

Maximising Binder Functionality in Selective Agglomeration

A Thesis Submitted for the Degree of

Doctor of Philosophy

By

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December 2015



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.....
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.....
Roberto Moreno-Atanasio

ACKNOWLEDGEMENTS

I would like to thank my supervisors, Roberto Moreno-Atanasio and Kevin Galvin, for their continued support, guidance, and friendship. It was greatly appreciated.

I would also like to give a special thanks to Mark Mason for all his help. His tireless efforts kept all the research in the lab moving forward.

For the construction of equipment and advice I would like to thank Antonio Moreno, Bill Grant, and Dave Roberts.

Also, the financial support from the Australian Research Council and the Australian Coal Association Research Program was greatly appreciated.

Finally, I would also like to thank my father, Bert, and my brother, Jamie. You can't choose your family but if you could, I would choose you.

And for his support, encouragement, love, and preparation of delicious meals throughout all of my studies I would like to thank my partner, Sam.

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ABSTRACT

This study was concerned with improving this process of selective agglomeration using an immiscible binding liquid by maximising the functionality of the binder. In the past, research into the area of selective agglomeration has focussed on the use of only pure oils as binders. Pure oils are highly suitable, in a technical sense, as they are hydrophobic, immiscible with water and will preferentially wet hydrophobic particles in a mixture of hydrophobic and hydrophilic particles. However, pure oils are equally highly unsuitable due to their cost when combined with the dosages required in the agglomeration process. Therefore, to address this issue and thus reduce the costs associated with the organic binder, a high internal phase water-in-oil emulsion was introduced as the binder. This type of emulsion was selected as it possessed the hydrophobic surface functionality of oil while the space filling functionality of the binder was primarily satisfied by the dispersed water droplets within the emulsion. In other words, it was considered that by replacing the majority of the oil with water within the binder and subsequently the agglomerate structure, the overall organic liquid requirement would be substantially reduced.

The solid feed material used throughout all of the work was a naturally occurring mixture of coal and mineral particles, coal being naturally hydrophobic and minerals such as clays, being generally hydrophilic. Initial experiments indicated that the emulsion could selectively agglomerate coal in the same manner as pure diesel. Moreover, by comparing the organic liquid dosage required to achieve agglomeration when using the emulsion with the dosage required when using pure diesel it was established that a 2-fold reduction in the organic liquid requirement was achieved. A series of investigations was then carried out which examined the influence of the composition of the emulsion and process parameters on the performance of the emulsion. It was found that the initial result could be improved by reducing the level of degradation the emulsion experienced during the agglomeration process. The highlight of this work was the result for a 3 wt% aqueous NaCl-in-kerosene emulsion which achieved a 10-fold reduction as compared to the benchmark diesel case. This emulsion achieved agglomeration in only 7 s and thus experienced the lowest level of degradation which resulted from mixing in the turbulent, aqueous environment of the agglomeration process. Moreover, it was shown that if the emulsion was pre-dispersed in water prior to the combination of the emulsion with the coal slurry the mixing time required to achieve agglomeration was only 3 s.

Following on from the development of the emulsion binder, a fundamental investigation into binder functionality was carried out. It was found that the organic liquid requirement to achieve agglomeration was a function of the specific surface area of the material to be agglomerated and the voidage within the agglomerate material. Moreover, it appeared that the dispersed, water droplets within the emulsion played a space filling role within the void spaces, as hypothesised, however the thin film which formed around the particles comprised only of organic liquid and thus the water droplets did not play a space-filling role. That being said, the results indicated that the film formed when using the emulsion was 178 nm which was approximately 4-times thinner than the film formed when using pure kerosene. Therefore, the results from this investigation indicated that the reduction which may be achieved is a function not only of the dispersed phase of the emulsion but also of the surface area of the feed.

Due to the successful development of the agglomeration process using the emulsion a final investigation was carried out to study the potential application of this work in an industrial coal processing setting. It was found that the ash% and moisture content of the agglomerated product was sufficiently low to meet market requirements. In particular it was found that the emulsion binder consistently produced a product with an ash of 10 – 11% leaving behind reject with an ash of 80% from a feed with an ash of 61%, providing that the emulsion dosage was sufficient.

Overall, the work in this study has resulted in the development of a rapid agglomeration process with reduced organic reagent requirements. This work has provided a foundation for further and exciting work in this new area.

PUBLICATIONS

- van Netten, K., Moreno-Atanasio, R., & Galvin, K. P. (2013). Preparation of Coal Agglomerates Using a Water-in-Oil Emulsion, *Proceedings, Annual Australasian Chemical Engineering Conference, Chemeca 2013*, Brisbane, Australia.
- van Netten, K., Moreno-Atanasio, R., & Galvin, K. P. (2014). Fine Particle Beneficiation through Selective Agglomeration with an Emulsion Binder. *Industrial and Engineering Chemistry*, 53, 15747 - 15754.
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NOMENCLATURE

<i>Symbol</i>	<i>Definition</i>	<i>Units</i>
<i>A</i>	Area	m ²
<i>a</i>	Assay	-
<i>D</i>	Dosage	wt%
<i>d</i>	Diameter	m
<i>F</i>	Force	mN
<i>f</i>	Scalar variable	-
<i>G</i>	Gibbs Free Energy	mJ
<i>k</i>	First Order Coefficient	1/wt%
<i>l</i>	Perimeter	m
<i>P</i>	Pressure	mPa
<i>R</i>	Recovery	-
<i>S</i>	Entropy	mJ/K
<i>SA</i>	Specific Surface Area	m ² /m ³
<i>s</i>	Liquid Saturation	-
<i>T</i>	Temperature	K
<i>V</i>	Volume	m ³
<i>v</i>	Specific volume	m ³ /m ³
<i>w</i>	Work	mJ
<i>Y</i>	Yield	wt%

Greek Letters

<i>Symbol</i>	<i>Definition</i>	<i>Units</i>
γ	Surface energy	mJ/m ²
γ	Surface tension	mN/m
δ	Film thickness	m
θ	Contact angle	°
μ	Viscosity	Pa s
ρ	Density	kg/m ³
ϕ	Phase volume ratio	-

Subscripts

<i>Symbol</i>	<i>Definition</i>
32	Sauter mean
<i>attach</i>	Energy of attachment
<i>c</i>	Continuous phase
<i>F</i>	Feed
<i>G</i>	Gas phase
<i>i</i>	Index
<i>L</i>	Liquid phase
<i>M</i>	Maximum
<i>O</i>	Organic phase
<i>oil</i>	Organic component
<i>P</i>	Product
<i>R</i>	Reject
<i>r</i>	Relative
<i>S</i>	Solid
<i>s</i>	surface
<i>spread</i>	Energy of spreading
<i>void</i>	Void space component
<i>W</i>	Aqueous Phase

Chapter 1

Introduction

1.1 Introduction

In this study, agglomeration through the addition of an immiscible, binding liquid was investigated. Agglomeration is a process of size enlargement which results in larger assemblies of small, primary particles. In practice, agglomeration is used to improve the utility of fine particles in further processing operations or to produce a final product of agglomerated material (Capes, 1980). In this work, agglomeration was used to facilitate the separation of an aqueous mixture of finely dispersed particles in a downstream processing operation. More specifically, selective agglomeration was carried out to agglomerate only one type of particle from the mixture such that it could be separated with relative ease from the other unwanted and still finely dispersed particles in the mixture. To achieve this selective agglomeration, as mentioned above, a liquid binder was used and it was the functionality of this binder which was the main focus of this work.

This chapter begins with a description of the aim of this thesis. Following this, background material on agglomeration using a liquid binder and, in particular, the selective agglomeration process and its applications is presented. Then, a discussion about maximising binder functionality in the agglomeration process is presented. The chapter concludes with a short description of the thesis objectives and an outline of the remaining chapters.

1.2 Aim of the Thesis

This study is concerned with improving the process of selective agglomeration by maximising the functionality of the binder. The selective agglomeration took place within an aqueous mixture, the aim being to separate hydrophobic and hydrophilic particles. In general, a hydrophobic binder is required for such a separation as it is immiscible with the suspending liquid and it will preferentially agglomerate only the hydrophobic particles in the mixture. In this work, a mixture of coal and mineral particles was used as the feed material as coal is naturally hydrophobic and minerals are hydrophilic. As mentioned, the binder must be hydrophobic to process this type of feed. A sufficient volume of binder must also be present to allow for agglomeration of all the hydrophobic particles in the feed. However, beyond these two indispensable conditions, the functionality of the binder may be maximised so

that certain aspects of the process are improved, such as processing time, raw materials usage and agglomerate size.

Therefore the aim of this study was to maximise the functionality of the binder to allow for the effective treatment of a mixture of coal and mineral particles. The effect of binder composition and process parameters were investigated.

1.3 Background on Agglomeration using a Liquid Binder in Three Phase Systems

Agglomeration of solid particles using a liquid binder may be carried out in a continuum of gas or liquid (Capes, 1980). Agglomeration carried out in a gas results in a solid-liquid-gas three phase system and agglomeration carried out in liquid results in a liquid-solid-liquid three phase system. Both types of agglomeration systems will be presented in this section with a discussion on their applicability for use in different applications.

1.3.1 Solid-Liquid-Gas Three Phase Systems

Figure 1.1 presents a schematic of a solid-liquid-gas three phase agglomeration system.

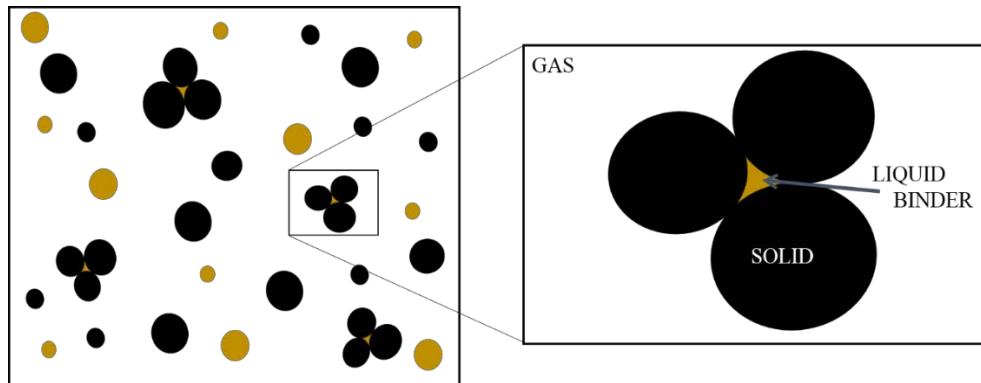


Figure 1.1: Solid-liquid-gas three phase agglomeration system

As depicted in Figure 1.1, the liquid binder is dispersed throughout the fine solid particles. Then, during intimate contacting of the system constituents, the liquid binder wets and agglomerates the dry powder through the development of capillary and viscous bonding forces (Iveson, Litster, Hapgood, & Ennis, 2001). In these systems both aqueous based and solvent based binders may be appropriate for use depending on the material to be agglomerated and the desired product.

Agglomeration in the solid-liquid-gas three phase system is also referred to as wet granulation and experiences a wide usage in a variety of industries such as pharmaceuticals, food manufacturing, fertiliser manufacturing, ceramics formation and chemical manufacture (Capes, 1980; Iveson, et al., 2001). The use of wet granulation in these industries is usually the preferred method for the processing of fine particles as it improves the physical characteristics and handling properties of the dry powder. That is, by performing the size enlargement: the flow and compression characteristics are improved; the segregation of particles is reduced; useful structural forms and shapes are created; excessive amounts of fine particles are eliminated; dusting losses are reduced; and content uniformity is improved (Capes, 1980; Tousey, 2002).

1.3.2 Liquid-Solid-Liquid Three Phase Systems

Figure 1.2 presents a schematic of a liquid-solid-liquid three phase agglomeration system.

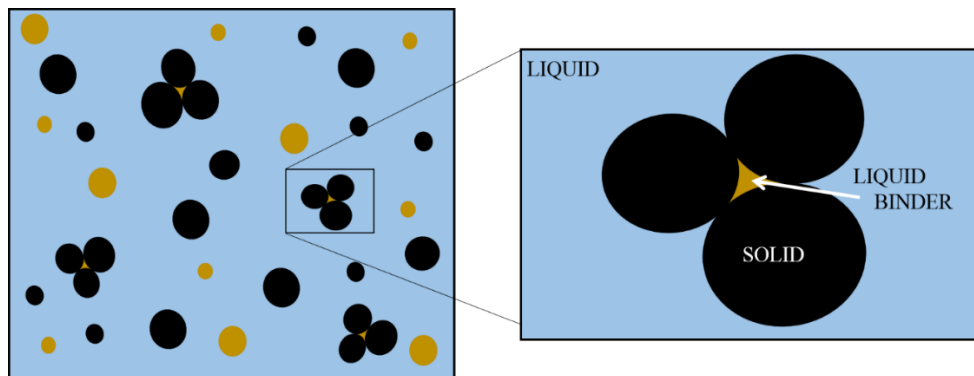


Figure 1.2: Liquid-solid-liquid three phase agglomeration system

As can be seen in the schematic, the fine particles are dispersed in a suspending liquid while a secondary liquid, the binding liquid, is added through the application of agitation. As similar to wet granulation, agglomeration is achieved as a result of the capillary and viscous forces which develop between the binding liquid and the solids. Also, as similar to wet granulation, the liquid binder must be selected with a consideration to the type and end-use of the solid to be agglomerated. However, because this agglomeration takes place in a liquid medium, consideration must also be given to the possible interaction between the two liquids and how the solid-liquid interaction changes. Therefore, the liquid binder must be selected such that it

preferentially wets the particles to be agglomerated and is immiscible with the suspending liquid (Capes, 1980).

Agglomeration of fine particles in suspension is generally used when particles must be separated or retrieved from the liquid medium. Ordinarily this operation is quite difficult as the particles are very small, and thus the efficiency of traditional separation methods is low (Gupta & Yan, 2006). However, by performing the size enlargement, the use of separation processes such as filtration and gravity separations become feasible. This type of agglomeration, which is also known as spherical agglomeration, therefore finds applications in areas such as: rapid clarification of liquids; pelletisation and sphere formation; and beneficiation of coal and mineral particles (Kelsall & Pitt, 1987; Szymocha, Pawlak, & Kramer, 1999). Agglomeration using a liquid binder is the preferred method for processing the fine particles in these applications as it can produce a compact and discrete granular solid with good structural integrity, provided a suitable amount of binding liquid is used. A considerable displacement of the suspending liquid from the product agglomerates is also achieved as the liquid binder occupies the void space in the interior of the agglomerates (Capes, 1980).

Many applications of agglomeration in suspension also utilise the liquid binder to perform a separation on a mixture of particles (Dawei, Kewu & Jicun, 1986; Cebeci & Sonmez, 2004; Nicol & Swanson, 1980). This separation can be achieved if the particles in the mixture differ in their ability to be wetted by certain liquids. For example, hydrophobic particles can be selectively agglomerated from an aqueous mixture of hydrophobic and hydrophilic particles using a hydrophobic binding liquid. The hydrophobic binding liquid, with the aid of agitation, will preferentially wet and agglomerate only the hydrophobic particles. The hydrophilic particles do not take part in the agglomeration as they have a higher affinity for the aqueous phase. As the size of the hydrophobic particles has been upgraded they can then easily be retrieved from the suspending liquid and the hydrophilic particles (Steedman & Krishnan, 1987).

Table 1.1 presents some examples of both selective and non-selective agglomeration in suspension using a liquid binder. As is made clear in the table, the process has been applied in a variety of aqueous and organic systems.

Table 1.1 Applications of agglomeration in suspension using a liquid binder

Separation	Suspending Liquid	Binding Liquid	Product(s)	Ref.
Soot from waste water originating from oil gasification plants	Aqueous	Hydrocarbon	Grey water and soot agglomerates	(Higman, Bajohr, & Reimert, 2002)
Hydrocarbon contaminants from soil through the addition of finely dispersed coal/coke	Aqueous	Hydrocarbons from soil	Remediated soil and coal agglomerates	(Szymocha, et al., 1999)
Wolframite* (tungsten ore) from quartz	Aqueous	Iso-octane	Wolframite agglomerates	(Dawei, et al., 1986; Kelsall & Pitt, 1987)
Coal from ash-forming mineral particles	Aqueous	Light and/or heavy hydrocarbons	Coal agglomerates	(Nicol & Swanson, 1980; Steedman & Krishnan, 1987)
Ash-forming minerals from a coal	Hydrocarbon	Aqueous	Coal-in-oil slurry	(Capes, Germain, McIlhinney, Puddington, & Sirianni, 1977)
Sand from bitumen solution extracted from oil sands	Hydrocarbon	Aqueous	Bitumen	(Farnand, Meadus, & Sparks, 1985)
De-inking toner-printed paper	Aqueous	Hydrocarbon	Recycled paper (cellulose slurry)	(Huang & Berg, 2003)
Celestite* (strontium ore) from gypsum	Aqueous	Hydrocarbon	Celestite agglomerates	(Cebeci & Sonmez, 2004)

* solid requires surface modification to render it hydrophobic

In some applications of selective agglomeration, the particles to be treated do not differ sufficiently in their wettability and, thus a conditioning agent is required to modify the surfaces of the particles which are to be separated. For example, dodecylamine is required in the selective agglomeration of wolframite, a tungsten ore, from quartz. The dodecylamine renders the surface of the wolframite hydrophobic such that it can be agglomerated by a hydrophobic binder (Kelsall & Pitt, 1987)

1.4 Selective Agglomeration in Coal and Mineral Beneficiation

As can be seen in Table 1.1 there has been a great interest in the potential use selective agglomeration in the area of coal and mineral beneficiation. This interest was based on the need for a method to efficiently separate the finely dispersed mineral ores or coal from the unwanted material with which it is mined. This unwanted material, also known as gangue, must be removed as its presence reduces the grade and, therefore, value of the resource. In many cases if the gangue cannot be efficiently and economically separated from valuable material, the entire fine fraction of feed is classified as waste and discarded (Osborne, 2012).

The field of coal processing, in particular, has had a long-term interest in the process of selective agglomeration as significant amounts of fine coal are still being discarded into tailings ponds (Osborne, 2012). Moreover, coal is known to respond remarkably well to selective agglomeration as coal is naturally hydrophobic and the gangue, which consists of clays and other minerals, is generally hydrophilic. Indeed, this high suitability to the process was the reason a naturally occurring feed of coal and mineral particles was selected for study in this work. Furthermore, by maximising the functionality of the binder with respect to a coal feed the potential to address the continuing problems encountered in fine coal processing was presented. However, it should be noted, that while coal was used in this work, the general findings can be applied to any application of selective agglomeration in suspension using a liquid binder.

1.4.1 Previous Research on the Selective Agglomeration of Coal

As described in Section 1.3.2, the agglomeration of fine coal involves the addition of a hydrophobic binding liquid, usually oil, to an aqueous suspension of coal and mineral particles under constant agitation. The oil preferentially wets the surface of the coal, selectively forming product coal agglomerates which are recoverable using a screen separation. The unwanted mineral matter, which remains finely dispersed, is not collected on the screen and continues with the water to form the reject (Steedman & Krishnan, 1987).

A substantial amount of research has been done on the selective agglomeration of coal since its first application early in the twentieth century (Perrott & Kinney,

1921). The process experienced wide-spread attention, especially during the energy crisis of the 1970's, as it appeared to be the most promising method for processing fine coal; the fraction of the coal feed which was, and remains to be, the most difficult to handle. The great appeal of the selective agglomeration process came from its ability to: effectively separate coal and mineral particles; drastically improve the ability to dewater the coal fines; and upgrade the size and thus, handlability of the coal product. In addition, selective agglomeration appeared to have no lower limit on the size of the particle that could be processed and was not hindered by the presence of large amounts of clays and other minerals, two attributes which are not shared by any other coal processing technique (Capes & Germain, 1982; Mehrotra, Sastry, & Morey, 1983).

As with any process, a main focus of the past research has been to understand the effect of the various operating parameters on the quality of the product. The variable parameters of the agglomeration process are: the oil (liquid binder) dosage and type; pulp density and; agitation duration and intensity. In general, it was found that an excellent separation (mineral matter rejection) and product recovery was possible over a broad range of pulp densities and mixing conditions (Capes & Germain, 1982). High quality coal agglomerates have been produced from slurries with pulp densities in the wide range of 5 wt% to 50 wt% (Mehrotra, et al., 1983; Swanson, Nicol, & Bensley, 1977). A considerable flexibility in the mixing conditions, *i.e.* agitation duration and intensity, applied in the process has also been displayed as the two parameters are linked via an inverse relationship (Capes, McIlhinney, & Coleman, 1970). This means a consistent product yield can be maintained if a change in agitation duration, for example, is compensated by inverse change in agitation intensity, or vice versa.

Conversely to the process conditions described above, the correct selection and dosage of the oil binder has been shown to be of great importance in ensuring a high quality product. The selection of oil type is critical as it determines the quality of the product agglomerates. Light oils such as diesel and kerosene have been shown many times over to possess excellent mineral matter rejection capabilities and produce high quality product agglomerates (Aktas, 2002; Capes & Germain, 1982; Capes, McIlhinney, & Sirianni, 1977; Tsai, 1982). Heavy oils, however, do not

consistently produce a low mineral matter product and this behaviour has been attributed to the complex and variable composition that is common of heavy oils such as, tars, bunker fuels, heavy crudes, coal tar and its derivatives (Capes, et al., 1977; Keller & Burry, 1987).

Furthermore, the oil dosage used in the process has been shown to determine the quality of the agglomerated product and the extent to which the coal is recovered. Indeed, the oil dosage is perhaps the parameter of paramount importance and this importance is reflected in the large volume of research which has been dedicated to investigating the optimum binder dosage (Aktas, 2002; Garcia, Vega &, Martinez-Tarazona, 1995; Sirianni, Capes, & Puddington, 1969). The emphasis on this parameter has also been accentuated by its dependence upon the characteristics of the coal to be agglomerated. As the oil must be present in sufficient volume to both, spread over the surface of the coal and, fill the void space within the agglomerates, the dosage parameter becomes dependent upon the chemical and physical characteristics of the coal. This dependence means that there is no universal dosage that is appropriate for every feed. However through the extensive testing that has been completed, some general regimes have emerged that can predict the structure of the agglomerate product depending on the amount of oil added (Capes & Germain, 1982; Sirianni, et al., 1969). In general, 10 – 20 wt% (dry coal feed basis) is the optimal range for producing strong, discrete and recoverable agglomerates (Swanson, et al., 1977). At this dosage the agglomerates reach a peak in strength and sphericity as the void space in the interior of the agglomerate is saturated with oil. At concentrations below this range there is not sufficient oil present to provide surface coverage of the particles and void saturation within the interior of the agglomerates. As a result, the product at low oil dosages is only weakly agglomerated and is, therefore, difficult to recover. At dosages beyond the optimal range, the agglomerates become over-saturated and the product is effectively a coal-in-oil paste (Capes & Germain, 1982).

Therefore, it is clear that the extensive research that has been carried out has resulted in a thorough understanding of the agglomeration process as applied to coal. However, regardless of this understanding and the subsequent capability to design an effective coal separation process, there have been no long term

commercial applications of the process. This lack of applications can be attributed, in a large part, to the prohibitive cost of the oil binder. As aforementioned, to successfully agglomerate a fine coal feed 15 wt% of oil is needed. In other words, to process one tonne of saleable coal 150 kg of oil is required. Following on, a comparison of the sale price of one tonne of coal with the cost price of 150 kg of oil reveals a significant financial deficit. This deficit often means that it is more cost effective to classify the fine coal as waste and dispose of it rather than process it for sale (Osborne, 2012). Indeed, many authors have identified this shortfall in the process and acknowledged that for agglomeration of coal to be commercially viable the dosage of the oil needs to be significantly reduced (Mehrotra, et al., 1983; Darcovich, Capes, & Talbot, 1988; Shrauti & Arnold, 1994). One possible route for achieving this goal is to maximise the functionality of the binder.

In the past, research in the area of fine coal agglomeration has been carried out with the use of only pure oils as binders (Aktas, 2002; Capes & Germain, 1982; Mehrotra, et al., 1983). Pure oils are highly suitable, in a technical sense, as they are naturally hydrophobic, immiscible with water and will preferentially wet coal in a mixture of coal and mineral particles. However, pure oils are equally highly unsuitable due to their cost when combined with the dosages required in the agglomeration process. Therefore, the maximisation of the binder functionality that will be presented in this work is multi-faceted. That is, it incorporates the need for a high quality product with the need for a low cost process.

1.4.2 Binder Functionality Maximisation

It has been established in the previous section that selective agglomeration of coal requires a hydrophobic binder that will preferentially wet only the hydrophobic coal particles in a feed. In a more general sense it can be said that the binder must satisfy a surface functionality. It has also been established that the binder must be present in sufficient volume as to allow for saturation of the void space in the interior of the agglomerates. Void saturation is necessary as it allows for the agglomerates to reach a peak in strength and sphericity and, in a practical sense, be recoverable and of high quality. Therefore it can be said that the binder must also satisfy a space-filling functionality. Finally, it was established that the binder must be low cost if it is to be used for the processing of fine coal and it was acknowledged that costs can be

reduced if the amount of oil required in the process is reduced. Therefore, a new binder had to be developed that could satisfy the surface functionality, the space-filling functionality and the low cost/low oil requirement.

In the development of the new binder it was considered that pure oil would still be required to provide the surface functionality of the binder, i.e. create a hydrophobic material. However, pure oil was not necessarily required to provide the space-filling functionality. This functionality could be performed by another low cost material, such as water. Therefore, a water-in-oil emulsion was created for use as the binder.

The emulsion that was used was a high internal phase (HIP) emulsion. A HIP emulsion is one in which the dispersed phase has a volume fraction of greater than 0.74 (Cameron, 2005). Presented in Figure 1.3 is a light microscope image of a HIP water-in-oil-emulsion with a dispersed phase volume fraction of 0.84. Also depicted is a schematic representation of one of the dispersed water droplets stabilised by an emulsifier.

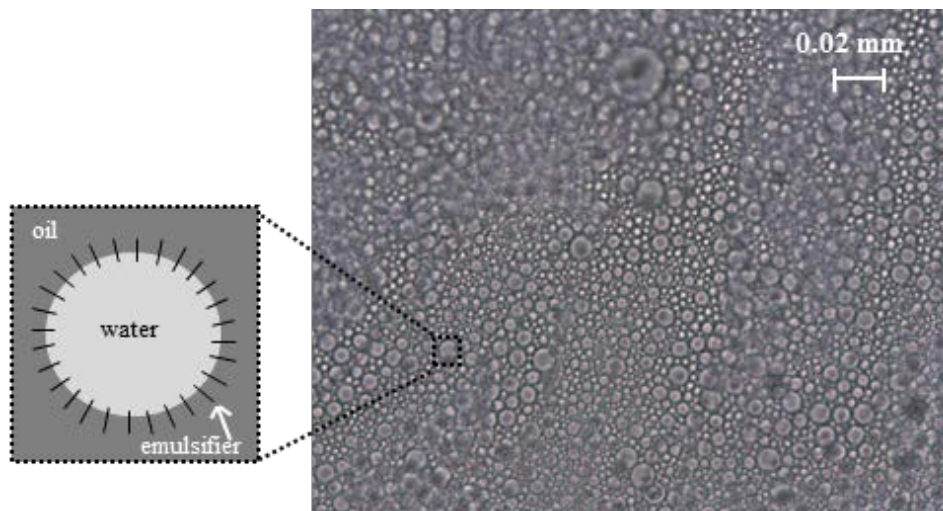


Figure 1.3: A light microscope image of a high internal phase water-in-oil emulsion with a dispersed phase volume fraction of 0.84. A schematic representation of a dispersed water droplet stabilised by emulsifier is also presented.

As shown in Figure 1.3, a thin, continuous layer of oil separates the tightly packed water droplets that make up the majority of the emulsion. Figure 1.4 now presents a comparison between the proposed emulsion binder and a traditional pure oil binder and illustrates the potential of the emulsion to reduce the amount, and thus cost, of the oil required in the process.

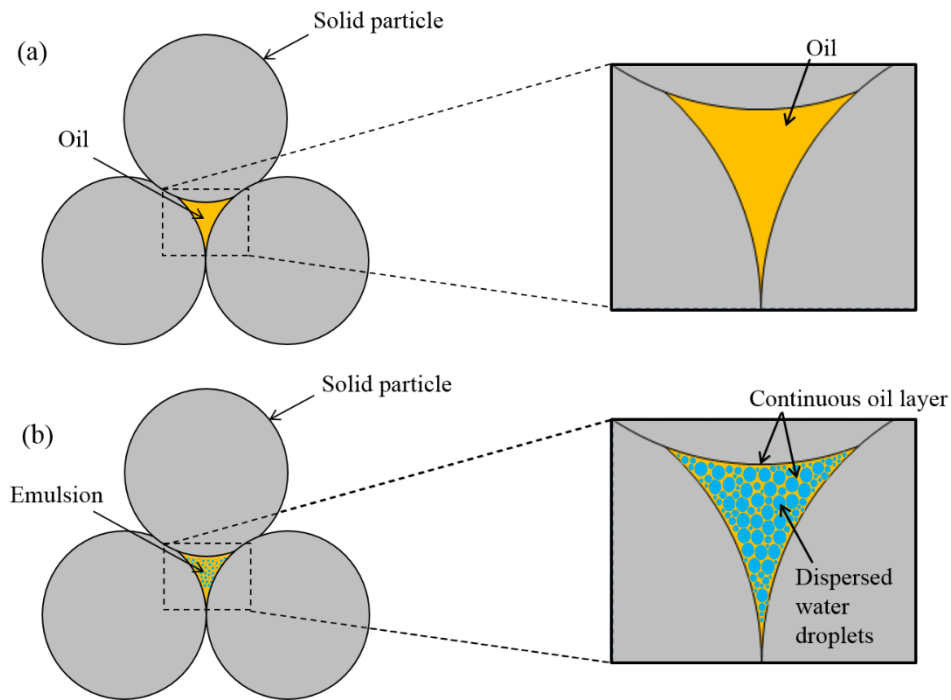


Figure 1.4: Schematic representation of agglomerated particles joined together using a) pure oil and b) a high internal phase water-in-oil emulsion.

As depicted in Figure 1.4, both the pure oil and the emulsion satisfy the surface and space-filling functionalities required of the binder. The surface functionality is satisfied in each case as both are hydrophobic materials which can selectively adhere to the surface of hydrophobic coal particles. Oil is inherently hydrophobic and the emulsion is hydrophobic as oil forms the continuous phase. Furthermore, the space-filling functionality is satisfied by both the pure oil and the emulsion as both fill the void space in the interior of the agglomerate. However, as can be seen in Figure 1.4b, water, in the form of dispersed droplets, replaces the majority of the oil in filling the void space when using the HIP water-in-oil emulsion. This substitution, therefore, means that the oil is required to fill only a small fraction of the void space.

This theorised concept of replacing the majority of the oil with dispersed water droplets is referred to as the substitution theory from here on in and forms the basis for assuming that a reduction in the oil requirement is possible through the use of the emulsion. Moreover, realisation of these reductions would mean that the HIP water-in-oil emulsion satisfies the previously unreconciled specification for a binder in the agglomeration process: reasonable processing costs.

1.5 Objectives of the Thesis

The main objective of this work was to develop a binder based on a HIP water-in-oil emulsion which could produce a high quality, agglomerated product at a significantly reduced oil dosage. The work of this thesis, in the first instance, was therefore to determine whether a HIP emulsion could agglomerate fine coal and produce a high quality product. Subsequently, the work focused on determining and maximising the reduction in oil dosage achievable through the use of the HIP water-in-oil emulsion.

To achieve the objective of reducing the oil dosage a series of investigations were carried out to understand the agglomeration process when the binder consisted of the HIP water-in-oil emulsion. Due to the distinct physical disparities between pure oil and a HIP water-in-oil emulsion this work was necessary to investigate the behaviour of the emulsion in the agglomeration process. Investigations were carried out into the influence of various properties of the emulsion in addition to the influence of operating parameters of the agglomeration process such as mixing time.

1.6 Thesis Outline

This thesis commences with a literature review in Chapters 2 and 3. The fundamental aspects of the selective agglomeration process are presented in Chapter 2. This section of the review therefore provides the basis for understanding the wetting and interfacial phenomena that underpin the agglomeration process. The review also provides a general description of agglomeration using a liquid binder. Chapter 2 concludes with an introduction to the fundamental theory of emulsions. In this section there is a particular focus on high internal phase emulsions and emulsion stability.

Chapter 3 provides a comprehensive review of the previous work on selective agglomeration of coal, in particular the influence of the various operating parameters. The operating parameters of greatest importance in the fine coal agglomeration process are oil dosage and type, agitation duration and intensity and pulp density. Consideration is also given in this chapter to other variations to the selective agglomeration process which have been examined previously.

The original work carried out with the emulsion binder is presented in Chapter 4. Therefore this chapter begins with a performance comparison between the emulsion and a pure diesel binder. In this section, the ability of the two binders to selectively agglomerate and recover coal is compared. As a part of this work the extent that the emulsion reduces the oil dosage required to achieve agglomeration is also established. Finally, an investigation into the effect of the composition of the emulsion on its functionality as a binder in the agglomeration process is presented.

Chapter 5 explores the mixing regimes within the agglomeration process and the emulsion preparation procedure as a means of maximising the functionality of the emulsion. The influence of mixing duration on the performance of the emulsion is examined and compared to that of a pure diesel binder. Furthermore, a new homogenisation device is introduced and used in an effort to improve the stability, and thus functionality, of the emulsion

Chapter 6 explores composition modifications as a means of maximising the functionality of the emulsion binder within the selective agglomeration process. The influence of various properties of the emulsion on its performance as a binder are presented. These properties include: the aqueous phase content, the emulsifier type and the continuous phase oil type.

Chapter 7 presents an analysis of the fundamental functionality of the binder in the agglomeration process. Within this chapter the functionality of the emulsion is described in detail and compared to the functionality of a pure kerosene binder.

A discussion around the potential application of the selective agglomeration process developed in this work is presented in Chapter 8.

Finally, Chapter 9 is the concluding chapter which presents a summary of all the findings of this work. Recommendations for future work are also presented in this chapter.

Chapter 2

Surface Chemistry, Agglomeration, and Emulsions

2.1 Introduction

Presented initially in this chapter is a review of the fundamental surface chemistry which underpins the mechanism of selective agglomeration. The concepts of surface energy, surface tension, interfacial tension and contact angle are introduced along with wettability and hydrophobicity. These concepts are then extended in the following section to describe the surface chemistry of the selective agglomeration process. This description considers the attachment of a hydrophobic binder to a solid surface in an aqueous environment and the spreading of a hydrophobic binder over a solid surface in an aqueous environment.

The following section in this chapter then describes the mechanism of formation of agglomerates via the attached liquid binder. The influence of liquid content on agglomerate formation is described along with the kinetics of agglomerate growth.

Finally, as a water-in-oil emulsion will be used as the binder in this work, this chapter concludes with a review of fundamental emulsion theory. This review includes a discussion on the properties of emulsions including structure, stability and viscosity. A particular emphasis is placed in this section on the properties of high internal phase emulsions because this type of emulsion will be used in this work.

2.2 Concepts in Surface Chemistry

2.2.1 Surface Energy and Surface Tension

A well-known variation exists in the energies between the molecules at the surface of a material and the molecules in the bulk phase of a material (Hunter, 2001). This variation arises due to the relative interactions the molecules of a material may have with surrounding molecules. Molecules in the bulk material experience cohesive (attractive) energies with immediate neighbours in all directions making their total energy more negative than their counterparts on the surface (Israelachvili, 1991). The molecules on the surface of the material experience a larger, *i.e.* less negative, attractive energy than molecules in the bulk as they only experience a cohesive energy on one side. An implication of this energy difference is that the creation of new surfaces is not energetically favourable as energy must be added to a molecule to move it from the bulk to a surface (Hunter, 2001). Therefore materials will intrinsically aim to minimise their surface area as this results in the maximum number of molecules in the bulk. Now, if the surface area of a material was to increase a disruption of intermolecular bonds between some of the bulk molecules would occur and there would be an overall energy change as a result. Hunter (2001) describes the work, dw , to create this new surface as proportional to the number of molecules brought from the bulk to the surface, and hence to the area, dA , of the new surface,

$$dw \propto dA \quad \text{or} \quad dw = \gamma dA \quad (2.1)$$

where γ , the proportionality constant, is defined as the surface energy. Now, if the work to create the surface is reversible and is carried out at constant pressure, P (mPa), and temperature, T (K), γdA coincides with the increase in the Gibbs free energy of the system, G (Adamson & Gast, 1997). This link can be illustrated by considering the differential expression for Gibbs free energy,

$$dG = -SdT + VdP + \gamma dA \quad (2.2)$$

where S (mJ/K) and V (m³) are the entropy and volume of the system, respectively. Now, under the conditions of constant temperature and pressure Equation 2.2 simplifies to,

$$dG = \gamma dA \quad (2.3)$$

From Equation 2.1 and Equation 2.3 it can be seen that surface energy can have the dimension of energy per unit area or force per unit length. For solids it is conventional to use the former units to express their surface energy, whereas the latter units are usually used when considering liquids (Hunter, 2001; Israelachvili, 1991). In the case of liquids it is common for γ to be called surface tension (mN/m) which is numerically and dimensionally the same as surface energy (mJ/m²) but slightly different conceptually.

As the name would suggest, surface tension includes forces in the description of surface creation as opposed to energies. The definition of surface energy can, therefore, be rephrased to make it specifically relate to liquids and their surface tension in the following manner; surface tension is a measure of the free energy required to increase the surface area of a liquid by a unit of area and is the result of an imbalance of intermolecular attractive (cohesive) forces. That is, a molecule in the bulk liquid experiences cohesive forces with the neighbouring molecules in all directions whereas a molecule at the surface of a liquid only experiences a net inward cohesive force. This creates an internal pressure and makes liquid surfaces contract to minimal area. Now, in order to make a new surface in a liquid the work to be done, dw , must be the result of a force, F (mN). Hunter (2001) shows that the magnitude of this force can be related to the surface tension of a liquid in the following way,

$$\gamma = \frac{F}{l} \quad (2.4)$$

where l (m) is the perimeter over which the force acts. It should be noted that the term ‘surface tension’ is usually used when one phase is gas. When the second phase is also a liquid, ‘interfacial tension’ is used.

2.2.2 Interfacial Tension

In general terms, the definition of interfacial tension is the same as surface tension; however it is used in the specific context of two immiscible liquids in contact. This condition, that the two phases in contact are liquids, implies that interfacial tension is synonymous with interfacial energy, as discussed in the previous section. Therefore, the interfacial tension may be defined as the free energy change associated with expanding the interfacial area between two immiscible liquids in contact by a unit area (Israelachvili, 1991).

2.2.3 Contact Angle

Thus far the discussion has focussed on the mechanics of a surface formed between two fluid phases (either gas and liquid or two liquids). In this section the discussion is extended to include a third solid phase. In a three phase system of two fluids and one solid the interface formed will depend on the surface and interfacial energies of the constituents (Israelachvili, 1991). To explore this concept a droplet of liquid (L) on a solid surface (S) in a continuous phase of gas (G), as depicted in Figure 2.1, will be used as the model system.

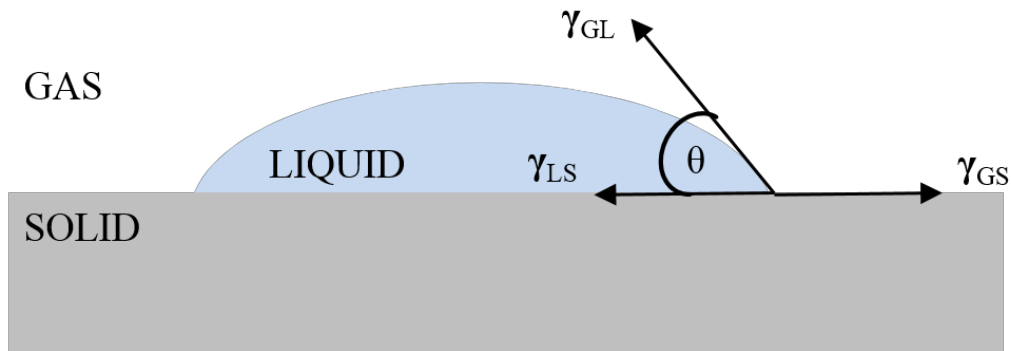


Figure 2.1: The forces acting at the triple interface for a drop of liquid on a flat solid surface.

Depicted in Figure 2.1 is an angle, θ , formed between the solid and the tangent to the liquid surface at the line of contact. This angle formed at the triple interface is called the contact angle and by convention is measured in the liquid phase (Barnes & Gentle, 2005). It may seem, from previous discussions, that the natural process would be for the droplet to be as rounded as possible as to minimise the liquid-solid

interfacial area. However this neglects the fact that the solid-vapour interface must increase and this process is also associated with a free energy change (Hunter, 2001). The contact angle therefore measures the compromise that occurs between the competing interfacial forces and represents the equilibrium position at the lowest free energy.

Obviously, the position of the triple interface and thus contact angle will depend on the horizontal components of the interfacial tensions acting on it (Barnes & Gentle, 2005). At equilibrium these interfacial tensions will be in balance;

$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL}\cos\theta \quad (2.5)$$

Equation 2.5 is called Young's Equation and is generally used to determine the shape of the interface at equilibrium when three phases are in contact, as described above (Adamson & Gast, 1997). It is important to note that the description above is not limited to the system in which there are three different phases (solid, liquid and gas). The description can also apply to a system in which the gaseous phase is replaced by a second immiscible liquid phase.

2.2.4 Wettability/Hydrophobicity

Equation 2.5 describes the equilibrium contact angle in terms of interfacial tensions between the solid and gas and solid and liquid. However, no insight has been given as to why different interfacial tensions exist and, in turn, why a certain value for contact angle is reached for a given system. For example, it can be observed that some solids form a very large contact angle with water, the smooth treated surface of heptadecafluorodecyltrimethoxysilane has a contact angle of 115° , whereas other solids can form a very low contact angle (Arkles, 2006; Barnes & Gentle, 2005). The difference observed between these cases can be explained by considering the relative wettability of the solids. Wettability is defined as the ability of a liquid to maintain contact with a solid surface. This ability is a result of intermolecular interactions when the two phases are brought together and represents a balance between the cohesive forces, between the molecules in the drop, and the adhesive forces, between the liquid molecules and the solid surface (Barnes & Gentle, 2005). Now, it should be remembered that when the term 'adhesive forces' is used, a broad

grouping of more specific and well-defined forces has occurred as they all contribute to the work of adhesion of liquid to solid. The most important forces that contribute to this adhesion include, van der Waals dispersive forces, interactions due to hydrogen (polar) bonds and, if the surface is charged, an electrical force contribution (Laskowski, 2001).

Therefore, for a liquid to wet a solid surface with relative ease it must have some way in which the liquid molecules can interact with the solid surface. A liquid that is capable of this interaction is usually called lyophilic and has a very low contact angle (Barnes & Gentle, 2005). A liquid that is not capable of adhesion is said to not wet the solid surface well and is usually called lyophobic. For a non-wetting liquid, in a practical sense, the contact angle is usually greater than 90° (Adamson & Gast, 1997). The definitions introduced in this paragraph are applicable for any liquid; however a substantial effort has gone into defining the wettability of different solids when the liquid is water.

In general, surfaces have been divided into two categories based on how they interact with water. Solids over which water spreads with relative ease are said to be hydrophilic, whereas surfaces over which water does not spread easily are called hydrophobic. The main difference between hydrophilic and hydrophobic surfaces is the presence (or absence) of surface charge. An interaction between water molecules and a solid surface is favourable when surface charges are present. Therefore hydrophilic surfaces usually bear an electric charge or polar groups, for example hydroxyl groups (Sendner, Horinek, Bocquet, & Netz, 2009). These hydrophilic surfaces can therefore impart strong adhesive forces, which hydrophobic surfaces are not capable of as they, in general, lack a source of surface charge.

2.3 Surface Chemistry of Selective Agglomeration

As discussed in Chapter 1, selective agglomeration is a special application of agglomeration in suspension in which the liquid binder is also used to perform a separation on a mixture of particles. It was also noted that the basis for this separation is a difference in the ability of the solids within the mixture to be wetted by certain liquids. This section, therefore, extends the fundamental chemistry

presented in the previous section to describe the interactions which occur in the selective agglomeration process. Presented initially is a description of the attachment of a hydrophobic binder to a solid surface in an aqueous environment. This is followed by a discussion on the spreading of the hydrophobic binder over a solid surface in an aqueous environment.

It should be noted that the description in this section relates, in particular, to the selective agglomeration of fine, hydrophobic coal particles from an aqueous mixture of coal and mineral particles using a hydrophobic binder, *i.e.* the system to be studied in this work. Also, the hydrophobic binder will be referred to as oil from here on in.

2.3.1 Attachment of Oil to a Solid Surface in an Aqueous Environment

The factor of foremost importance in selective agglomeration is whether the binder, *i.e.* the oil will attach to the surface of a particle in the suspension as this, in turn, determines selectivity. Figure 2.2 presents this solid-oil interaction before and after attachment (Laskowski, 2001).

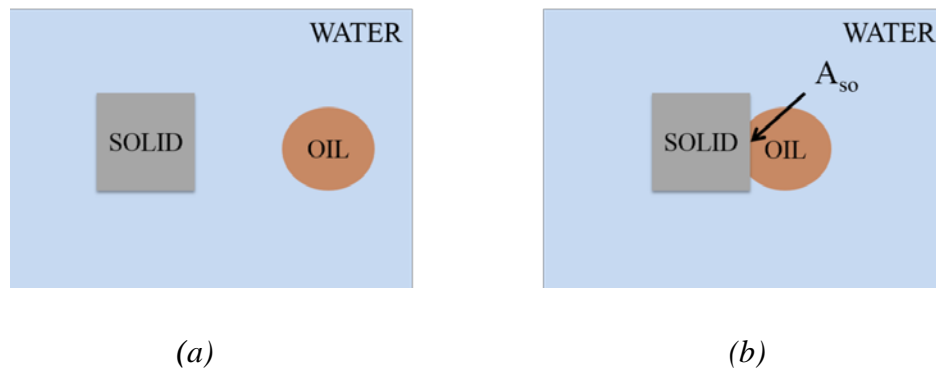


Figure 2.2: Attachment of oil droplet to solid particle in water. Adapted from Laskowski (2001).

As can be seen in Figure 2.2a, the solid particle and the oil droplet are discrete and separate in the aqueous suspension. Whereas, in Figure 2.2b the oil droplet has attached to the solid surface as a result of contact or coming into very close proximity. The resulting interfacial area A_{so} (m^2), has also been depicted in Figure 2.2b. The Gibbs free energy change associated with going from state a to state b is (Laskowski, 2001),

$$\Delta G_{attach} = G_2 - G_1 \quad (2.6)$$

Now, if the droplet is assumed to have attached isothermally and in a reversible way with the solid surface immersed in water the work performed is the same as the free energy change of the system, as described by Equation 2.3. Therefore, G_1 can be described as,

$$G_1 = A_{SW}\gamma_{SW} + A_{OW}\gamma_{OW} \quad (2.7)$$

where A_{SW} and A_{OW} are the interfacial areas between the solid particle and water and the oil droplet and water, respectively. Also, γ_{sw} and γ_{ow} are the solid/water and oil/water interfacial tensions. If it assumed that A_{SO} (the area of the interface formed as a result of contact) is equal to 1 then

$$G_2 = (A_{SW} - 1)\gamma_{SW} + (A_{OW} - 1)\gamma_{OW} + 1 \cdot \gamma_{SO} \quad (2.8)$$

where γ_{so} is the solid/oil interfacial tension. Now, by substituting Equation 2.7 and Equation 2.8 into Equation 2.6 an expression for ΔG_{attach} in terms of interfacial tensions can be obtained,

$$\Delta G_{attach} = \gamma_{SO} - \gamma_{OW} - \gamma_{SW} \quad (2.9)$$

Also, by introducing Equation 2.5, Young's equation, modified slightly, an expression for Gibbs free energy in terms of the contact angle can be attained. The modifications to Young's equation were necessary as the system presented in this section is slightly different to that described in Figure 2.1. Figure 2.3 presents this modified system, in which there are two liquid phases (water and oil) and one solid phase along with the corresponding interfacial tensions and the resulting contact angle.

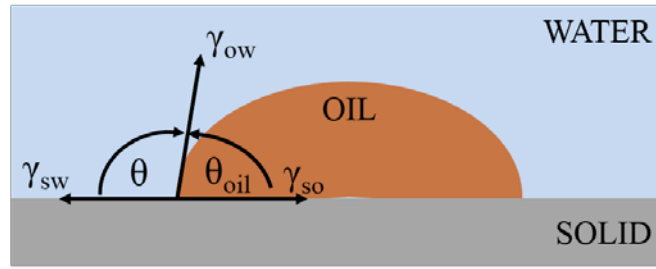


Figure 2.3: The contact angle at the triple interface for an oil droplet on a solid surface in an aqueous environment.

As shown in Figure 2.3, two different contact angles are presented, θ_{oil} and θ . By convention the contact angle for the system should be defined as the angle through the liquid droplet formed between the solid and the tangent to the liquid (oil) surface at the line of contact; the angle labelled θ_{oil} . In this case Young's equation for this system is

$$\gamma_{sw} = \gamma_{so} + \gamma_{ow} \cos \theta_{oil} \quad (2.10)$$

However, it was considered by the author to be more straightforward for the reader if the contact angle for the system was the angle between the solid and the tangent which passes through the aqueous water phase; the angle labelled θ . This was considered more straightforward as solids are so frequently referred to in literature in terms of their hydrophilicity or hydrophobicity, *i.e.* interaction with water. Considering,

$$\theta_{oil} = 180 - \theta \quad (2.11)$$

Young's equation, for this system in terms of the water contact angle, θ , becomes,

$$\gamma_{sw} = \gamma_{so} - \gamma_{ow} \cos \theta \quad (2.12)$$

Now, using Equation 2.12 an expression for the change in Gibbs free energy of attachment can be formulated in terms of the water contact angle and the oil/water interfacial tension,

$$\Delta G_{attach} = \gamma_{ow} (\cos \theta - 1) \quad (2.13)$$

Equation 2.13 shows that the attachment of an oil droplet to the surface of a particle in an aqueous environment is likely to take place if the water contact angle is greater than zero. Whereas, if the water contact angle is 0 then it would be impossible for attachment to occur, even if the droplet was forced against the surface, as there would be no interaction between the solid surface and the oil molecules.

As a result of the discussion above, it may appear that an oil droplet should attach to effectively any surface it encounters in an aqueous system, provided the contact angle is greater than zero. However, it should be noted that a negative ΔG_{attach} value indicates that attachment is possible but will not necessarily happen. This conditional result is because Equation 2.13 considers only the initial and final states if an attachment were to occur and does not account for the intermediate stages (Laskowski, 2001). In practice, for attachment to occur the intervening liquid layer between the solid particle and oil droplet must be displaced and the three phase contact line must be expanded (Chipfunhu, Zanin & Grano, 2011). Therefore, attachment can only occur if the kinetic energy of the particle is equal to, or more than, the energy required to thin the intervening liquid film and expand the three phase line of contact.

The energy required to overcome these intermediate stages is referred to as the energy barrier to attachment. Now, due to the influence of the relative interfacial tensions on the magnitude of this energy barrier, the likelihood of attachment is often characterised by a critical contact angle (Crawford & Ralston, 1988). That is, if the contact angle of a solid surface is below the critical angle, attachment is not likely to occur. Whereas, if the contact angle of the solid surface is above the critical angle, attachment is likely. Theoretical considerations and experimental data have been published which illustrate this effect of contact angle and appear to confirm the existence of a critical angle below which attachment does not occur (Chipfunhu, Zanin & Grano, 2012; Crawford, 1986; Gontijo, Fornasiero & Ralston, 2008; Miettinen, Ralston, Fornasiero, 2010).

Now, it should be noted that the published work described above relating to the energy barriers to attachment was carried out in the context of flotation systems. However, the comparison with the selective agglomeration system has been

considered to be qualitatively appropriate as flotation is similar to selective agglomeration except that air bubbles are used in the place of oil droplets to collect hydrophobic particles. Therefore, the tendency of oil to preferentially wet and agglomerate only the hydrophobic coal particles in an aqueous environment may be explained by considering the different contact angles and, in turn, differential energy barriers to attachment, for the coal and mineral particles.

2.3.2 Spreading of Oil on a Solid Surface in an Aqueous Environment

It is often assumed that on attachment oil droplets at a hydrophobic solid/water interface will spread onto the surface to form a thin film. However, contrary to this, Brown, Gray and Jackson (1958) showed that, even in the presence of surfactants, oils do not spread spontaneously on coal when immersed in water. The reason for this is because, as shown in Figure 2.4, the spreading of oil between a solid/water interface requires a change in free energy.

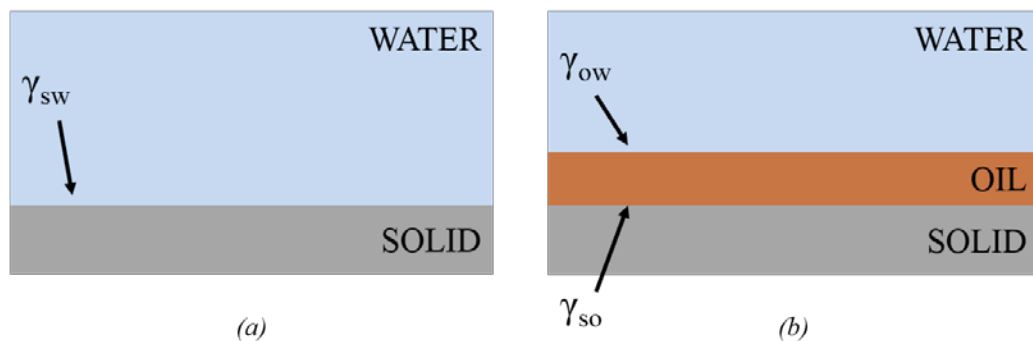


Figure 2.4: Schematic modelling of oil spreading between the water and solid interface.

Figure 2.4a depicts the water/solid interface and the interfacial tension between the two phases in the initial state, prior to oil spreading on the surface. Figure 2.4b then depicts the three phase system in which oil has spread between the solid surface and the water. As can be seen there are now two interfaces, one between the water and oil and a secondary interface between the solid and oil.

Laskowski (2001) describes this spreading of oil as resulting in the free energy change, ΔG_{spread} , given by

$$\Delta G_{spread} = \gamma_{SO} + \gamma_{OW} - \gamma_{SW} \quad (2.14)$$

which relates the interfacial tension, γ (mN/m), between the three different phases, water (W), oil (O) and solid (S). Now, by introducing the modified Young's equation, Equation 2.12, the water contact angle of the solid can be related to the Gibbs free energy change associated with the spreading.

$$\Delta G_{spread} = \gamma_{OW}(1 + \cos\theta) \quad (2.15)$$

By considering the result in Equation 2.15 it can be concluded that ΔG_{spread} will always be a positive number, indicating that the spontaneous spreading of oil over a surface in an aqueous environment is thermodynamically unlikely. It should also be noted that the free energy due to the oil spread would be zero if the water contact angle was 180° , a condition which never occurs in practice (Laskowski, 2001); confirming the results of Brown et al. (1958).

It may also be deduced from Equation 2.15 that the agglomeration of coal in an aqueous suspension through the addition of a hydrophobic binder, such as oil, would be less effective than previously imagined due to the tendency of the oil to remain as a droplet. However, fortunately, other characteristics of coal and the agglomeration system help to overcome this tendency for oil to remain as droplets. For example, a study by He and Laskowski (1992) showed that the pores on the surface of coal particles immersed in water may stay filled with air for a very long time due to micro capillarity effects. The presence of this trapped air promotes the spreading of oil on the coal surface as it effectively increases the hydrophobicity of the coal. Conversely, the pores on hydrophilic surfaces (such as minerals and lower rank coals) quickly fill with water serving to increase their wettability (by water) even further. The role of air on the surface of particles in aiding in selective agglomeration, specifically, was explored in a study by Allen and Wheelock (1992). In the study the effect of preparation techniques on the kinetics of oil agglomeration of fine coal was examined to establish whether air adsorbed on fresh coal particle surfaces affected the subsequent agglomeration. It was found that the presence of the air film appeared to increase both the initial rate and final extent of agglomeration. Therefore it was concluded in the study that the air facilitated the

wetting of the coal surface and simultaneously reduced the amount of oil required as the oil did not stay in droplet form (Allen & Wheelock, 1992).

2.4 Agglomerate Formation

In the previous section it was established that an oil droplet may attach to the surface of a particle in an aqueous environment if the conditions, thermodynamic and kinetic, allow for it. This adhesion of oil to the solid surface represents the first step in the formation of an agglomerate as the oil can then serve as a liquid binder between the particles on subsequent collisions. This liquid binder can hold particles by a combination of capillary and viscous forces (Iveson, et al., 2001).

This section explores the formation of agglomerates through the application of a liquid binder. The formation of agglomerates is primarily controlled by two factors: liquid content/availability and contacting time. Therefore this section is broken down into two sub-sections. The first section explores the effect of liquid content/availability on the formation and structure of agglomerates and the second section explores the kinetics of agglomeration in suspension.

2.4.1 Influence of Liquid Content

Newitt and Conway Jones (1958) and Barlow (1968) formulated a general description for the influence of liquid content on the mechanism of agglomeration using a liquid binder. This general description considered a three phase system of air (continuous phase), liquid (dispersed discrete droplets) and solid particles. However, it has become generally accepted to use this mechanism in selective agglomeration which involves a three phase system of water (liquid continuous phase), oil (secondary immiscible liquid in the form of dispersed discrete droplets) and solid particles (Capes & Germain, 1982; Capes & Sutherland, 1967). In this description, the influence of liquid content on the formation of agglomerates is described using four different regimes. These regimes are presented in Figure 2.5 and are in order of increasing liquid content.

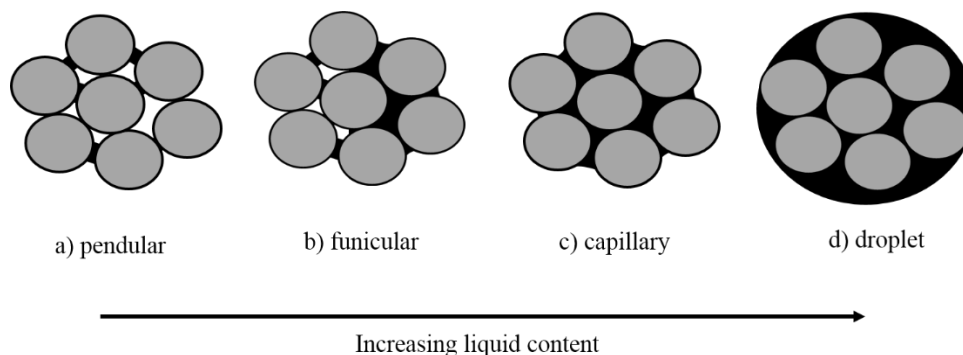


Figure 2.5: Schematic of an agglomerates in the a) pendular, b) funicular, c) capillary and d) droplet state. The solid particles (grey) are held together by a liquid binder (black) which either partially or completely fills the void space within the agglomerate. The liquid content of the agglomerates increases from left to right. Adapted from Drew (1978).

As depicted in Figure 2.5 the four states can be distinguished by the relative amount of oil within the agglomerate. A variable called the liquid saturation, s , can be used to relate the volume of the liquid in the void to the total void space of the agglomerate. In the pendular state, Figure 2.5a, the liquid saturation is about 0.25 and the particles are held together by discrete bridges or lens-shaped rings of oil at the point of contact (or the point of close approach), water being the continuous phase (Kapur, 1978; Kristensen & Schaefer, 1987). Once the liquid saturation exceeds 0.25 the liquid bridges begin to coalesce and the agglomerate structure changes from pendular to funicular, as depicted in Figure 2.5, and the agglomerate is held together by both liquid bridges and via capillary pressure (Pietsch, Hoffman, & Rumpf, 1969). When the liquid saturation moves past 0.8, discrete bridges can no longer exist however capillary pressure acts to hold the agglomerate together, and this is shown in Figure 2.5c as the capillary state. In the capillary state the strength of the agglomerate is at a maximum as any applied tensile stress has to overcome both the capillary pressure difference and surface tension of the liquid along the circumference of the agglomerate (Kapur, 1978). In this state, it is no longer useful to consider the individual particle-particle bonds but, rather, to consider the cohesive strength of the agglomerate as a whole. The final diagram in Figure 2.5 represents the result of over saturation of the binder. In this droplet state

the solids are suspended in oil and, thus, effectively completely removed from the continuous aqueous phase.

In practice, the optimum operating regime for a selective agglomeration process is the capillary state (Capes, 1980). This state is the preferred product state as the aim of an agglomeration process is to form spherical, discrete and large agglomerates which have considerable structural integrity. It should be noted, however, that the capillary state in Figure 2.5 represents an ‘equilibrium’ state in which there is sufficient time for the binder to achieve this distribution. This influence of time on the structure of the agglomerated product is considered further in the following section.

2.4.2 Kinetics of Agglomeration

Numerous fundamental investigations into the kinetics of agglomeration in suspension using a liquid binder have been carried out previously (Bemer, 1979; Blandin, Mangin, Subero-Couroyer, Rivoire, Klein & Bossoutrot, 2005; Bos & Zuiderweg, 1985; Kawashima & Capes, 1974; Kawashima & Capes, 1976). In each case, model systems were used to detail the growth of agglomerates. For example, Bemer (1979) agglomerated glass and Al-silicate powders suspended in carbon tetrachloride using glycerol/water mixtures as the liquid binder. Kawashima and Capes (1974; 1976) also investigated the agglomeration behaviour of silica sands, glass and calcium carbonate powders suspended in carbon tetrachloride. However, in these studies an aqueous calcium chloride solution was used as the liquid binder. Bos and Zuiderweg (1985) investigated the converse configuration with the aqueous phase constituting the suspending liquid. In this study, CaCO_3 suspended in water was agglomerated with kerosene (Bos & Zuiderweg, 1985).

From these fundamental studies, Bemer (1979) was one of the first to propose a model describing the kinetics of agglomeration in suspension. The model broke the agglomeration process down into a number of stages or regimes. Figure 2.6 depicts a general description of the growth regimes with a plot of agglomerate size as a function of agglomeration time.

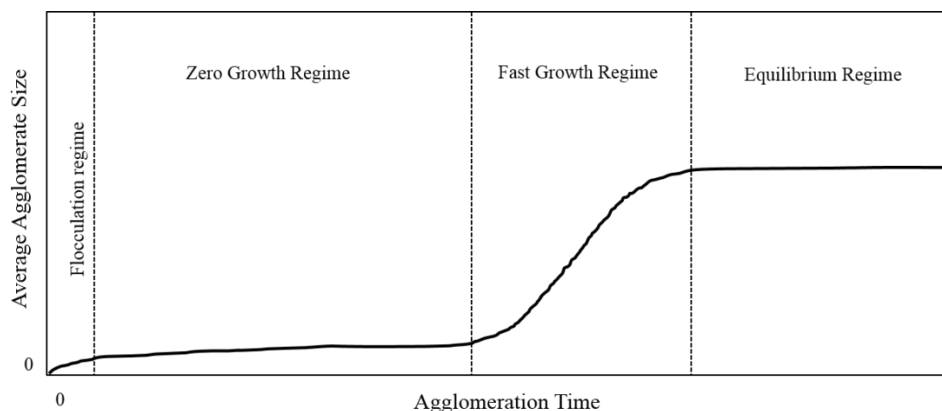


Figure 2.6: Growth regimes in agglomeration in suspension using a liquid binder. Adapted from Bemer (1979).

As can be seen in Figure 2.6, the first stage was called the flocculation regime. This flocculation stage was shown by Bemer (1979) to be quite rapid compared to the stages which follow. The second stage was denoted as the period of zero growth. The duration of this stage was considered to relate to the time required for the flocs to consolidate and for the excess binder to be squeezed out from the internal voids to the surface of the agglomerate, *i.e.* agglomerate compaction (Bemer, 1979). The movement of binder to the surface of the agglomerates signified the beginning of the next regime: the period of fast growth. It was proposed fast growth occurred in this stage due to agglomerate-agglomerate coalescence (Bemer, 1979). After the period of fast growth an equilibrium period was reached. As a result of this work, Bemer (1979) concluded that coalescence and breakage were the relevant mechanisms to describe the kinetics of agglomeration.

More recently, Blandin et al. (2005) formulated another general description of the kinetics of agglomeration in suspension. The model developed in this study generally agreed with that proposed by Bemer (1979). However, the authors of the former study distinguished only two stages, a wetting and nucleation stage followed by a period of growth and consolidation (Blandin et al., 2005). The authors also noted that the mechanism of wetting varied with the relative sizes of the particle and binder droplet diameters.

A limited number of studies have also been carried to specifically investigate the kinetics of agglomeration of coal in suspension using a hydrophobic binder (Cebeci,

2003; Rao & Vanangamudi, 1984; Skarvelakis & Antonini, 1995; Vanangamudi & Rao, 1984). These studies also formulated descriptions of the kinetics of agglomeration. However, in these studies, the growth of agglomerates was classified using the concept of rate equations. In each study it was found that the growth followed second order kinetics and a considerable effort was placed on describing the effect of process parameters such as binder dosage on the two constants of the second-order kinetic equation.

2.5 Emulsions

As mentioned in the introduction, a water-in-oil emulsion will be used as the hydrophobic binder in this work. Therefore, this section provides a review of fundamental emulsion theory. A general description of emulsion properties is presented initially. This is followed by a discussion on emulsion characteristics such as stability, surfactant type and viscosity. A particular focus will also be placed on high internal phase emulsions as it is this type of highly concentrated emulsion which will be used in this work.

2.5.1 General Properties

An emulsion is a dispersion of two partially miscible or immiscible liquids. The phase which is dispersed in the form of small droplets is referred to as the inner phase and the phase which remains continuous is referred to as the outer phase. The size of the droplets which constitute the inner phase are usually $>0.1\ \mu\text{m}$ in size (Adamson & Gast, 1997). Micro-emulsions can also be formed, however, in which the droplet size is in the range $0.01 - 0.1\ \mu\text{m}$ (Shaw, 2000).

The two common types of emulsions are oil-in-water and water-in-oil and a schematic representation of these is presented in Figure 2.7.

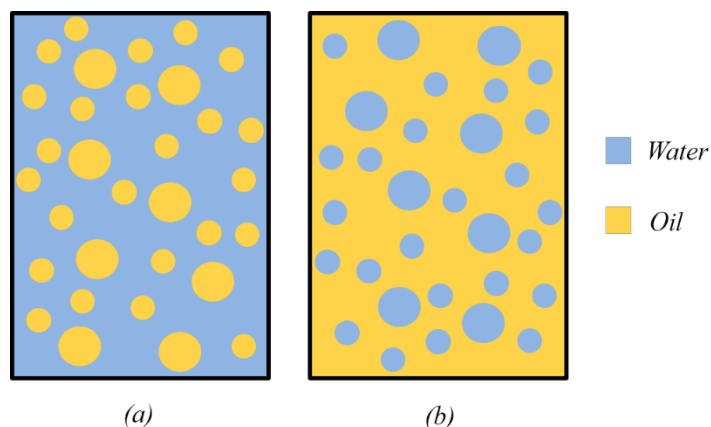


Figure 2.7: The two types of emulsions: a) oil-in-water and b) water-in-oil.

Figure 2.7a depicts an oil-in-water emulsion as droplets of oil are dispersed in a continuous phase of water. Figure 2.7b displays the opposite configuration of that in Figure 2.7a, showing water droplets dispersed in a continuous phase of oil, *i.e.* a water-in-oil emulsion. Effectively all applications of emulsions, for example in pharmaceuticals, cosmetics, food and paints, consist of one of these two types of emulsions. The two types of emulsions may be distinguished by their texture, ability to disperse oil or water-soluble dyes, dilution with oil or water and conductivity (Shaw, 2000).

Other than the composition of each phase, the relative volumes of the inner and outer phases are also important in describing an emulsion. A parameter called phase volume ratio, ϕ , is usually used to characterise this property and is calculated by the ratio of the volume of the inner, dispersed phase to the total volume of the emulsion (Cameron, 2005). For example in an emulsion where $\phi = 0.4$, 40% of the volume of the emulsion is occupied by the dispersed phase. This property is important as it influences the state of the droplets in the internal phase which, in turn, affects the viscosity of the emulsion (Adamson, 1990). The viscosity of emulsions is considered in further detail in a subsequent section.

2.5.2 Stability

Emulsions are inherently thermodynamically unstable mixtures. Indeed, if an emulsion is produced by simply mixing the two immiscible phases together, phase separation will usually be rapid, especially if the concentration of the dispersed

phase is high. This fast phase separation occurs because coalescence of the dispersed phase is favourable as it results in a reduction in the total interfacial area and hence in the total free energy of the system (Galvin, et al., 2001).

Therefore, to create a more stable emulsion a surfactant or emulsifier is required. However, even in the presence of surfactants, emulsion stability is still an issue of paramount importance. De-stabilising processes such as creaming and droplet coalescence occur which act to break down the emulsion. Creaming results from density differences in the phases and causes the emulsion to separate into a more concentrated and a more dilute emulsion phase (Adamson, 1990). Droplet coalescence results from droplet collisions and can, therefore, be associated with creaming (Shaw, 2000). The continuation of droplet coalescence can result in the complete separation of the two immiscible phases such that only a single, continuous interface exists. The assessment of emulsion stability usually involves methods which count either the number or size distribution of the dispersed droplets within the emulsion (Adamson, 1990).

As mentioned above, the use of emulsifiers substantially improves the stability of the emulsion. Emulsifiers enhance stability by forming an adsorbed film around the dispersed droplet and by reducing the interfacial tension between the phases. Other factors which also contribute to the stability of emulsions include: a mechanically strong interfacial film, a relatively small internal phase volume ratio ($\phi < 0.74$), a narrow droplet size distribution, and a high Newtonian viscosity (Shaw, 2000).

2.5.3 Surfactants/Emulsifiers

As mentioned in the above section, surfactants are required to improve the stability of emulsions by acting at the interface between the two immiscible phases. Figure 2.8 presents a schematic representation of an oil droplet in water stabilised by an emulsifier.

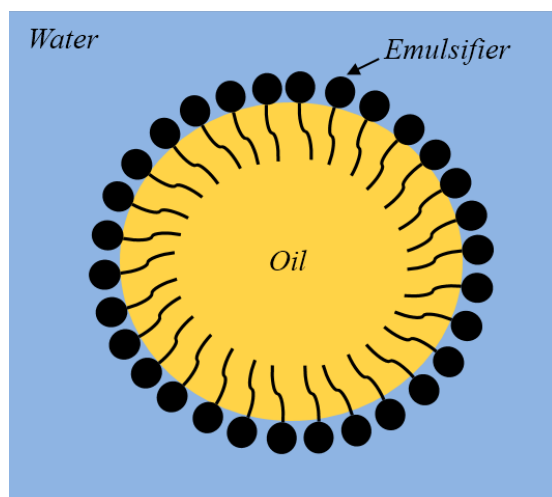


Figure 2.8: An oil droplet in water stabilised by an emulsifier.

Surfactants or emulsifiers are usually organic compounds which are amphiphilic which means they have a hydrophobic group, the ‘tail’ of the emulsifier depicted in Figure 2.8, and a hydrophilic group, the ‘head’ of the emulsifier depicted in Figure 2.8. In the reverse configuration of that depicted in Figure 2.8, *i.e.* a water droplet dispersed in oil, the hydrophilic head sits inside the water droplet and the hydrophobic tail extends into the continuous phase of oil.

The hydrophobic component of an emulsifier usually consists of a hydrocarbon chain which can be branched, linear or aromatic. The hydrophilic component of the emulsifier consists of a polar group which can be ionic or non-ionic (Shaw, 2000). Depending on the structure of the surfactant, it may be oil-soluble, water-soluble or both. An example of a water-soluble surfactant which is commonly used is sodium stearate. This surfactant consists of a carboxylate head and a long hydrocarbon chain.

As there are many different types of emulsifiers the appropriate selection for a given application is essential. The main criteria for this selection is the desired configuration of the emulsion, *i.e.* water-in-oil or oil-in-water. That criteria is based on Bancroft’s rule which states that the phase which will most readily remain continuous is also the phase in which the emulsifier should be more soluble (Bancroft, 1913). So, if the continuous phase is organic, an organic-soluble

emulsifier must be selected. However, if an aqueous solution is to form the continuous phase, a water-soluble emulsifier must be selected.

The tendency for an emulsifier to be water-soluble or oil-soluble has been expressed on an empirical scale of HLB (hydrophile-lipophile balance) numbers to facilitate the selection of the appropriate emulsifier for a given application (Shaw 2000). The HLB scale goes from 0 – 20, with a zero value corresponding to the most lipophilic emulsifiers and a value of 20 corresponding to the most hydrophilic emulsifiers. Following on, Table 2.1 presents the HLB values for various applications.

Table 2.1: HLB values for various applications.

<i>HLB Number</i>	<i>Application</i>
3 - 6	Water-in-oil emulsion
7 - 9	Wetting Agent
8 – 15	Oil-in-water emulsion
13 – 15	Detergent
15 – 18	Solubiliser

As shown in Table 2.1, to create a water-in-oil emulsion an emulsifier with a low HLB number is required. However, to create an oil-in-water emulsion an emulsifier with a relatively high HLB number, in the range of 8 – 15 is required.

2.5.4 High Internal Phase Emulsions

2.5.4.1 Description

Shaw (2000) states that there are two main factors which determine the configuration of an emulsion. The first factor was discussed above and relates to the nature of the emulsifier. The second factor relates to the relative volume of the two phases. That is, the phase with the higher volume is more likely to form the continuous phase but it does not necessarily have to.

Emulsions can be made in which the volume of the dispersed phase is greater than the continuous phase. These emulsions are called high internal phase (HIP) emulsions and are usually defined by an internal, dispersed phase volume ratio, ϕ ,

greater than 0.74 (Cameron, 2005). This value of $\phi = 0.74$ is significant as it represents the maximum volume fraction the dispersed phase could occupy if the internal droplets were closely packed mono-sized spheres (Shaw 2000). Now, as HIP emulsions exceed this limit and, in fact, can be made up to volume fractions in excess of $\phi = 0.95$ it is generally assumed that the droplets within the emulsion are not uniform in size and/or are deformed into polyhedra (Cameron, 2005, Lissant, 1970). A non-uniform droplet size distribution allows for high internal, dispersed phase volumes as smaller droplets can pack inside the gaps of larger droplets. Deformation of the internal droplets into polyhedra also allows for high internal phase volumes as the contact area between droplets becomes a flat surface (Adamson, 1990). This deformation is considered to occur as the thin film separating the two dispersed droplets may have a lower surface tension than that of the bulk.

2.5.4.2 Applications

High internal phase emulsions find applications in a diverse range of areas such as food preparation, fuels, oil recovery, cosmetics, explosives and polymer chemistry (Cameron, 2005; Reynolds, McGillivray, Mata, Yaron and White, 2010). HIP emulsions are used in these various applications due to the benefits which result from their unique formulation and structure. For example, the concentrated nature of the droplets means that the emulsion behaves more like a gel, therefore suppressing instabilities which result from sedimentation or creaming (Shaw, 2000). Also, water-in-oil emulsions contain a lower organic content than their non-HIP emulsion alternatives which is beneficial in an environmental and economic sense (Dunstan, Fletcher & Mashinchi, 2012). Furthermore, it has been shown recently that chemically incompatible aqueous species can be compartmentalised in separate droplets of a mixed water-in-oil emulsion (Dunstan & Fletcher, 2011). Also, when using water-in-oil emulsions, the continuous oil layer can be used as a barrier between the water droplets and the external surrounds. Finally, HIP emulsions have been used as a means of templating highly porous material (Cameron, 2005). In this application, the porous material is formed by solidifying the continuous phase of the emulsion before removing the dispersed droplets by drying.

2.5.4.3 Preparation

As HIP emulsions defy the natural tendency for the phase with the higher phase volume to form the continuous phase certain measures must be taken during their preparation. These measures are required to ensure catastrophic phase inversion does not occur. Catastrophic phase inversion occurs when the dispersed phase rapidly becomes the continuous phase and usually results from a sudden shift in the relative volume fractions of the two phases (Dunstan, et al., 2012). Therefore, to avoid catastrophic phase inversion during the preparation of HIP emulsions the dispersed phase must be added incrementally to the continuous phase. Careful selection of the emulsifier is also essential to avoid phase inversion at high dispersed phase volume fractions, for the reasons described in the section on emulsifiers. Furthermore, due to the extremely high interfacial area of between the two phases of the emulsion a high concentration of emulsifier is usually required.

Numerous accounts can be found in the literature for batch, lab-scale preparation of HIP emulsions and, as discussed above, involve the incremental, usually drop-wise, addition of the dispersed phase to the continuous phase under constant agitation from a mixing device (Cameron, 2005; Peker, Bora, & Över, 2001; Reynolds et al., 2010). A continuous process for the preparation of high internal phase water-in-oil emulsions has also been developed which involves sparging air into a two phase system of oil and water (Galvin et al., 2001). In this case, the air sparging provided a mechanism for the incremental addition of the dispersed aqueous phase into the oil phase.

2.5.5 Emulsion Viscosity

In dilute emulsions, $\phi < 0.74$, the inner phase exists as spheres and as such, the viscosity, μ (Pa s), of the emulsion is often treated using the Einstein limiting law (Adamson, 1990),

$$\mu = \mu_c(1 + 2.5\phi) \quad (2.16)$$

where μ_c is the viscosity of the continuous phase.

Also, using Equation 2.16 and the definition for the relative viscosity of an emulsion, μ_r , which is,

$$\mu_r = \frac{\mu}{\mu_c} \quad (2.17)$$

the relative viscosity of the emulsion can be shown to increase linearly with the volume fraction of the dispersed phase (Einstein, 1906, 1911),

$$\mu_r = 1 + 2.5\phi \quad (2.18)$$

Now, as mentioned, the above relation is only useful for dilute emulsions. The more concentrated, high internal phase emulsions are not Newtonian and, therefore, their viscosity exhibits a dependence upon shear rate (Adamson, 1990). That being said, there is still a link between the viscosity of high internal phase emulsions and ϕ but it relates to the droplet size and size distribution (Pal, 2006).

2.6 Summary

This chapter provided a review of relevant surface chemistry concepts. Of particular importance was the concept of wettability which described the ability of a liquid to maintain contact with a solid surface. This phenomenon was important as it highlighted the underpinning mechanism for selective agglomeration of hydrophobic particles from an aqueous mixture of hydrophobic and hydrophilic particles.

The fundamental process of agglomeration in suspension using a liquid binder was also considered in this chapter. The influence of the liquid content on the structure of the agglomerated material was illustrated using four different regimes. The capillary state in which the void space within the agglomerate is effectively saturated was discussed to be the desired regime for the selective agglomeration process. The influence of contacting time on the growth and structure of agglomeration, *i.e.* agglomeration kinetics was also reviewed.

The chapter concluded with a discussion on emulsions. It was demonstrated that the stability and structure of an emulsion was primarily dependent upon the selection of the correct emulsifier. To make a water-in-oil emulsion an emulsifier

with a low HLB value is required which means it is soluble in organic liquids. A description of high internal phase emulsions was also presented along with a discussion of their applications and method of preparation.

Chapter 3

Selective Agglomeration of Fine Coal

3.1 Introduction

The purpose of this study was to establish an economic binding agent suitable for selective agglomeration, achieved by recognising the required functionality of the liquid binder, and in turn maximizing the necessary attributes. It is noted, however, that the performance of the selective agglomeration process is not only influenced by the liquid binder but also other process parameters such as the pulp density, agitation duration and agitation intensity. This chapter therefore reviews previous work on the selective agglomeration process to illustrate the influence of each of these operating parameters. In particular, this chapter focuses on the application of the selective agglomeration to the processing of fine coal, *i.e.* the system to be studied in this work. Indeed, the majority of the literature in this area has focused on the practicalities of the selective agglomeration process with reference to fine coal due to its potential application in industry. It should be noted, however, that selective agglomeration is usually referred to as ‘oil agglomeration’ as oil has traditionally always been used as the liquid binder.

This chapter begins with a discussion about the important parameters in the selective agglomeration of fine coal including: binder concentration, binder type, pulp density and agitation intensity and duration. The chapter then concludes with a review of variations on the traditional fine coal agglomeration process which have been investigated in the past.

3.2 Important Parameters

As mentioned in the introduction to this thesis, the process of selective agglomeration has received considerable attention in the field of coal processing due to its impressive selectivity and separation efficiency. Therefore, an extensive volume of literature exists on the subject of fine coal agglomeration (Aktas, 2002; Bensley, Swanson, & Nicol, 1977; Brisse & McMorris, 1958; Garcia, et al., 1995; Swanson, et al., 1977). This section reviews the findings of this work and summarises the influence of the important process parameters on the outcome of an agglomeration process. It should be noted that in this section, the terms ‘oil’ and ‘binder’ are synonymous because in all previous studies the binder was a pure oil.

3.2.1 Binder dosage

As the majority of the previous work into the selective agglomeration of fine coal was from an industry standpoint, a considerable emphasis was placed on the quantity of binder required to process a given coal feed. This emphasis existed as the cost of the oil required per tonne of coal was one of the decisive factors in the economic feasibility of the process. Consequently, a large volume of literature exists which illustrates the effect of binder dosage (Aktas, 2002; Bensley, et al., 1977; Capes, et al., 1972; Cebeci & Sonmez, 2004; Garcia, et al., 1995; Laskowski & Yu, 2000; Shrauti & Arnold, 1994; Sirianni, et al., 1960).

As illustrated in the previous chapter, the binder acts on the surface of the hydrophobic particles. Therefore, the dosage of binder required to achieve agglomeration is a function of the composition and size distribution of the feed. The composition, or ash content, of the feed influences the binder dosage as it indicates the portion of the feed which will participate in the agglomeration process. The size distribution of the feed, or more specifically the size distribution of the carbonaceous material, influences the dosage as it determines the specific surface area on which the binder must act. Now, due to the influences of these coal feed characteristics, there is no universal dosage which is appropriate for all feeds. However, through the extensive testing which has been completed, some general regimes have emerged that can predict the structure of the agglomerate product depending on the amount of oil added (Capes & Germain, 1982;

Sirianni, et al., 1969). These more practical regimes can be compared to those presented in the previous chapter in Section 2.4.1 to illustrate the fundamental structure of the agglomerate at a particle level. To facilitate the discussion of these dosage regimes, Figure 3.1 presents the product structure in the three different regimes. Also presented in the figure is a fine coal feed to serve as a comparison.

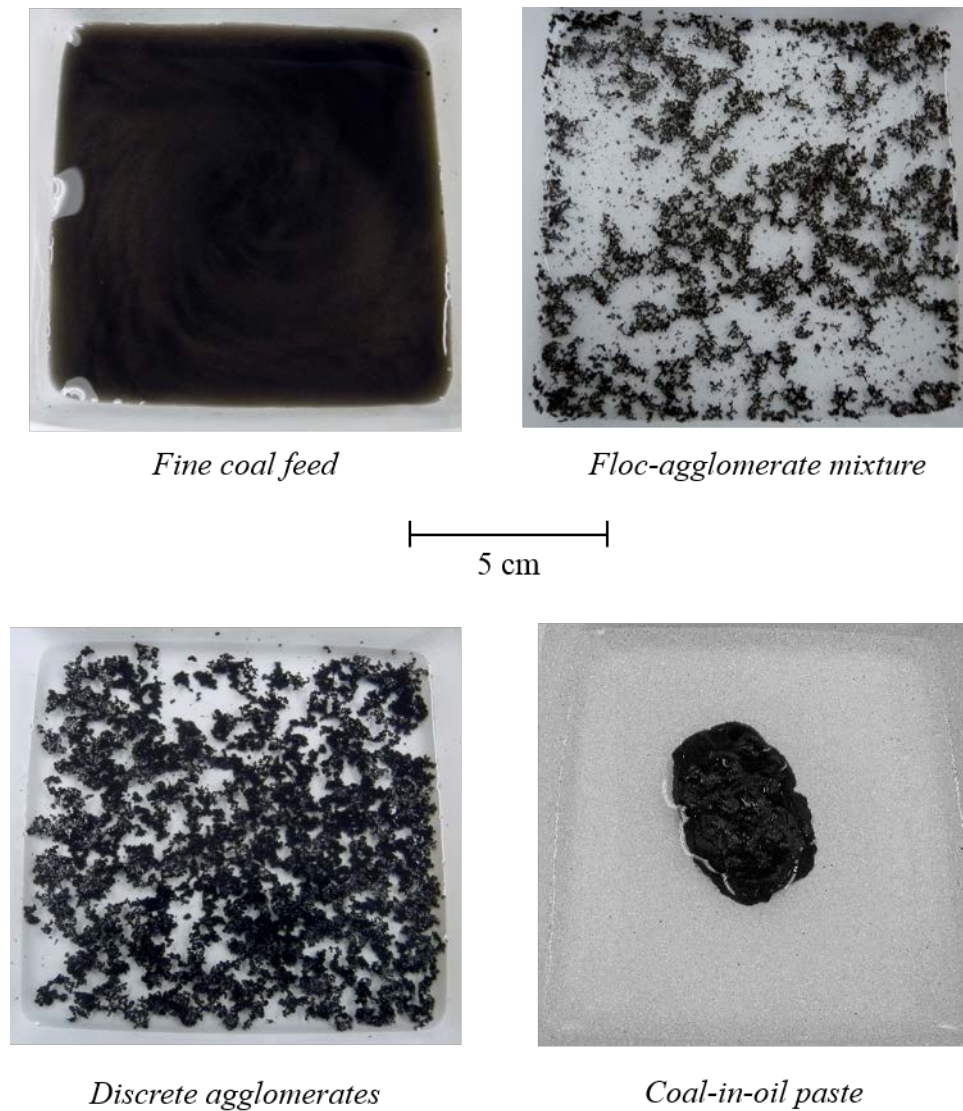


Figure 3.1: Product structure regimes as a function of binder dosage.

The coal feed presented in Figure 3.1a clearly shows that initially the individual, discrete particles cannot be differentiated from the bulk liquid due to their small size. Moreover, the liquid appears black due to the dispersion of these fine particles. Considering now Figure 3.1b, the floc-regime, a distinct variation in the appearance of the coal can be seen.

Even at the low dosages which characterise this first regime, discrete particle structures can be distinguished from the surrounding liquid. Furthermore, due to the collection of the fine particles, it can be seen that the suspending liquid now appears clear. Generally, dosages of 3 – 5 wt% result in the unconsolidated product pictures in Figure 3.1b (Darcovich, et al., 1988). By now comparing the structure observed in Figure 3.1b to the growth mechanism presented in Section 2.4.1 it can be assumed that this low binder dosage is equivalent to a liquid saturation less than 0.25 where only pendular bridges exist between the particles (Capes & Germain, 1982). These floc-like agglomerates are difficult to recover due to their poor integrity. In addition, there is usually considerable moisture in the final product because of the tendency to retain water (Steedman & Krishnan, 1987). Due to these undesirable product attributes dosages of this low level are not practical to use.

As the binder dosage is increased beyond 5 wt% the flocs observed in the floc-regime consolidate and form more compact agglomerates. This structural change occurs because the increased binder availability means that there can be an increased number of oil junctions per particle. Moreover, as explained in the growth mechanism in Section 2.4.1, as the binder dosage and, thus, liquid saturation increases the pendular bridges between the particles begin to coalesce into a network structure (Steedman & Krishnan, 1987). At dosages in the range of 5 – 15 wt% particles will be joined via both pendular bridges and capillary pressure and agglomerates will be small as their size is limited by oil availability and agglomerate strength. However, as the oil dosage reaches 15 – 20 wt% a peak in strength and sphericity is observed (Capes & Germain, 1982). This well agglomerated state is depicted in Figure 3.1c and represents the attainment of the capillary state in the growth mechanism. As can be seen in the figure, these agglomerates are visibly discrete and due to their large size can be de-watered and separated from the still finely dispersed mineral particles with relative ease. Due to these desirable characteristics, dosages in the range of 10 – 20 wt% are generally used in practice.

Finally, Figure 3.1d represents the result of an excessive binder dosage as the agglomerates have entered the droplet regime in the growth mechanism. This means the agglomerates exist as pasty lumps in which the solids are essentially dispersed in a continuous phase of oil (Capes & Germain, 1982). This regime usually results from

dosages in excess of 20 wt%. Dosages this high are not used in practice due to the difficulties associated with the recovery of the product. Moreover, the cost of the oil binder at these high levels is exorbitant.

3.2.2 Binder Type

As mentioned previously, the only type of binder used in the past for the selective agglomeration of coal was pure oil. However, within this range a large variety of oils were tested. This section, therefore, reviews the influence of oil type on the selective agglomeration process.

The type of oil used in a selective agglomeration process has been shown to significantly influence the outcome of the process. This influence exists because the oil must not only be able to effectively recover the combustible material in feed, but simultaneously reject the mineral matter. In other words, the oil must possess a certain degree of selectivity. To achieve this selectivity it must be thermodynamically favourable for it to wet the surface of the hydrophobic coal particles but not favourable for it to wet the surface of the mineral particles. Section 2.3 explored the conceptual and fundamental nature of wetting in an aqueous environment and this section now goes on to explore how these fundamental concepts apply to selective agglomeration in a more practical sense. Also presented in this section is a description of how other characteristics, such as the density and viscosity, of the oil selected affect its performance as a binder in selective agglomeration.

Sun and McMorris (1959) investigated the influence of oil density and viscosity on the recovery of coal in an agglomeration process. As a result of the findings in this study it was concluded that oils of medium density were the most suitable for optimal recovery as heavier oils could not be readily dispersed under the conditions of the experiment, *i.e.* short mixing times and lighter oils did not have the strength to form and hold good agglomerates (Sun & McMorris, 1959). However, it was subsequently demonstrated by Capes and Germain (1982) that heavy oils can achieve comparable recoveries to that of medium density oils if the heavy oils are given sufficient agitation time. Through the application of extended mixing times for the heavy oils, Capes and Germain (1982) were able to show that the decrease in recovery attained by Sun and McMorris (1959) was related to the agglomeration kinetics of the system rather than the surface chemistry of

heavy oils. Indeed, several investigators have reported high recoveries with heavy oils when used in combination with the suitable operating parameters such as long mixing times or intense mixing conditions to optimise the droplet-particle contact (Robbins, Winschel, Amos, & Burke, 1992; Tsai, 1982).

Thus far the ability of different oils to recover combustible material has been discussed; however no indication was given as to whether this recovery was achieved in a selective manner. The ability of an oil to be selective, *i.e.* reject mineral matter is of equal importance to product recovery as the overriding goal of the selective agglomeration process is to achieve a separation.

Lighter oils, such as pentane, hexane and diesel fuel oil, have been shown many times over to have good ash rejection capabilities and therefore the required selectivity for the beneficiation of coal (Aktas, 2002; Capes & Germain, 1982; Capes, et al., 1977; Tsai, 1982). However, the results for heavier oils, $\rho > 900 \text{ kg/m}^3$, are not so consistently good. In an investigation into the selectivity of different oils, Capes, et al. (1977) illustrated that the product ash levels were, in general, substantially higher for heavy oils than those obtained for lighter oils; however, at the same time, the results for heavy oils were somewhat erratic. Some heavy oils displayed ash rejection capabilities comparable to that of light oils, whereas others clearly had lower selectivity (Capes, et al., 1977). The authors of the work attributed this behaviour to the complex and variable composition that is common of heavy oils such as, tars, bunker fuels, heavy crudes, coal tar and its derivatives. The complex composition they refer to is the mix of aromatics, naphthenes, and to a lesser extent paraffins, olefins, along with high amounts of nitrogen, sulfur, oxygen and heavy metals. The presence of this high level of inorganic constituents was suggested as the reason for the decreased selectivity of the heavy oils as they are considered to have the ability to condition to surface of the ash particle (Capes & Germain, 1982). This conditioning would render the ash particles hydrophobic, thus making them undiscernible from the hydrophobic coal particles.

The idea that the presence of polar compounds in the oil may affect the ash content of the final agglomerated product was considered in more detail in a study by Keller and Burry (1987). They were able to show that a linear relationship exists between the ash content in the agglomerated clean coal and the oil/water interfacial tension. More specifically,

they found that the ash content was higher for hydrocarbons within the 30 – 40 mJ/m² interfacial tension range and decreased for oils with a higher interfacial tension with water. This result agreed with and further explained the results obtained by Capes, et al. (1977) and confirmed the proposition that lighter oils have better ash rejection capabilities. That is, the interfacial tension between aliphatic hydrocarbons and water slightly exceeds 50 mJ/m² and any deviation from this indicates the presence of polar compounds which can interact with water (Laskowski, 2001). As mentioned in Section 2.2.4, this interaction between the heavy (polar) constituents and the water may be via dispersion forces and hydrogen bonding. Aromatic hydrocarbons also have an additional means of interacting with water which results in their interfacial tensions dropping a further 15 mJ/m² (Laskowski, 2001). This interaction is a polar pi interaction which occurs between a polar molecule (such as water) and a quadrupole moment in a pi system (such as in benzene). Now, even though this section has focussed on the interaction of the hydrocarbon with water it should be remembered that the very same interactions can also act to form associations between heavy oil and polar mineral surfaces.

Therefore, to ensure good selectivity highly refined and light oil should be used. This is because the heavy constituents can not only lower the interfacial tension between the oil and water phases but also interact with hydrophilic, polar surfaces in a similar manner as water *i.e.* through hydrogen bonding and dispersion forces. Moreover, it may be concluded that pure paraffin oils would be most efficient as they have the highest interfacial tension with water and this has been shown in literature (Capes & Germain, 1982; Sun & McMorris, 1959).

3.2.3 Pulp Density

The pulp density of an agglomeration system is defined as the concentration of solids in the suspension. A wide range of pulp densities have been studied in the past. This range extends from as low as 5 wt%, for example in the laboratory scale Trent Process; to high pulp densities of 50 weight%, for example in the laboratory scale Spherical Agglomeration Process and the pilot scale process developed by BHP (Mehrotra, et al., 1983; Swanson, et al., 1977). As a result of the wide range examined it has been concluded that the pulp density does not have a major influence on the final product of a selective agglomeration process. That is, it has been demonstrated that product

agglomerates can be dewatered and de-ashed to comparable levels regardless of pulp density providing other process variables are modified to compensate (Capes & Germain, 1982). For example, if a low pulp density is used, which is desirable to reduce entrapment of mineral particles in the agglomerates, prolonged mixing is required to ensure that the necessary number of contacts between particles can occur (Steedman & Krishnan, 1987). Indeed, it is more common for a high pulp density to be used as it ensures adequate contact between the constituents within a reasonable time and reduces the volume of water that must be handled.

3.2.4 Agitation Intensity and Duration

The kinetics and mechanics of agglomerate growth has been described in detail already in Section 2.4.2. This section, therefore, provides a review on the link between agitation intensity and duration and the consequences of the selected mixing regime on the quality of the product.

In general, an inverse relationship exists between the agitation speed and duration as there must be an increase in one when the other experiences a decrease if a consistent product recovery and quality is to be maintained. Capes, et al., (1970) demonstrated this relationship quantitatively when they showed that the time required to complete agglomeration in a blender is approximately 8 min when operating at 6000 rpm and increases to 18 min when operating at 3000 rpm. This flexibility in the mixing scheme has meant that various sets of operating conditions have been employed in the past in selective agglomeration studies.

In early applications of the selective agglomeration process, for example the laboratory Trent process low agitation rates combined with extended agitation times were employed. However, more recently, the use of high speed blenders has been favoured due to the more rapid processing times required. Although, it has also been shown that higher agitation rates combined with relatively long mixing times increase the combustible recovery and decrease the ash content of the final product (Sirianni, et al., 1969). These conditions produced a high quality product as the high shear allowed for a high level of re-dispersion and reformation of the agglomerates which in turn increased the rejection of hydrophilic material (Sirianni, et al., 1969). It should be noted, however, that high

shear usually limits the final size of agglomerates to relatively small diameters (Steedman & Krishnan, 1987).

It is important to remember that while agitation speed and duration are linked and can be made to compensate each other; individually, both parameters have the capability to affect product quality and recovery. Capes and Germain (1982) highlighted the importance of agitation time on the ability of various oils to recover bituminous coals. They were able to improve the results of Sun and McMorris (1959), who had reported a decrease in combustible recovery for oils with a high specific gravity ($> 0.85 \text{ g/cm}^3$) for a constant agitation rate and duration. This improvement in combustible recovery was achieved by increasing the agitation time relative to the time used for the lighter oils as to allow for complete dispersion of the heavy oil.

3.3 Variations to Traditional Selective Agglomeration Processes

The introduction of the water-in-oil emulsion as the binder in the selective agglomeration of coal is highly innovative, representing a variation to the traditional selective agglomeration process. This section reviews other variations to the traditional process which have been investigated in the past.

3.3.1 Oil-in-Water Emulsions

A common criticism of the traditional selective agglomeration process is the high energy inputs needed to cause phase separation¹. So in an attempt to address this problem some agglomeration processes, most notably the one developed by BHP, included a pre-emulsification of the oil (Nicol & Swanson, 1980). Bensley et al., (1977) showed that energy efficiency could be increased through efficient emulsification of the oil phase prior to its addition to the raw coal pulp. In the study the authors employed a Silverson mixer/emulsifier operating at 13800 rpm (free running speed) for 3 min to produce emulsion droplets of approximately 3 – 5 μm in size. Their results illustrated a dramatic reduction in inversion time for low oil dosages when pre-emulsification was used.

¹ In this context phase separation is defined as the point at which all the combustible material has been effectively removed from the aqueous phase by becoming part of an oil-based agglomerate. Phase separation in selective agglomeration can be observed visually as the aqueous suspension changes colour from a dark grey/black liquid to a light grey/white liquid. The mixing time required to reach the phase separation is commonly called the inversion time.

However this advantage diminished at higher oil dosages. A small improvement (2-3%) in recovery of carbonaceous material as a result of emulsification was also observed for the entire range of oil dosages. Interestingly, they found that decreasing the size of the emulsion droplet led to an even shorter inversion time and that the reduction to sizes as small as 3 – 5 μm appeared to have no kinetic penalties through electric double layer repulsion hindering the coalescence rate.

In the study by Bensley, et al., (1977), no surfactants were used in the formation of the emulsion, only high shear mixing. In contrast, Laskowski and Yu (2000) investigated the effect of a surfactant induced emulsification of oil on the selective agglomeration process. The authors suggested that if an appropriate surfactant was selected, the interfacial tension between oil and water may be reduced and this would facilitate the spreading of oil droplets on the coal surface. The surfactants used in this study were sodium dodecyl sulfate (SDS) and dodecylamine (DDA). Both surfactants were prepared in an aqueous solution to concentrations of $3.4 \times 10^{-4} \text{ M}$ and $5.4 \times 10^{-4} \text{ M}$ respectively. The results from this study showed that a high recovery of coal could be obtained using very low oil dosages (0.5-5 wt%). This result represented a significant reduction in the oil dosage that was thought to be needed in agglomeration. Laskowski and Yu (2000) also noted that the surfactant emulsified droplets were smaller than in the emulsion produced by only mechanical agitation.

In the same work, Laskowski and Yu (2000) described the change in electrokinetic properties of the oil droplet and thus the particle-droplet interaction as a result of the surfactant addition. It was this change in electro-kinetic potential which also allowed the authors to suggest that the addition of an appropriate cationic surfactant may lead to the recovery of low-rank/oxidised coals (as they are characterised by more negative electrokinetic potential values). These coals are normally more difficult to retrieve by agglomeration due to the reduced hydrophobicity of their surfaces.

3.3.2 Other Reagents

In the study by Laskowski and Yu (2000) discussed in the preceding section, other types of reagents were also tested in the agglomeration process. Several flocculants were used including, polyacrylamide (PAM) and polyethylene oxide (PEO) and totally hydrophobic

lattices (FR-7A and UBC-1). The results of the tests showed that hydrophobic lattices and the conventional flocculants can aggregate very hydrophobic coals (but not lower rank coals). Also, the less hydrophobic coals could be agglomerated by the PAM flocculent.

An interesting study conducted by Raichur, Misra, Bukka and Smith (1996) involved the use of a highly hydrophobic and negatively charged bacterium called *Mycobacterium phlei* in an attempt to recover coal. In agglomeration experiments *M.phlei* displayed a high level of selectivity and resulted in the formation of heavy compact flocs which settled out of suspension quite quickly. The result of the flocculation was processed using a column flotation cell and a successful separation was achieved as a result. No comparison was made, however, between the results obtained using *M.phlei* and conventional oil.

3.3.3 Ash Agglomeration

Ash (or reverse) agglomeration was developed on the laboratory scale in an attempt to avoid waste slurries of fine tailings (Capes, et al., 1977). In this process the ash-forming material is removed from a hydrocarbon suspension of feed coal as discrete agglomerates, while the cleaned coal remains in the oil suspension. As with the conventional process, the agglomeration results from intensive mixing, but in this case the removal of oil from the ash surface is the goal. The binder added is, therefore, an aqueous bridging liquid and the quantity required depends on the moisture content of the feed slurry (Capes & Germain, 1982). Coarse inert adsorbents are also used in the reverse agglomeration process to seed the agglomerates and are usually added in a secondary process of gentle mixing. The product from ash agglomeration is an oil slurry which may be transported by pipeline, used as colloidal fuel or as a feed to another conversion process (Capes, et al., 1977)

3.4 Summary

In this chapter a review of the past experiences with the selective agglomeration process was presented. In particular, the review focused on the application of the selective agglomeration process to fine coal.

The parameters of paramount importance were shown to be the composition and dosage of oil used in the process because these parameters determined the structure and quality of the agglomerated product. Pulp density and the mixing regime used were also shown to influence the outcome of an agglomeration process. However, these were illustrated to be less significant in defining the quality of the product as excellent separation and product recovery were shown to be possible over a broad range of pulp densities and mixing conditions.

Variations to the traditional selective agglomeration process were also discussed in this chapter. Pre-emulsification of the oil binder into the suspending liquid was shown to reduce the time and oil required to achieve agglomeration. A discussion on the other binders which have been tested in the past was also presented. These included polyacrylamide, polyethylene oxide, totally hydrophobic lattices and a hydrophobic, negatively charged bacterium.

Chapter 4

Agglomeration using Proposed Water-in-Oil Emulsion

Contribution to the Research

The table below indicates the contribution of each person to the research.

Contributor	Primary Contribution
van Netten, K.	Collaborator in design of experimental program of work, carried out experimental program of work, and data analysis
Galvin, K. P.	Co-supervisor, collaborator in design of experimental program of work, proof reading of thesis chapter
Moreno-Atanasio, R.	Supervisor, proof reading of thesis chapter

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Roberto Moreno-Atanasio

.....
Kim van Netten

4.1 Introduction

Pure oil binders have been shown to be highly effective in separating coal from an aqueous mixture of coal and mineral particles through selective agglomeration (Capes & Darcovich, 1984). Pure oil binders, such as diesel, preferentially wet and agglomerate only the hydrophobic coal particles, thus allowing for recovery using a screen separation (Steedman & Krishnan, 1987). However, as noted in Chapter 1, the processes in which pure oil binders are used suffer very poor economics and hence, cannot be used in commercial coal preparation (Swanson, et al., 1977). Therefore, this work focused on the development of a new, cost-effective binder; a high internal phase (HIP) water-in-oil emulsion.

This chapter details the initial work carried out with the new emulsion binder. As this was a novel application of a HIP emulsion, this work was vital in forming a basis for understanding the new agglomeration process. The work also gave an indication to whether the aim of producing a high quality, agglomerated product at a greatly reduced oil dosage was achievable. Presented initially however is a quantitative description of the substitution theory which illustrates the reductions in the oil dosage which may be achieved using the new emulsion binder.

4.2 The Substitution Theory

Figure 1.4 in Chapter 1 first introduced the concept behind the substitution theory with a comparison between agglomerates made from a pure oil binder and a HIP water-in-oil emulsion binder. In this figure, both binders were shown to fill the void space within the agglomerates such that the space was effectively saturated. Now, as was noted in Chapter 1, this comparison was important because it illustrated the function of the dispersed water droplets within the emulsion in filling a space and thus, the potential for a reduction in the amount of oil required to form agglomerates. Following on from this qualitative description, this section presents a theoretical quantification of the reduction in the oil dosage required to achieve agglomeration.

A theoretical quantification of the reduction can be calculated by considering the composition of the emulsion used. For example, a HIP water-in-oil emulsion which has a dispersed, aqueous phase volume fraction of 0.90 could theoretically achieve a 10-fold reduction as only 1/10 th of the binder is organic liquid. In other words, only 1/10 th of the void space within the agglomerate is filled by oil as opposed to all of the void space when a pure oil is used. This calculation was repeated for emulsions of varying compositions and the results were used to produce Figure 4.1. Figure 4.1 depicts the relationship between the aqueous phase volume fraction of the emulsion and the theoretical reduction in the volume of oil required to form agglomerates relative to pure oil.

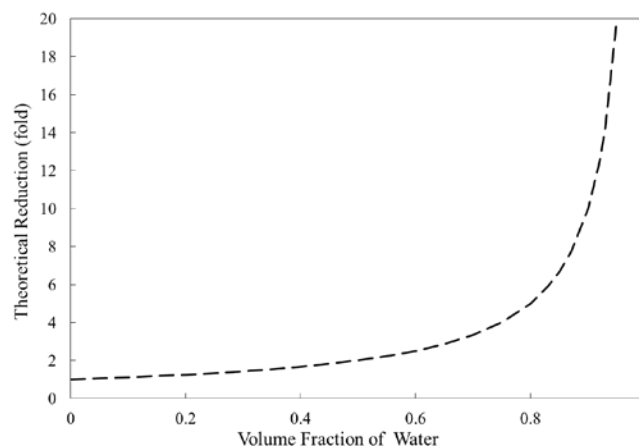


Figure 4.1: Theoretical reduction in the volume of oil required to form agglomerates through the use of the HIP water-in-oil emulsion binder, as compared to pure oil, as a function of the volume fraction of water within the emulsion.

Figure 4.1 shows that as the volume fraction of water within the emulsion, and thus within the void space of an agglomerate, increases, the theoretical reduction in the volume of oil required increases. In particular, Figure 4.1 shows that a 10 – 20 fold reduction can be achieved if an emulsion with a dispersed, aqueous phase volume fraction of 0.90 – 0.95 is used.

It should be recognised, however, that the reduction values presented in Figure 4.1 are representative of a limiting case as they were formed under the assumption that a HIP water-in-oil emulsion is as effective as pure oil in agglomerating fine coal. This means that the emulsion binder is assumed to: agglomerate coal using the same mechanism as pure oil; selectively adhere to the surface of coal in the same manner as pure oil; be effectively dispersed throughout the coal slurry and; be sufficiently stable such that it does not break down during the agglomeration process. In any case where these assumptions are not valid, the reduction achieved through the use of the emulsion binder will be limited.

The initial experiments described in this chapter were therefore used to establish the extent to which these assumptions were valid and, subsequently, the reduction that was achievable. Agglomeration experiments using pure diesel were also carried out to set a benchmark for the oil dosage required in the process.

4.3 Experimental Methodology

4.3.1 Materials

The diesel was sourced from a local fuel distribution centre. The density and viscosity of diesel are 830 kg/m³ and 0.0025 Pa.s, respectively (ExxonMobil, 2009). The emulsifier used in the emulsion binder was an ethanolamine derivative of polyisobutylene and was sourced from Orica Pty Ltd. This emulsifier, which will be referred to as the PIB emulsifier from here on in, was used without any physical or chemical modifications. Tap water was used as the suspending liquid in all agglomeration experiments. Tap water was also used for the dispersed phase in the emulsion binder. Table 4.1 presents a typical analysis of tap water in the Hunter region, NSW, Australia. Of particular importance is the pH, conductivity and total solids.

Table 4.1: Typical analysis of tap water in the Hunter region, Australia (Hunter Water Corporation, 2012)

<i>Parameter</i>	<i>Units</i>	<i>Hunter Tap Water - Average</i>
pH	(units)	8.6
Conductivity	($\mu\text{m}/\text{cm}$)	200
Total Solids	(mg/L)	151
Turbidity	(NTU)	0.2
Sodium	(mg/L)	21

Two different Australian coals were used in the experimental work described in this chapter. Two different types were selected to emphasise the specific functionality of the emulsion which was being examined.

In the first instance, the focus of the work was to demonstrate the ability of the emulsion to simply form agglomerates and recover fine coal at a given binder dosage. Therefore, a high quality, bituminous coal was used in these experiments. The coal was considered high quality as it was a flotation product and, thus, had a low ash% of 9.7%. The size distribution of the feed sample was measured using a Mastersizer 2000 (Malvern Instruments, Malvern, UK). In the Mastersizer 2000, laser diffraction is used to measure particle size distributions. A laser is passed through a dispersion of particles and the angular variation in the intensity of the scattered light is measured. A 50% w/w ethanol/water mixture was used to disperse the particles. The inclusion of ethanol into the liquid dispersion medium facilitated the submersion of the dry coal particles. The results from the size analysis are presented in Figure 4.2. As depicted in the figure, the feed had a significant proportion of ultra-fine, $<100\ \mu\text{m}$, material and had a d_{50} of $105\ \mu\text{m}$.

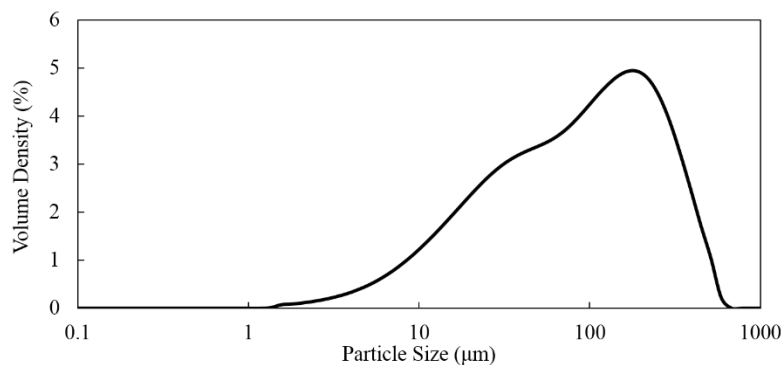


Figure 4.2: Size distribution of the high quality feed used in the majority of the experimental work

On confirmation of the ability of the emulsion to recover coal, the focus shifted to demonstrating the ability of the emulsion to recover coal selectively, i.e. reject the fine mineral particles. Therefore, a low quality coal was introduced for this phase of the work. This feed was considered low quality because it was a hydrocyclone overflow and, thus, had a high ash% of 57.5%. The size distribution of this feed was also measured using laser diffraction in the Mastersizer 2000 and is presented in Figure 4.3. As depicted in the figure, this feed consisted primarily of ultra-fine particles and had a d_{50} of 14 μm .

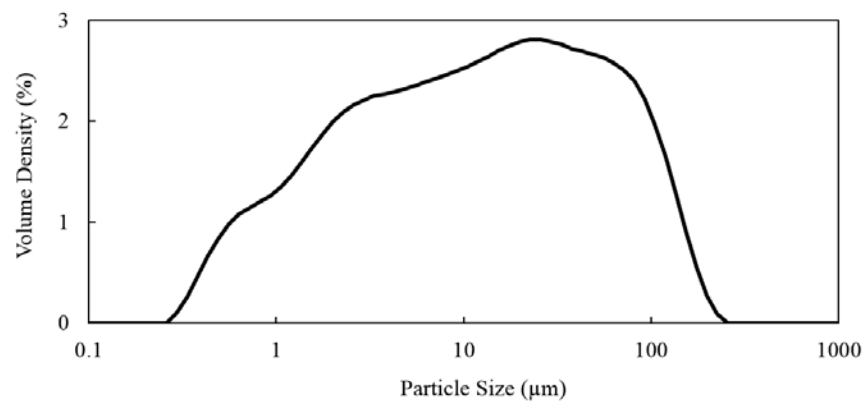


Figure 4.3: Size distribution of the low quality feed used in the investigation into the selectivity of the emulsion.

In a coal processing setting this type of finely dispersed feed would be considered difficult to process because of the high mineral (ash) content and the substantial proportion of ultra-fine material.

4.3.2 Coal Feed Preparation

Throughout the duration of this work all coal samples were received, processed and stored submerged in water. This storage procedure was adopted to maintain the surface hydrophobicity of the coal by limiting surface oxidation. The oxidative aging process is hindered by this method as the water provides a barrier between the surface of the coal and the air (Iveson & Galvin, 2012).

A wet-screening process was used to prepare the high quality coal feed for use in experiments. A circular vibratory screen with an aperture size of 260 μm , sourced from Kason Corporation, was used. The <260 μm fraction was subsampled to form the feed for the experiments. The low quality feed was subsampled and used as received.

4.3.3 Preparation of High Internal Phase Emulsion

In the work described in this chapter, the high internal phase emulsion was made from tap water, diesel and the PIB emulsifier. Via the preparation process described below, the water is formed into discrete droplets which are dispersed through a continuous phase of diesel. The PIB emulsifier acts at the interface between the two phases and stabilises the emulsion. The dispersed, aqueous phase volume fraction of the emulsion was typically 0.85; however other volume fractions between 0.67 and 0.93 were investigated. The continuous organic phase typically consisted of diesel and the PIB emulsifier in a 1:1 ratio; however other ratios were also investigated.

To prepare the HIP emulsion, the organic components were placed into a stainless steel mixing bowl. The comparably large volume of water was then added in small increments under continuous mixing provided by a Russell Hobbs Electric Hand Mixer (350 W motor) set at maximum speed. To ensure phase inversion of the emulsion did not occur, the incremental volume of water was limited to half of the initial volume of the organic phase. Furthermore, the incremental volume of water was completely incorporated into the organic phase prior to the addition of the next increment of water. An increment of water was deemed to be incorporated into the organic phase when water droplets were no longer visible on the surface of the hydrophobic emulsion. The total time taken to add the water was typically 360 s.

The emulsion began as a transparent, orange liquid and progressively turned lighter as the water was added; finally forming an opaque, white, and viscous material on the completion of the water addition. Figure 4.4 presents the emulsion at different stages during preparation. The volume fractions of the water, diesel and PIB emulsifier in the final emulsion presented in Figure 4.4 are 0.85, 0.075 and 0.075, respectively. It should be noted that the only difference between the stages of preparation presented in Figure 4.4 is the volume fraction of water within the emulsion, which increases as time progresses.

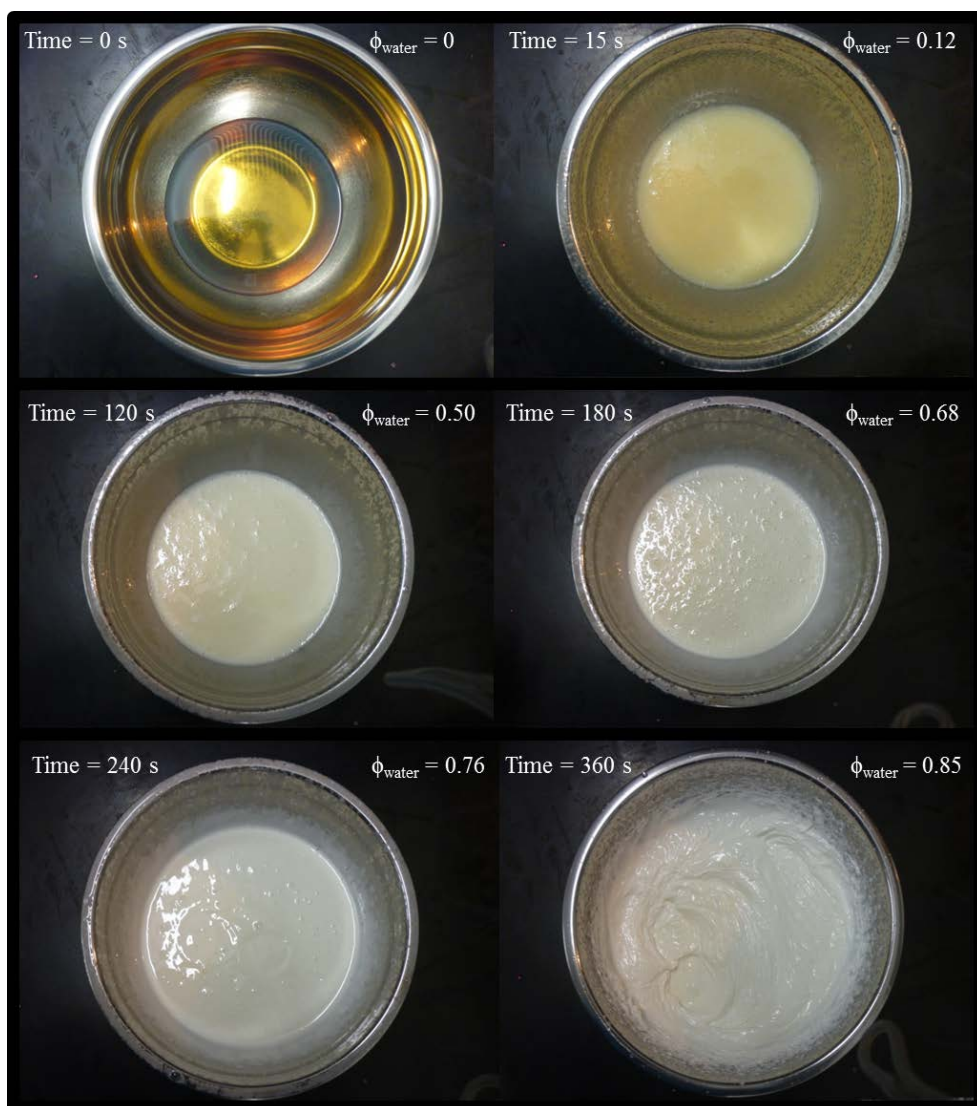


Figure 4.4: The emulsion at different stages during preparation. It should be noted that the only difference between each of the stages is the dispersed aqueous volume fraction of the emulsion.

The average internal droplet size of the final emulsion was in the range of 1 – 10 μm . The internal droplet size of the emulsions was measured using a Mastersizer S (Malvern Instruments, Malvern, UK). The liquid medium used to dilute the emulsion and thus disperse and mobilise the internal water droplets was diesel.

4.3.4 Selective Agglomeration

In agglomeration experiments, 1 L of coal slurry was added to a cylindrical mixing vessel. The height and diameter of the vessel were 40 cm and 17 cm, respectively. The vessel was constructed from polyvinyl chloride and had three baffles evenly spaced around the inside wall. Agitation was then applied to the slurry by a Heidolph RZR 2102 Control

overhead mixer. The coal slurry was dispersed at 2000 rpm for 1 min prior to the addition of the binder. The binder, either the emulsion or pure diesel, was then added and the mixing was continued at 2000 rpm for 10 min. The agglomerated slurry was then poured over a screen with aperture size of either 500 μm or 180 μm . The former was used in experiments in which the high quality coal was used and the latter was used in experiments using the low quality coal. The agglomerated material which remained on top of the screen formed the product and the material which reported to the underflow of the screen formed the reject. The yield of a given agglomeration experiment was defined as the mass of the dried agglomerated product as a fraction of the total dry coal feed. Figure 4.5 displays the product and reject, prior to drying, from a successful agglomeration experiment. It can be seen that the coal agglomerates have been separated from the mineral matter which remains finely dispersed in the water.



Figure 4.5: The product and reject from a successful agglomeration experiment.

Both the product and reject samples were dried in an oven set at 110 °C. The dried samples were then weighed and packaged for storage. Where noted, ash analysis was performed on the dry samples to determine the mineral matter content in the product and reject material.

4.4 Performance of Emulsion Binder

In the first phase of the initial work, it was necessary to evaluate the performance of the emulsion binder with respect to a pure diesel binder. Therefore, experiments were carried out which focused on the ability of the emulsion to recover fine coal at a given binder dosage and, the ability of the emulsion to be selective. As aforementioned, these properties were evaluated in separated experiments. Initially the ability of the emulsion to recover carbonaceous material was examined. To achieve this, the influence of the oil

dosage on the yield of product coal was examined and compared against experiments in which pure diesel was used as the binder. As a consequence of these experiments, the first indication of the reduction in the oil dosage which could be achieved through the use of the emulsion was ascertained. The raw data for the agglomeration experiments presented in this chapter as well all of the following chapters can be found in Appendix A. Results which involved further, more in-depth analysis are presented in separate appendices, as noted.

4.4.1 Fine Coal Recovery

Prior to the introduction of the emulsion binder, agglomeration experiments were carried out using a pure diesel binder. In these experiments, pure diesel was dosed at different levels to investigate the influence of oil dosage on the yield of product coal. The results from these experiments are presented in Figure 4.6. These results served as a benchmark for all future experiments using the high quality coal feed. It should be noted that, for this feed, the maximum yield was approximately 90 wt% due to the mineral matter content.

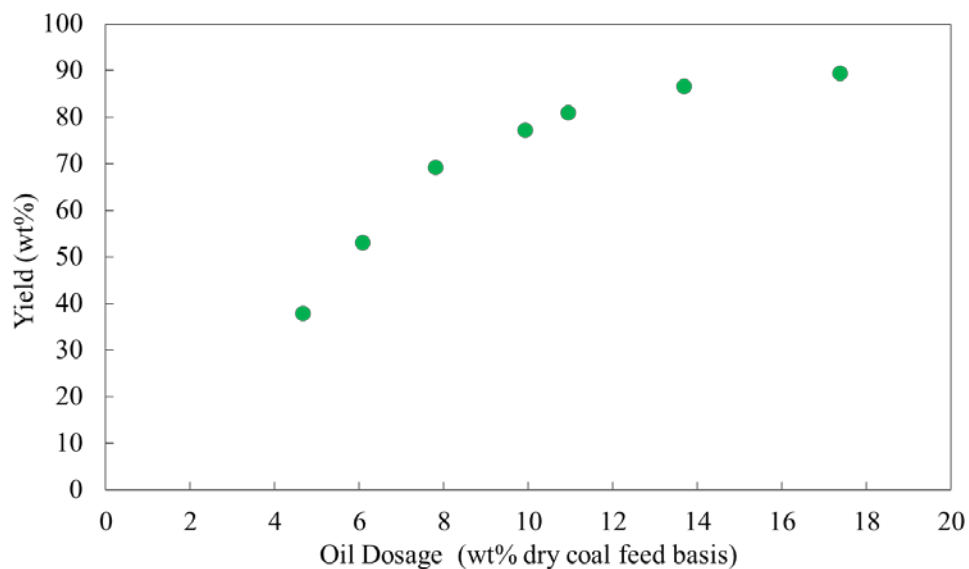


Figure 4.6: Yield of product coal as a function of oil dosage for a pure diesel binder. The coal feed had an ash% of 9.7%

As depicted in Figure 4.6, increases in the oil dosage result in increases in the yield of agglomerated product. However, a plateau in yield is observed after an oil dosage of approximately 16 wt%. In general these results are consistent with results presented in the literature and can be explained by considering the state of the bridging liquid between

the particles (Bensley, et al., 1977; Capes & Germain, 1982; Mehrotra, et al., 1983). At low oil dosages, only pendular bridges form between the particles resulting in an unconsolidated and loosely agglomerated structure. Loosely agglomerated material is not easily recovered using a screen and thus low yields are experienced. This phenomenon is reflected in the results presented in Figure 4.6 as poor yields are obtained for oil dosages less than 8 wt%. Observations of the experiments also indicated that the product consisted of a loose chain-like structures rather than large, discrete agglomerates.

As greater amounts of oil binder are added, the loosely agglomerated material begins to consolidate and some compact agglomerates begin to form. Eventually, the oil dosage reaches a level in which all of the particles are formed into discrete, strong agglomerates and thus, the maximum possible yield is achieved. As a result, further increases in the oil dosage beyond this point do not serve to increase the yield appreciably; thus explaining the observed plateau in yield in Figure 4.6. The dosage at which the plateau commences, therefore, represents the minimum dosage required to achieve complete agglomeration of all the recoverable, carbonaceous material in the feed. The minimum oil dosage required for this feed is 16 wt% when using pure diesel.

Following the agglomeration experiments using the pure diesel binder, experiments were carried out using an emulsion binder. Table 4.2 presents the composition of the emulsion used in this experiments described in this section. It should be noted that in an attempt to achieve a fair comparison between the two binders, identical operating conditions were used in both sets of experiments.

Table 4.2: The volume fraction of each component within the emulsion used to investigate the ability of the emulsion to recover fine coal.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
Water	Diesel	PIB Emulsifier
0.85	0.075	0.075

To be a successful substitution for pure oil, the emulsion binder had to have the ability to recover fine coal and produce a high quality, granular product. Presented in Figure 4.7 are the results for the emulsion binder together with the results from Figure 4.6 for the

pure diesel binder. It should be noted that the binder dosage value is now presented as organic liquid dosage, rather than oil dosage, and is defined as:

$$\text{Organic Liquid Dosage} = \frac{\text{mass of organic liquid}}{\text{mass of dry feed solids}} \times 100\% \quad (4.1)$$

Furthermore, it should be noted that the pure diesel comprises entirely of organic liquid. However, only a small fraction (0.15) of the emulsion binder is organic liquid. Therefore the mass of the PIB emulsifier and diesel within the emulsion are considered in the calculation but not the mass of the water.

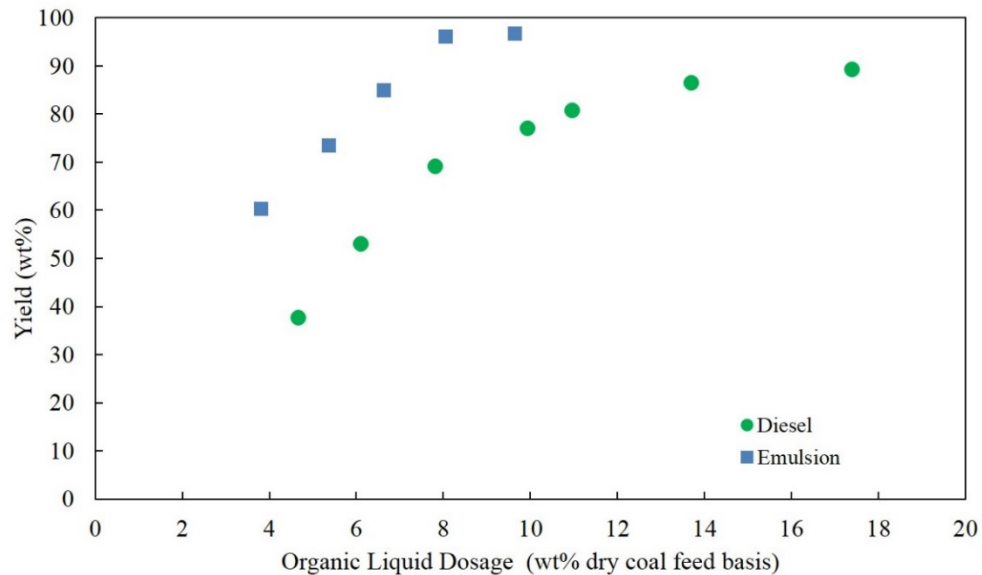


Figure 4.7: Yield of product coal as a function of organic liquid dosage for a pure diesel binder and an emulsion binder. The emulsion binder had a dispersed, aqueous phase volume fraction of 0.85. The coal feed had an ash% of 9.7%

The general trend presented in Figure 4.7 for the emulsion binder is the same as displayed by the pure diesel binder. That is, at low organic liquid dosages there is insufficient binder present to form all of the carbonaceous material into agglomerates and thus, low yields are observed. However, at higher organic liquid dosages there is sufficient binder and high yields are observed as all of the coal has been formed into large, discrete, recoverable agglomerates. Observations of the experiments also indicated similar product structures for both binders, at all organic liquid dosages. That is, at low dosages, the product formed

using the emulsion also exhibited an unconsolidated loose chain-like structures and at high dosages agglomerates were observed.

These results indicated that the emulsion binder can agglomerate and recover fine coal in a similar manner to pure diesel. Also, importantly, these results indicated that when using the emulsion this agglomeration occurs at a lower organic liquid dosage than when using pure oil. That is, to achieve complete agglomeration and, thus, the maximum yield an organic liquid dosage of 8 wt% was required when using the emulsion binder. Whereas a dosage of 16 wt% was required to achieve the same yield and product state when using the pure diesel. Furthermore, by comparing these two values, the reduction in the organic liquid requirement can be quantified. That is, the use of the emulsion binder has resulted in a 2-fold reduction in the organic liquid dosage required for a given yield. This result was encouraging as it indicated that the emulsion binder was behaving somewhat like predicted. However, it was also clear that a 2-fold reduction was considerably less than the 7-fold reduction predicted in Figure 4.1 for an emulsion with a dispersed, aqueous phase volume fraction of 0.85.

At this stage in the study, the reason for achieving only a 2-fold reduction was not apparent and, as a result, subsequent investigations were undertaken in an attempt to understand and improve this finding. However, prior to these investigations, an investigation into the selectivity of the emulsion was crucial to confirm that the emulsion also rejected mineral matter during the formation of agglomerates.

4.4.2 Selectivity

In the second phase of the initial work, the selectivity of the emulsion was examined and compared against a pure diesel binder. As aforementioned, a low quality coal was introduced as the feed for these experiments to truly test the capability of the emulsion to be selective. In these experiments, the organic liquid dosage was varied to produce a number of product samples at different yields for both the emulsion binder and the pure diesel binder. Then ash analysis was performed on a representative feed sample and the product and reject samples to provide an indication of selectivity. The ash analysis was performed externally by ALS Global, the detailed results from which are presented in Appendix B.

Presented initially in Figure 4.8 is the yield of product coal as a function of the organic liquid dosage for the emulsion binder and the pure diesel. The composition of the emulsion remains unchanged from that presented in Table 4.2. Also, it should be noted that, for this feed, the maximum yield was approximately 40 wt% due to the high mineral matter content. This varies from the previously used high quality coal feed in which 90 wt% of the feed was carbonaceous and thus recoverable via the agglomeration process.

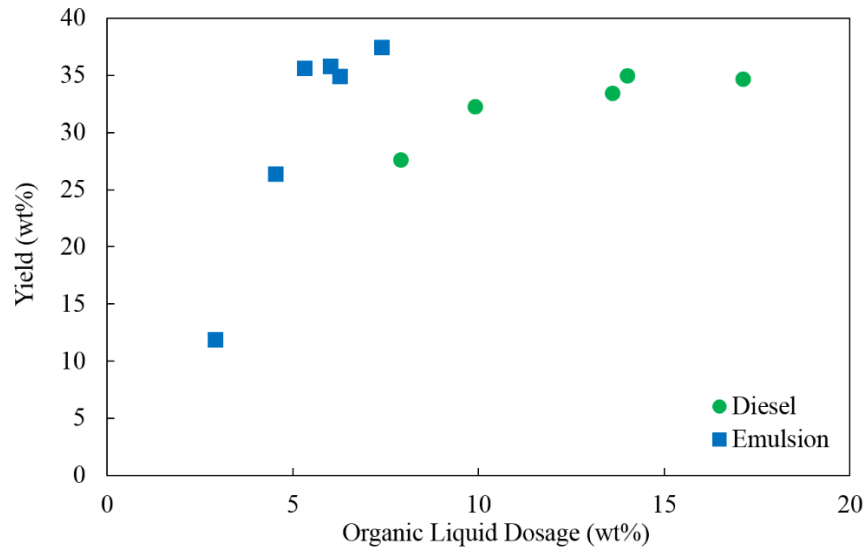
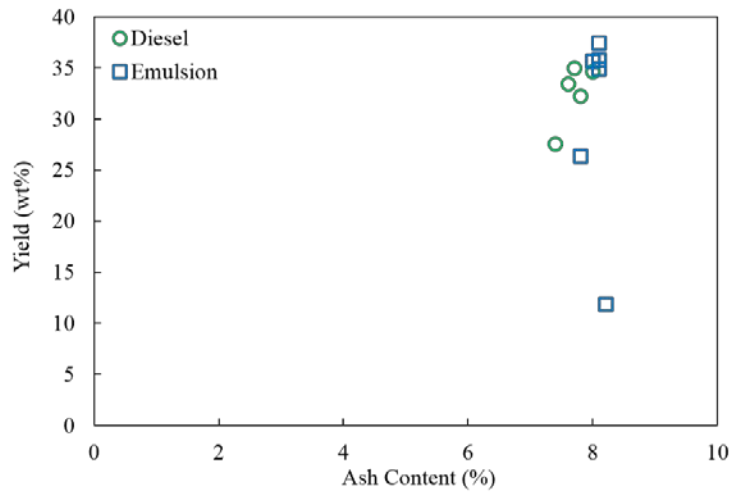


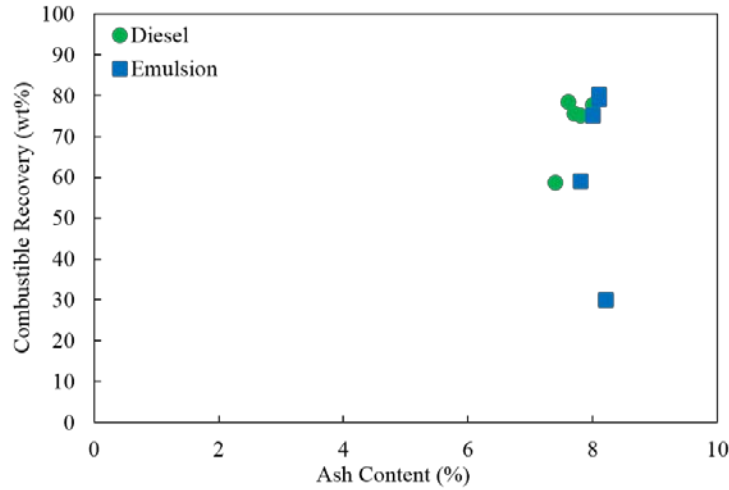
Figure 4.8: Yield of product coal as a function of organic liquid dosage for a pure diesel binder and an emulsion binder. The emulsion binder had a dispersed, aqueous phase volume fraction of 0.85. The feed had an ash% of 57.5%.

The results in Figure 4.8 display a similar trend to that observed in Figure 4.7. Initially, there is an increase in yield with increases in the organic liquid dosage. However, after a certain dosage, the yield plateaus at a constant, maximum value as all of the carbonaceous material has been formed into recoverable agglomerates. Therefore, for this feed, the dosage required to achieve agglomeration, i.e. the dosage at the commencement of the plateau, is 12 wt% when using pure diesel and 6 wt% when using the emulsion. It should be noted that these dosage values vary from that required when using the high quality feed due to the variation in the size distribution and ash% of the two feeds. However, regardless of this variation in the feed, it can be seen that a two-fold reduction in the organic liquid requirement has once again been achieved. This finding was actually quite important as it indicated that the ability of the emulsion to recover fine coal is not hindered by the presence of considerable amounts of clays and other minerals.

Following on, it was of interest to consider the ash% of each of the product samples from Figure 4.8. Therefore, presented in Figure 4.9a are the yield-ash curves for the emulsion and the pure diesel. The corresponding combustible recovery values, as calculated by the two product formula, are presented in the Figure 4.9b. The method of calculation for the combustible recovery values is also presented in Appendix B.



(a)



(b)

Figure 4.9: a) Yield and b) combustible recovery as a function of the ash% for the emulsion and pure diesel.

Figure 4.9a shows that the ash % is effectively constant in the range of 7 – 8 % over a wide range of yields for both the emulsion and the pure diesel. An ash % of this low level is remarkable for a single pass operation, especially when considering the feed had an ash% of 58 %. Of course, the results for the pure diesel binder were not surprising as they

agree with the result found by many others that light oils exhibit excellent mineral matter rejection capabilities (Aktas, 2002; Capes & Germain, 1982; Capes, et al., 1977; Tsai, 1982). More importantly, however, these results indicate that the selectivity of the emulsion effectively matches that of a pure oil binder.

Also presented in Figure 4.9 is the corresponding combustible recovery for each of the samples. It can be seen that the combustible recovery was high for both binders. However, even in the cases in which sufficient amounts of binder were used, the combustible recovery did not exceed approximately 80%. This limit on the maximum combustible recovery is a normal occurrence for a natural coal feed due to the presence of composite particles. The presence of composite particles limits combustible recovery as individual particles which consist of both carbonaceous and mineral material may not be agglomerated if the binder interacts with the mineral portion of the particle. Further liberation (particle comminution) may improve the combustible recoveries presented in Figure 4.9.

4.4.3 Summary

It has been shown that the emulsion can selectively recover fine coal in a similar manner to pure diesel. Moreover, it has been shown that the use of the emulsion has led to a 2-fold reduction in the organic liquid dosage required to achieve agglomeration, as compared to pure diesel. This 2-fold reduction was encouraging as it indicated that the use of the emulsion does reduce the organic liquid required in the process. However a reduction of this magnitude was well below the 7-fold reduction predicted at the start of the chapter for an emulsion with a dispersed phase volume fraction of 0.85. Therefore, the remainder of the work in this chapter, and indeed this thesis, focused on maximising the functionality of the emulsion such that the reduction value was improved.

4.5 Maximising the Functionality of the Emulsion through Composition Modifications

As previously mentioned, the reason for achieving only a 2-fold reduction in the work thus far was not apparent. However, it was acknowledged that if the reasoning presented in Section 4.2 was correct, modifying the internal aqueous phase volume fraction should result in different levels of reduction. Varying levels of reductions, as compared to the

pure diesel benchmark, should be observed as the void space in the interior of the agglomerate would be occupied to differing extents by the oil and water phases.

It should be noted that the high quality coal which was used in the first phase of experiments described in this chapter was also used for the remainder of the work described in this chapter. The high quality feed was used once again as the selectivity of the emulsion had been confirmed and the focus had returned to the ability of the emulsion to recover coal at a given organic liquid dosage.

4.5.1 Internal Aqueous Phase Volume Fraction

The volume of the dispersed, aqueous phase within the HIP emulsion is controlled by the amount of water that is added during the initial preparation. If care is taken during the water addition stage of the emulsion preparation, emulsions with dispersed, aqueous phase volume fractions in excess of 0.90 can be made. In this section, results for emulsions with dispersed phase volume fractions of 0.90 and 0.93 were investigated. Also, investigated was an emulsion binder with a dispersed phase volume fraction of 0.67. It should be noted that a dispersed phase volume fraction of 0.93 was the maximum volume fraction that could be achieved at this stage of the work. Attempts to make emulsions with higher dispersed phase volume fractions failed as the additional water would not form part of the emulsion. Rather, the water would remain on the outside or on the top of the bulk emulsion regardless of the duration of mixing applied.

Figure 4.10 presents the yield of product coal as a function of organic liquid dosage for an emulsion binder with a dispersed phase volume fraction of 0.90. Also presented in the figure is the diesel benchmark case and the results from Figure 4.7 for an emulsion with a dispersed phase volume fraction of 0.85. To draw attention to the new results, the results for the 0.85 case have been faded to grey.

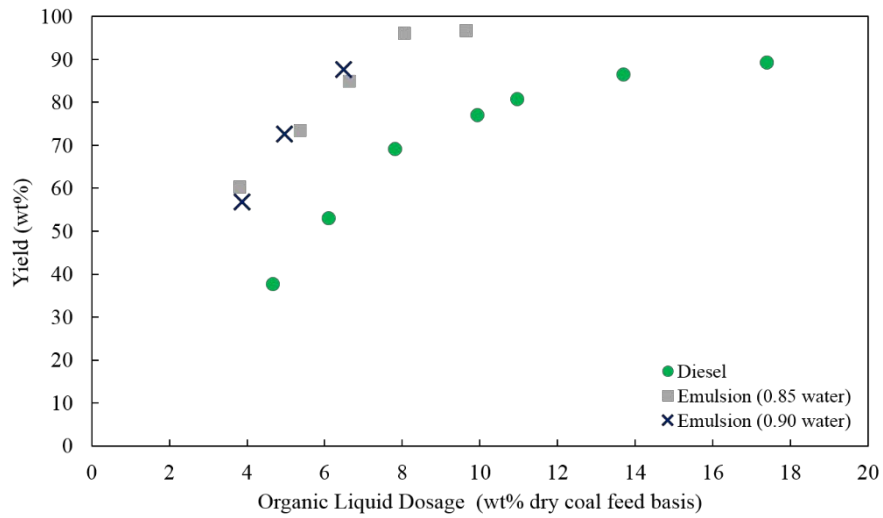


Figure 4.10: Yield of product coal as a function of organic liquid dosage for a pure diesel binder and two emulsion binders with aqueous, dispersed, aqueous phase volume fractions of 0.85 and 0.90, respectively

Contrary to expectation, Figure 4.10 shows that the results for the emulsion with a dispersed phase volume fraction of 0.90 coincide exactly with the results from the 0.85 case. Therefore, when comparing with the benchmark diesel case, the emulsion with a dispersed phase volume fraction of 0.90 also only achieved a 2-fold reduction. An increase in the reduction was expected as the use of an emulsion with a higher dispersed phase volume fraction should mean that the void space in the interior of the agglomerate is filled to a greater extent by the aqueous phase and to a lesser extent by the organic phase. However, it was considered that perhaps the dispersed phase volume fraction of the two emulsions did not differ sufficiently to produce a perceivable variation in agglomeration performance. Therefore, two extreme cases were also tested. Figure 4.11 presents the yield of product coal as a function of the organic liquid dosage for emulsions with dispersed phase volume fractions of 0.67 and 0.93.

Once again, the curve for the benchmark diesel case has been reproduced from Figure 4.6, along with the results from Figure 4.10 for the 0.85 and 0.90 cases. Furthermore, the results already presented in previous figures have been faded to grey to draw attention to the new results.

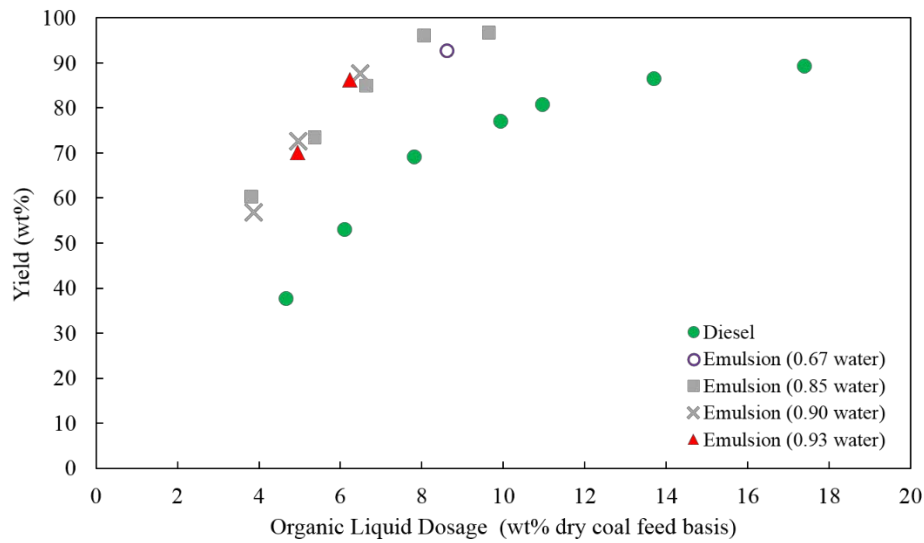


Figure 4.11: Yield of product coal as a function of the organic liquid dosage curves for a pure diesel binder and four emulsion binders with aqueous, dispersed, aqueous phase volume fractions of 0.67, 0.85, 0.90 and 0.93, respectively

As shown in Figure 4.11, the results for the emulsions made with dispersed phase volume fractions of 0.67 and 0.93 overlap the results of the 0.85 and the 0.90 cases. Therefore, all of the emulsion binders investigated only achieved a 2-fold reduction as compared to the benchmark diesel case. This level of consistency within the results was unexpected due to the emulsion composition variation and the implications of substitution theory described in Section 4.2. Of course it may have been overly ambitious to expect that the theoretical reductions presented in Section 4.2 would be realised, however some dependence of the performance of the emulsion on its composition was expected.

In an attempt to account for the results observed in Figure 4.11, the stability of the emulsion was brought into question. In this context, the stability of the emulsion related to the tendency for water to be released from the internal phase of the emulsion during dispersion of the binder in the agglomeration process. If the emulsion lacked stability, and the internal water was released from the emulsion, the enhanced space-filling functionality of the emulsion binder would be negated. Furthermore, it was recognised that release of the internal water was a real possibility as the emulsion binder must be dispersed under high shear in a turbulent, aqueous environment and only a thin layer of oil enclosed the dispersed water droplets. Now, it should be noted that the exact thickness of the continuous layer within the emulsion binders used in this work was not measured.

However, for concentrated emulsions the thickness of the continuous phase film has been shown to be in the range of 10 – 100 nm and to be highly dependent upon composition (Klizling, Kronberg, & Eriksson, 2006; Mukesh, Das, & Ghosh, 1992).

4.5.2 Organic Phase Composition

To investigate the issue of emulsion stability, attention was drawn, initially, to the composition of the organic phase, or more specifically, to the concentration of emulsifier. HIP emulsions inherently have an extremely large organic-aqueous interfacial area. For example, an emulsion with a dispersed phase volume fraction of 0.90 and an average internal droplet diameter of 10 μm would have an interfacial area of 540 000 m^2/m^3 ; assuming spherical droplets. Now, when this area is expanded, either through the incorporation of more water or through size reduction of the internal droplet diameter, excess emulsifier must be available. In instances in which the emulsifier is not available, the creation of the new interfacial area will not be possible due to the lack of lasting stabilisation at the interface.

At this stage in the study, it was not known whether the emulsifier was present in excess or deficit and, thus whether the concentration of the PIB emulsifier was the limiting factor in the results to this point. As such, the effect of the organic phase composition and the potential dependence of stability and, therefore, performance of the emulsion as a binder was considered. Table 4.3 presents the compositions of the emulsions tested for this investigation. It should be noted, that all of the emulsions used in this phase had a dispersed, aqueous phase content of 0.85.

Table 4.3: The volume fraction of each component within the emulsions tested during the investigation into the effect of the organic phase composition.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
Water	Diesel	PIB Emulsifier
0.85	0.075	0.075
0.85	0.105	0.045
0.85	0.045	0.105

Figure 4.12 presents the results for emulsions with PIB emulsifier volume fractions of 0.075, 50 % of the organic phase, and 0.045, 30 vol% of the organic phase. The results

for the former have been reproduced from Figure 4.7 in the previous section and, thus, have been faded to grey to draw attention to the new results. The results for benchmark diesel case are also reproduced in Figure 4.12.

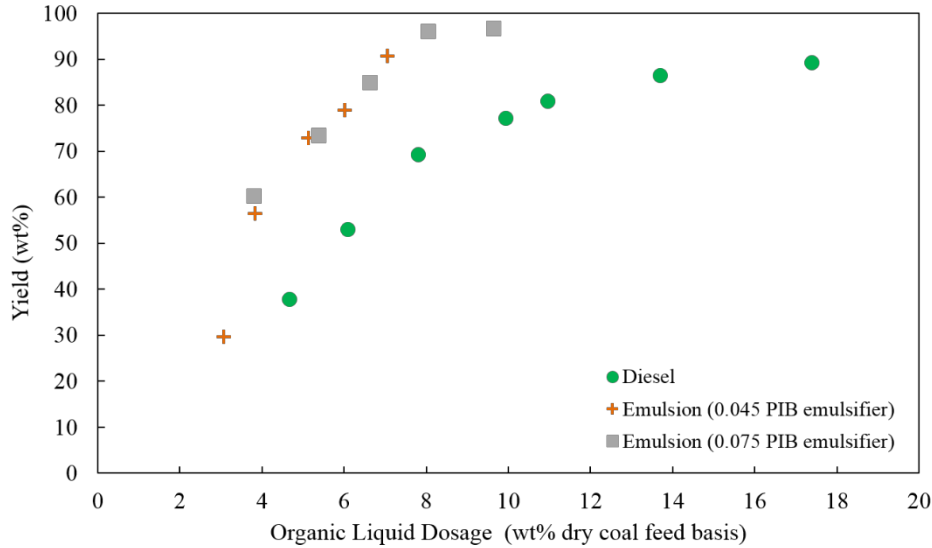


Figure 4.12: Yield of product coal as a function of organic liquid dosage for a pure diesel binder and two emulsion binders with organic phase compositions of: 0.85 water, 0.105 diesel, and 0.045 PIB emulsifier; and 0.85 water, 0.075 diesel, and 0.075 PIB emulsifier.

The results for the emulsion with a PIB emulsifier volume fraction of 0.045 have been shown to, once again, match the results for the original emulsion investigated at the commencement of this chapter. Therefore, the new emulsion, which had a reduced amount of PIB emulsifier also achieved a 2-fold reduction in the organic liquid dosage. Complimentary to the results presented in Figure 4.12, Figure 4.13 exhibits the performance of an emulsion with a PIB emulsifier volume fraction of 0.105. This emulsion had the highest level of PIB emulsifier of all the emulsions investigated in this stage. Also presented in Figure 4.13 are the results for the benchmark diesel case and the results for the emulsions with lower PIB emulsifier volume fractions, which have been faded to grey.

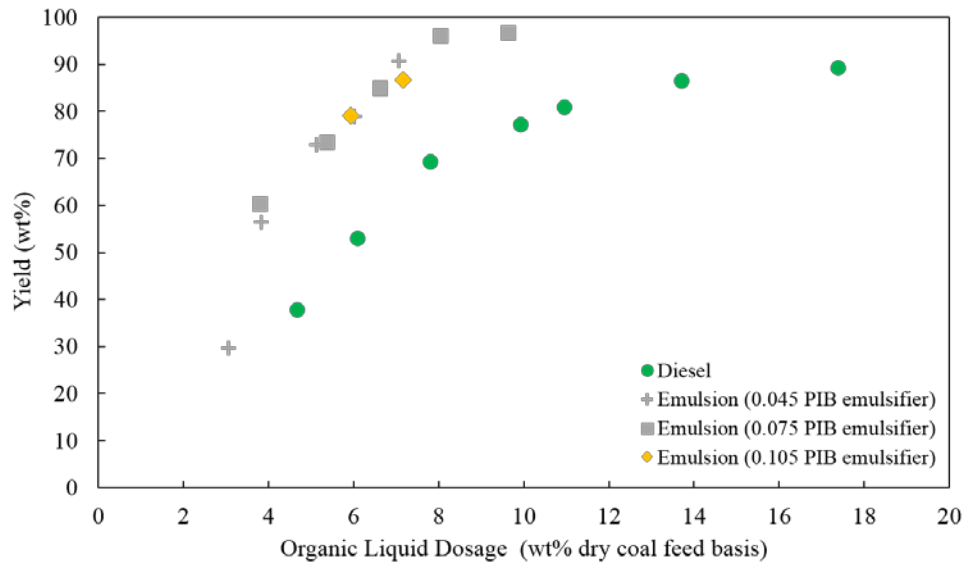


Figure 4.13: Yield of product coal as a function of organic liquid dosage for a pure diesel binder and three emulsion binders with organic phase compositions of: 0.85 water, 0.105 diesel, and 0.045 PIB emulsifier; 0.85 water, 0.075 diesel, and 0.075 PIB emulsifier; and 0.85 water, 0.045 diesel, and 0.105 PIB emulsifier.

Figure 4.13 shows that no advantage has been gained by increasing the volume fraction of PIB emulsifier within the organic phase. The results for the emulsion with a PIB emulsifier volume fraction of 0.105 have fallen on the same curve as formed by the results for the emulsions with the reduced PIB emulsifier volume fractions and, thus, a 2-fold reduction compared to the benchmark diesel case was once again achieved.

Overall, these results indicate that the volume fraction of the PIB emulsifier has no effect on the performance of the emulsion as a binder within the range investigated. Therefore, it appears as though the concentration of PIB emulsifier is not the limiting factor in the results obtained thus far. In fact, it is likely that all of the emulsions used in this section had excess emulsifier.

Therefore, to account for the consistency in all of the results obtained thus far, the issue of emulsion stability was once again considered. Emulsion stability, or lack thereof, would explain the consistency as a breakdown of the emulsion would nullify the effect of composition modifications and to some extent, the creation of the emulsion structure in the first place.

During the agglomeration process the emulsion must withstand a high level of mixing, and thus shear. This mixing is essential as it distributes the binder and facilitates the contact between particles and binder. However, it may very well be that this mixing is the cause of the apparent emulsion degradation. As aforementioned, the emulsion consists of tightly packed water droplets in a thin layer of oil and if this structure is subject to excessive shear in a turbulent, aqueous environment it is not unreasonable to assume that the structure will breakdown. Therefore, in the following chapter, the effect of mixing on the performance of the emulsion is explored. This investigation was carried out in an effort to further maximise the functionality of the emulsion with the aim of increasing the reduction in organic liquid dosage. This investigation was also essential prior to any further modifications to the composition of the emulsion.

4.6 Summary

The ability of the proposed emulsion binder to agglomerate fine coal in a similar manner to pure diesel was investigated initially in this chapter. An emulsion binder with a dispersed, aqueous phase volume fraction of 0.85 exhibited a similar ability to selectively recover fine coal as pure diesel. Furthermore, it was shown that the use of the emulsion led to a 2-fold reduction in the organic liquid dosage required to achieve agglomeration, as compared to using pure diesel. As this reduction was considerably less than predicted by the substitution theory, the remainder of the work in this chapter focused on maximising the functionality of the emulsion through composition modifications. Figure 4.14 re-exhibits the results presented throughout the chapter for all of the emulsions investigated.

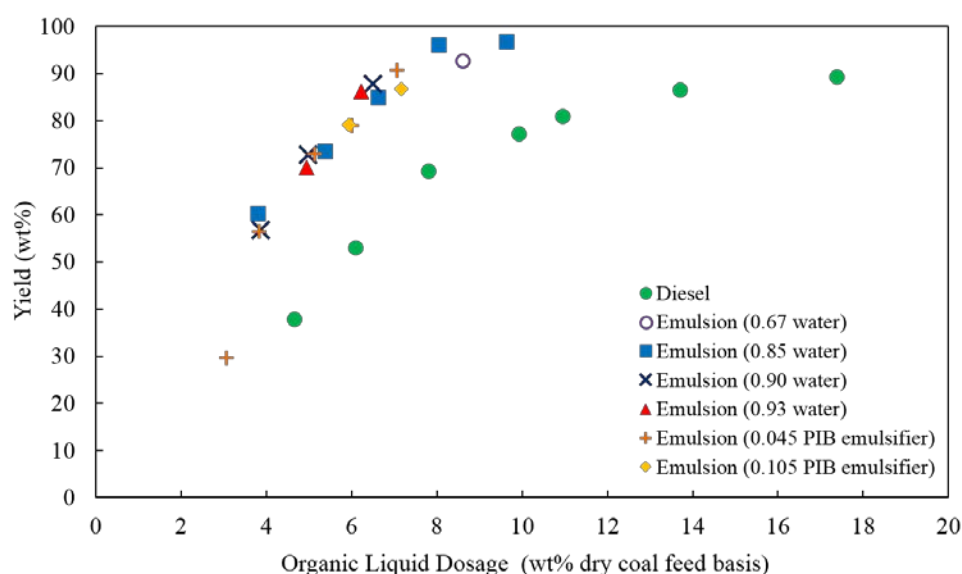


Figure 4.14: Yield of product coal as a function of organic liquid dosage for a pure diesel binder and six emulsion binders. The binders vary in their aqueous volume fractions and organic phase compositions.

Figure 4.14 shows that all of the results obtained thus far for the emulsion binder lie on one curve which represents a 2-fold reduction in the organic liquid dosage compared to the benchmark diesel case. These results indicate that the dispersed, aqueous phase volume fraction and the organic phase composition have no effect on the performance of the emulsion as a binder.

As a result of the findings in this chapter, it was considered that there was some limiting factor that was hindering the performance of the emulsion and this factor was considered to relate to the stability of the emulsion. That is, if the stability of the emulsion was insufficient to withstand the shear applied during the agglomeration process it may breakdown. Moreover, if this breakdown occurred to a constant level it would explain the consistency in results in Figure 4.14 and the lack of dependence upon the composition of the emulsion. Therefore, the following chapter explores the effect of mixing within the agglomeration process on the functionality of emulsion. This work was carried out in an effort to identity whether the emulsion was degrading due to excessive shear destroying the structure of the emulsion. It was essential that the limiting factor in the performance of the emulsion be addressed prior to any further modifications to the composition of the emulsion.

Chapter 5

Maximising Binder Functionality through Mixing

Contribution to the Research

Paper:

van Netten, K., Moreno-Atanasio, R., & Galvin, K. P. (2013). Preparation of Coal Agglomerates Using a Water-in-Oil Emulsion, *Proceedings, Annual Australasian Chemical Engineering Conference, Chemeca 2013*, Brisbane, Australia.

Contribution:

Author	Primary Contribution
van Netten, K.	Collaborator in design of experimental program, carried out experimental program of work, data analysis, and lead author of paper
Moreno-Atanasio, R.	Supervisor and collaborator in preparation of paper
Galvin, K. P.	Co-supervisor, collaborator in design of experimental program of work, and collaborator in preparation of paper

Paper:

van Netten, K., Moreno-Atanasio, R., & Galvin, K. P. (2015). A kinetic study of a modified fine coal agglomeration process. *Procedia Engineering*, 102, 508 - 516.

Contribution:

Author	Primary Contribution
van Netten, K.	Collaborator in design of experimental program, carried out experimental program of work, data analysis, and lead author of paper
Moreno-Atanasio, R.	Supervisor and collaborator in preparation of paper
Galvin, K. P.	Co-supervisor, collaborator in design of experimental program of work, and co-author of paper

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Roberto Moreno-Atanasio

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Kim van Netten

5.1 Introduction

It was clear from the work in Chapter 4 that the use of the emulsion adds new dimensions to the agglomeration process that are not present when a pure oil binder is used. Most importantly the binder results in a significant reduction in the level of organic liquid required. However, there was an indication that the stability of the emulsion may affect its functionality as a binder. More specifically, the results suggested that the emulsion was breaking down, limiting its potential. To account for this apparent degradation attention was directed to the level of mixing, and thus the shear rate, applied to the emulsion during the agglomeration process. If excessive, the emulsion structure would be degraded or even destroyed. Therefore, the work in this chapter focused on the effect of mixing on the functionality, and thus, performance of the emulsion.

To examine the influence of mixing the change in the size distribution of the feed was measured with respect to time. From this work it was possible to detail the kinetics of agglomeration when using the emulsion binder and compare to the kinetics of agglomeration when using a pure oil binder. It was anticipated that the functionality of the emulsion could be improved by identifying signs of emulsion degradation and in turn limiting the degradation through changes in the methodology.

Of course, from the outset of this work it was recognised that a certain level of mixing is essential in the agglomeration process, for dispersing the binder and facilitating contacting between the particles. Therefore, it was considered that it may also be beneficial to enhance the ability of the emulsion to withstand this mixing. To achieve this, a secondary investigation was launched which focused on the level of mixing applied during the preparation of the emulsion. The level of mixing applied to the emulsion binder during the preparation process is important as it may influence the level of shear the emulsion can then withstand during the agglomeration process. That is, if a high amount of shear is applied during the creation of the emulsion it will reduce the internal droplet size within the emulsion and hence create a more stable structure. Therefore, in the latter part of this chapter, a high shear homogenising device, a microniser, was introduced for use in the preparation of the emulsion. An evaluation of the effect of the device on the performance and thus functionality of the emulsion is presented.

However, prior to the investigation into the influence of mixing on the performance of the emulsion a new mixing device for use in the agglomeration experiments was introduced, the details of which are discussed below.

5.2 New Mixing Device

Previous applications of fine coal agglomeration have used mixers which operate over a wide range of agitation speeds from 150 rpm – 20 000 rpm (Laskowski & Yu, 2000; Perrott & Kinney, 1921). However, more recent applications have favoured high speed mixing devices as they facilitate the rapid formation of agglomerates, i.e. reduce residence time, and can be used on slurries with solids concentrations as high as 50 wt% (Capes & Germain, 1982). Now, the device described in the previous chapter could only impart relatively low intensity mixing as the maximum speed was 2 000 rpm. Therefore, to be consistent with the more recent applications of agglomeration, a new high speed blender was purchased; a Waring variable speed blender. This blender, pictured in Figure 5.1, was selected as it had the capacity to operate at mixing speeds in excess of 20 000 rpm.



Figure 5.1: The mixing device used in the second phase of the experimental work.

A secondary benefit was also realised through the introduction of the new mixing device. Due to the use of a glass mixing vessel in the new device, the colour change which occurs in the bulk liquid of the slurry could now be monitored as it progressed. The mixing vessel

used in the work described in the previous chapter had opaque walls and thus did not afford this opportunity.

During the course of mixing the bulk liquid of the slurry changes colour due to the agglomeration, and subsequent removal from suspension, of the coal particles. As pictured in Figure 5.2a, the slurry is initially black because of the high number of finely dispersed coal particles. However, as the agglomeration proceeds the slurry gradually becomes lighter in colour. At the completion of the mixing, the bulk liquid becomes light brown due to the clay and mineral particles which remain finely dispersed. Figure 5.2b displays the final state of the slurry in which large, black agglomerates can be seen in a mineral-rich liquid.

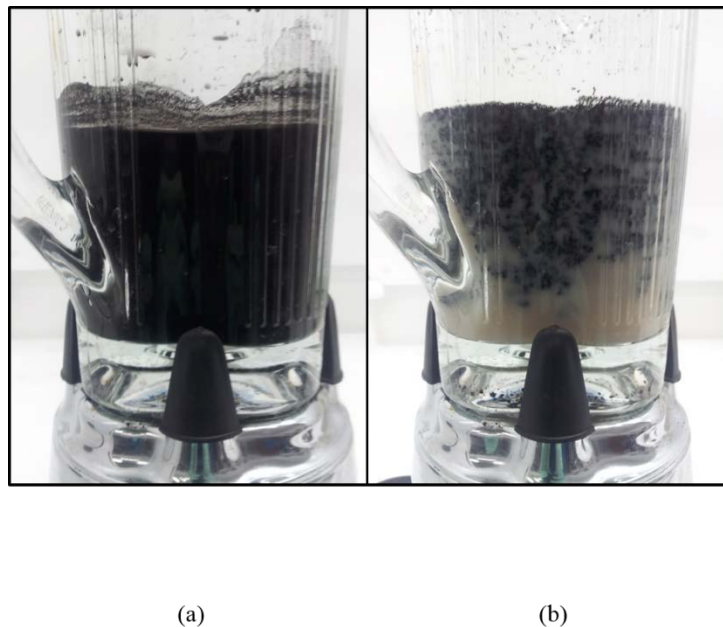


Figure 5.2: a) the feed slurry and b) the agglomerated slurry. Note the colour change of the bulk liquid of the slurry which results from the agglomeration of the fine coal particles.

As a result of the new mixing vessel and some preliminary observations, it became apparent that the emulsion binder agglomerated coal faster than pure diesel. More specifically, the agglomeration process appeared to take less than 1 min when using the emulsion binder. Whereas the pure diesel binder required 1.5 – 2.0 min to achieve the same agglomerated state. This result was significant because in the previous chapter the operating conditions which were appropriate for the diesel binder were applied directly

to the emulsion binder in the interest of a fair comparison. Now, as the new results indicated that the emulsion binder required only half the time of the diesel binder, it was concluded that the emulsion binder experienced excessive mixing in all the experiments in phase 1. Moreover, if the stability of the emulsion was indeed an issue, as previously suggested, this excessive mixing may have led to excessive degradation of the emulsion structure. These observations, therefore, reinforced the need for a detailed investigation into the effects of mixing on the performance of the emulsion binder. The results from this investigation are presented following the description of the new experimental methodology.

5.3 Experimental Methodology

The new methodology adopted as a result of the introduction of the Waring blender is presented in this section. The high quality coal feed which was used in the majority of the work in the previous chapter has been used once again in the current work. Consistency in the feed allowed for a comparison between the previous results and the current results. The emulsion used throughout the experiments described in this chapter had a composition of 0.075 PIB emulsifier, 0.075 diesel and 0.85 water. As the materials and preparation procedure for the HIP emulsion remained the same as in the previous chapter they have not been presented again here.

5.3.1 Selective Agglomeration

In all of the experiments, 500 mL of coal slurry, with a solids concentration of approximately 10 wt%, was placed in a 1 L glass beaker. The beaker was positioned on the Waring variable speed blender, as pictured in Figure 5.1, and the sample was agitated at 20 000 rpm to ensure even dispersion of the fine particles prior to the addition of the hydrophobic binder. The binder, either the emulsion or pure diesel, was then added in a single dose and the agitation was continued for a pre-determined period of time. In the experiments in which the influence of mixing time was explored, this agitation time was varied between 0 s – 120 s. The agglomerated sample was then either: dried and the size distribution was analysed using laser diffraction or; passed over a series of screens with aperture sizes 150 μm and 355 μm to obtain a measure of the size distribution of the feed. The former method was used initially to analyse the effect of mixing time on agglomeration using the emulsion binder. The latter method was used to compare the

effect of mixing time on agglomeration for the emulsion binder and a pure diesel binder. The need for two different analysis methods is discussed further in the results section below.

Following the investigation into the influence on mixing time, some standard agglomeration experiments were also carried out which focused on the product yield as a function of organic liquid dosage. In these experiments, the agglomerated slurry was passed over a 355 μm screen and the product coal agglomerates were subjected to wash water provided by a small spray bottle to remove any entrapped mineral matter. The product and reject material were then dried in an oven (110 °C) for 24 hr. The dried samples were weighed and packaged for storage.

5.4 Influence of Mixing on Agglomeration Process

5.4.1 Emulsion Binder

Through the introduction of the new mixing device, the agitation times for the agglomeration process were greatly reduced due to the higher mixing intensity provided. The glass mixing vessel in the new device also provided the capacity to monitor the agglomeration process. As a result, it was noted that the emulsion binder agglomerated fine coal particles more rapidly than pure oil and this observation reinforced the need for a detailed investigation into the effects of mixing on the performance of the emulsion binder. In this initial investigation the effect of mixing was examined by monitoring the changes in the size distribution of the particles as a function of time. As mentioned in the previous section laser diffraction was used to analyse the dried agglomerated samples. The Mastersizer 2000, described in the previous chapter, was once again used for this purpose and the dispersant was a 50% w/w ethanol/water mixture.

Figure 5.3 presents the size distribution of the sample measured by laser diffraction as a function of agitation time for the emulsion binder. It should be noted that the organic liquid dosage of emulsion used in each experiment was constant and equal to 8 wt%. This dosage was selected such that complete agglomeration of the particles was possible if time permitted.

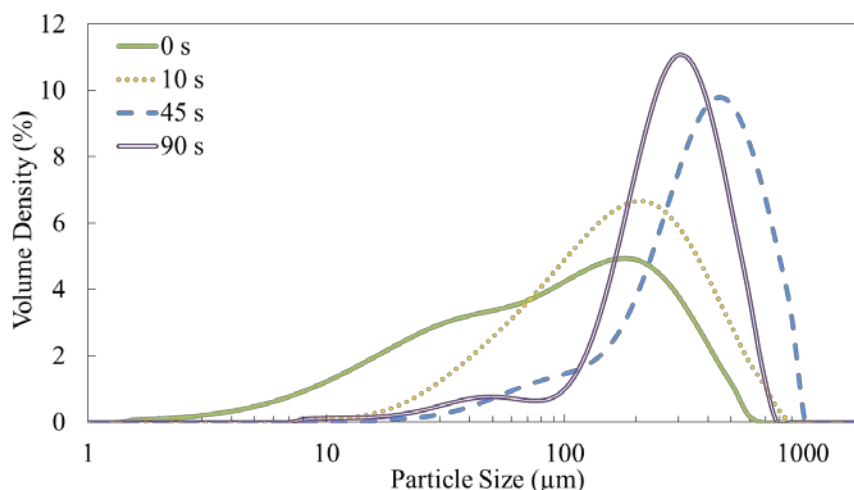


Figure 5.3: The influence of agitation time on the size distribution of the sample measured by laser diffraction using the Mastersizer 2000. The binder used was the water-in-oil emulsion. Note the logarithmic scale for particle size.

Figure 5.3 depicts four size distribution curves for the sample at 0 s, 10 s, 45 s and 90 s of agitation. It can be seen that the feed, at 0 s, had a high proportion of ultrafine, < 100 µm, material. However, after only 10 s of agitation, a considerable portion of these fine particles were joined together to form larger agglomerates. This rapid growth is indicated by the size distribution for the sample at 10 s shifting to the right along the horizontal axis. By 45 s, only a small proportion of the remaining particles were < 100 µm as shown by the contraction of the size distribution curve around a mean agglomerate size of approximately 400 µm. As aforementioned, the agglomeration process appeared to be complete at around 45 s because the colour change of slurry had concluded and the liquid was light brown. However, the mixing was allowed to continue for a total agitation time of 90 s to monitor the effect of excessive agitation. After 90 s of agitation, it can be seen that the size distribution curve contracts further with almost all of the fine particles now formed into larger agglomerates. Additionally, the curve has shifted back towards a lower mean agglomerate size, as compared to the sample at 45 s.

The results displayed in Figure 5.3 clearly depict a growth process as the mean size of the agglomerates generally increases with agitation time and the overall size distribution of the sample narrows. However, a decrease in agglomerate size can be seen at extended mixing times. Therefore, to further elucidate the influence of mixing time when using the

emulsion binder, Figure 5.4 presents the mean diameter of the sample as a function of time.

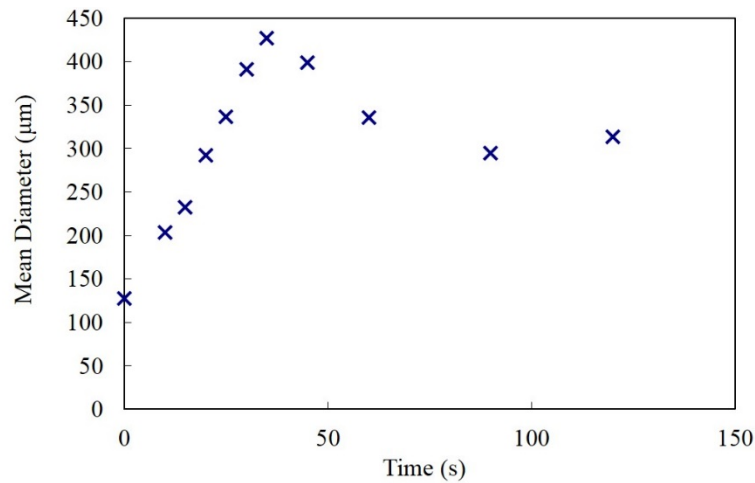


Figure 5.4: The mean diameter of the agglomerates as a function of agitation time using the emulsion binder.

It can be seen in Figure 5.4 that the growth of the agglomerates occurs rapidly when using the emulsion binder. Within 35 s, the feed particles, with a mean diameter of 128 μm, grow into agglomerates with a mean diameter of 427 μm. Following this growth, it is interesting to note, once again, the drop in the mean agglomerate size which occurs after about 40 s. This size reduction continues until about 60 s after which a plateau is reached at a mean agglomerate size of about 300 μm.

These results show that the emulsion binder can successfully agglomerate fine coal. However, importantly, these results also indicate that the best results can be achieved if the mixing time is limited to 40 s when using the emulsion binder because the size of the agglomerates decreases substantially after this time. At this point the cause of the decrease in agglomerate size with extended mixing times was unclear but it was considered that it may be the first indication of emulsion degradation due to excessive shear. Emulsion degradation, or break down, would result in a decrease in the size of agglomerates as there would no longer be sufficient binder present to maintain their structural integrity.

Therefore, to further clarify the cause of this decrease the subsequent phase of experiments was carried out to compare, in detail, the agglomeration kinetics of the emulsion binder with a pure diesel binder. In this way, it was possible to determine

whether the decrease in agglomerate size with extended mixing was unique to the emulsion binder or whether it was an artefact of the experimental conditions. A comparison of the two binders would also clarify the apparent variation in the time required to reach complete agglomeration.

5.4.2 Binder Comparison

The results presented in the previous section highlighted the influence of mixing for the emulsion binder and resulted in an improved understanding of the behaviour of the new binder. Unfortunately, results comparable to those in the previous section could not be obtained for the pure oil binder as the dried agglomerates formed using pure oil lacked the structural integrity required for the laser diffraction analysis. That is, when dried, these agglomerates would disintegrate back to a fine powder due to the evaporation of the diesel oil. This differed from the agglomerates made from the emulsion binder, which retained their form, even when dry. This enhanced structural integrity was found to result from the presence of the emulsifier as it did not appear to evaporate during the drying process.

Therefore, in order to compare the influence of mixing on the agglomeration process for the two binders, a different method of analysis was applied. This method, as described in Section 5.3.1, involved passing the agglomerated slurry over a series of screens with aperture sizes of 150 μm and 355 μm . By then calculating the yield in each size fraction versus time, an approximate measure of the agglomerate growth could be obtained. Presented in Figure 5.5 (a-c) are the results for the size fractions investigated which were -150 μm , +150 – 355 μm and + 355 μm . The -150 μm (less than 150 μm) size fraction was measured to display the agglomeration of the ultra-fine fraction of the feed. Whereas, the +355 μm (greater than 355 μm) size fraction highlighted the growth of the large agglomerates as the aperture size was larger than the top size of the feed originally and, was three times larger than the d_{50} of the feed. The +150 – 355 μm (greater than 150 μm and less than 355 μm) size fraction, therefore, presented the growth in the intermediate range. It should be noted, once again, that a sufficient and constant amount of binder was present in each case such that, if time permitted, complete agglomeration of the coal would occur. Therefore, the dosage used for the emulsion binder was 8 wt% and 16 wt% for the pure diesel binder.

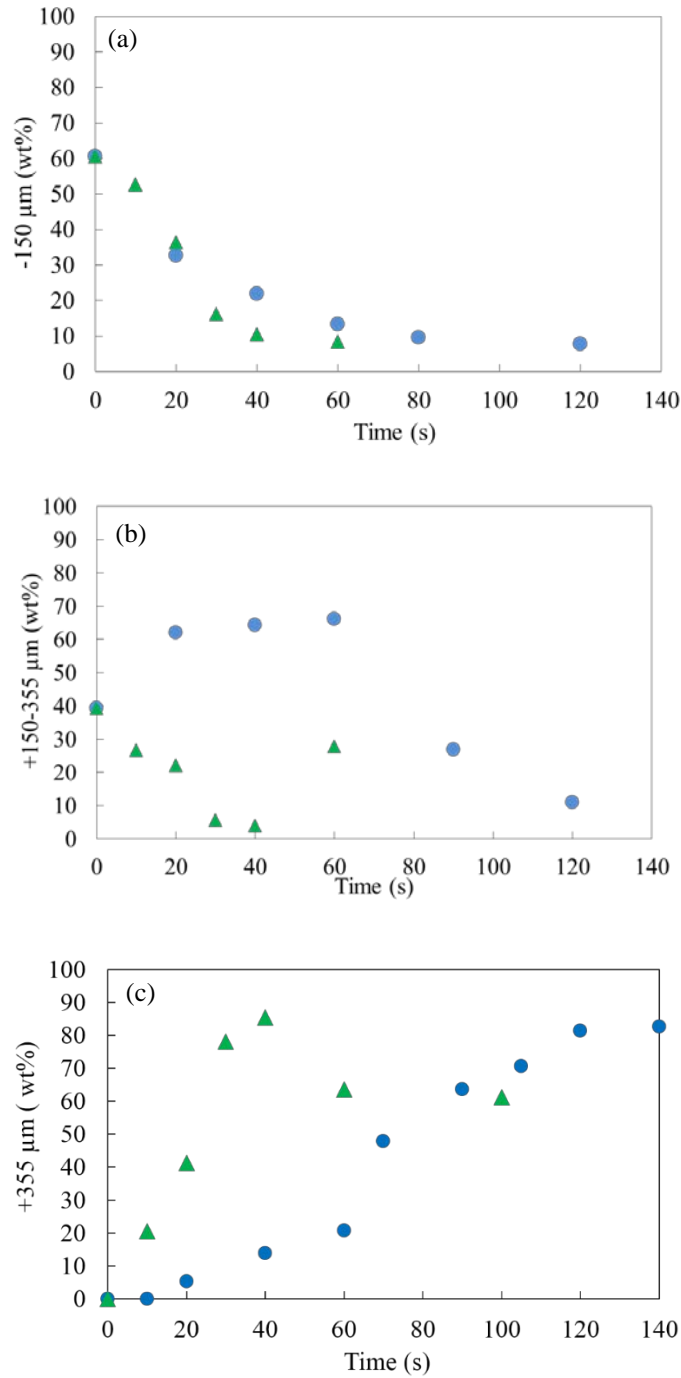


Figure 5.5: The mass percentage of particles within the a) $-150 \mu\text{m}$ size fraction b) $+150 - 355 \mu\text{m}$ size fraction and c) $+355 \mu\text{m}$ size fraction with time for a diesel binder (●) and the emulsion binder (▲) as a function of time.

Considering firstly Figure 5.5a, it can be seen that both binders display a similar trend. In both cases, there is a rapid decrease in the mass of particles in the $-150 \mu\text{m}$ size range indicating that the ultra-fine fraction of the feed is agglomerated very quickly. Within

40 s, the mass fraction of these particles falls from approximately 60 wt% to a minimum value of approximately 10 wt%. Of course, this minimum value represents the fraction of ultra-fine hydrophilic particles in the feed which are not wetted and, subsequently agglomerated, by hydrophobic binders.

Figure 5.5b presents the mass fraction of particles within the + 150 – 355 μm as a function of agitation time. Interestingly, in this size fraction, a marked difference can be seen for the two binders. That is, the diesel binder initially exhibits an increase in the mass of particles in this size range. Then, after approximately 60 s the mass of particles in the + 150 – 355 μm range falls rapidly. After 120 s of agitation, there is only a small fraction of particles remaining in the intermediate size range, indicating that the majority of the particles have been formed into agglomerates which are greater than 355 μm in size. This trend can be compared to the result for the emulsion binder which effectively shows the opposite. Initially, a rapid decrease in the mass of particles within the + 150 – 355 μm range can be seen. This decrease continues until 40 s, at which time there are almost no particles within this size range indicating that all of the particles have been formed into + 355 μm agglomerates. However, after 40 s, the mass of particles within the + 150 – 355 μm size range increases again, indicating that some of the agglomerates have been reduced in size.

Finally, Figure 5.5c presents the mass fraction of +355 μm agglomerates as a function of agitation time. Considering initially the diesel binder, it can be seen that the growth of large (+355 μm) agglomerates is quite slow in the early stages of mixing. However, it has been seen, in Figure 5.5b, that during this time growth was occurring in the fine fraction of the feed. Then, between 60 s – 120 s there is a period of rapid growth as an increasing mass of agglomerates become greater than 355 μm in size. This growth is followed by a plateau in the mass of +355 μm agglomerates which indicates that all of the carbonaceous material in the feed has been formed into large, recoverable agglomerates. Overall, the results for the pure diesel compare well with previous studies on the agglomeration kinetics of fine particles in suspension. As similar to works by Bemer (1979) and Blandin, et al. (2005), these results appear to display three main stages of growth: a period of wetting and wetting and flocculation (< 40 s), in which no considerable growth of agglomerates occurs; a period of rapid and substantial growth (40 s – 120 s) which is

indicated by the rapid increase in the mass fraction for +355 μm agglomerates; and finally, a plateau in the mass of +355 μm agglomerates after 120 s of agitation.

By now considering the results for the emulsion binder in Figure 5.5c it is clear that the general trend is, once again, different to that displayed for the pure diesel binder in the same figure. That is, it appears that large (+355 μm) agglomerates begin to form almost instantly when using the emulsion binder. Furthermore, the formation of these large agglomerates continues at a rapid rate such that all of the carbonaceous material has been formed into +355 μm agglomerates within 40 s, i.e. in one-third of the time required when the pure diesel binder was used. However, as similar to the results presented in the previous section for the emulsion binder, a decrease in the mass fraction of large agglomerates can be observed after 40 s. This decrease continues until 80 s, after which no further decreases are observed in the time period studied. It appears, therefore, that the size of these agglomerates has somehow been reduced such that they fall back into the size fraction of +150-355 μm ; a process which was not observed for the diesel binder.

Taken as a whole, the results in Figure 5.5 indicate that the influence of mixing duration on the growth of agglomerates for the emulsion binder is different to that displayed for the pure diesel binder. It has been considered that this difference may be, at least partially, attributable to the five orders of magnitude difference in the viscosities of the two binders. The diesel binder has a low viscosity of 0.0025 Pa s, whereas the emulsion binder, which is more like a gel, has an ultra-high viscosity of around 100 Pa s, depending on the composition. As such, it seemed logical to assume that this significant variation in the rheological properties would affect their behaviour in the aqueous, turbulent environment of the agglomeration process.

The role of binder viscosity in the growth of agglomerates in liquid suspension has not been investigated in the past. However, the role of binder viscosity in dry powder granulation has been studied extensively and comparisons between dry granulation and agglomeration in suspension have been shown to be valid to a certain extent (Blandin, et al., 2005; Mills, Seville, Knight, & Adams, 2000; Rough, Wilson, & Bayley, 2005). In dry powder granulation, it has been proposed that the viscosity of the binder influences the extent to which kinetic energy is dissipated during particle-particle collisions in the presence of the binder and, the rate of agglomerate compaction (Mills, et al., 2000).

Experimental observations of granulation systems support this proposal as binder viscosity has been shown to affect both the growth rate and mechanism of size enlargement of the granules (Rough, et al., 2005; Schæfer, 2000). In addition, Rough, et al., (2005) showed that the growth of granules can begin to occur instantly and proceed rapidly in dry powder granulation systems in which an ultra-high viscosity binder is used due to the tendency of the particles to stick to the surface of the high viscosity binder globules.

Therefore, the viscosity of the emulsion binder may explain the rapidity with which the large agglomerates are formed. However, it may not adequately explain the significant decrease in the mass fraction of +355 μm agglomerates at extended, >40 s, agitation times as observed in Figure 5.5 and similarly, in Figure 5.4 with the drop in mean agglomerate size. That being said, the process of granule compaction is observed in granulation systems and results from continued collisions of the granules with the impeller, vessel walls and, other granules (Rough, et al., 2005). However, this process has always been shown to cause continued granule growth through coalescence, as the binder migrates from the bulk to the surface of the granule (Rough, et al., 2005). Now, it may be that compaction of the agglomerates made from the emulsion binder is occurring, however as this continued growth is not observed it was concluded that the most likely explanation for the decrease in agglomerate size is indeed emulsion degradation.

As aforementioned, emulsion degradation is undesirable as the benefit gained through the creation of the emulsion structure is lost. Therefore, in an effort to improve the functionality of the emulsion and thus limit the level of degradation the mixing time was limited to 40 s when using the emulsion binder. The following section presents the results of agglomeration experiments in which this optimised mixing time was used.

5.5 Improved Mixing Time

In this section the influence of the organic liquid dosage on the yield of product coal was re-evaluated to determine the effect of the improved mixing time when using the emulsion binder. The agglomeration experiments were also repeated using the diesel binder to account for the introduction of the new mixing device. The mixing time required for the pure diesel binder was set at 2.0 min as a consequence of the results presented in Figure 5.5.

Figure 5.6 presents the yield of product coal for each binder as a function of the organic liquid dosage. Once again, it should be noted that the pure diesel comprises entirely of organic liquid. However, only a small fraction (0.15) of the emulsion binder is organic liquid and thus, the mass of the PIB emulsifier and diesel within the emulsion are considered in the calculation of the organic liquid dosage but not the mass of the water. Trend lines have been added to both data sets.

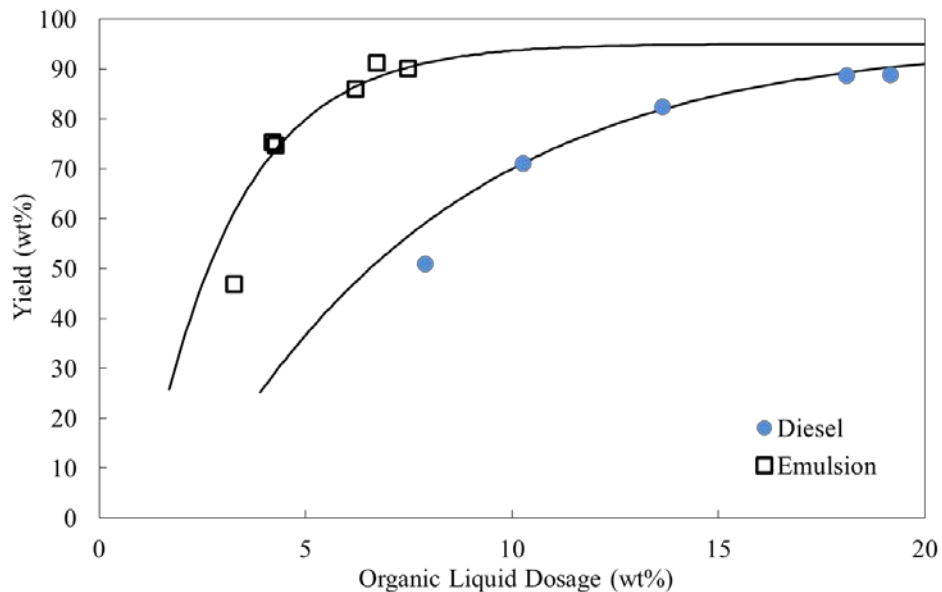


Figure 5.6: Yield of product coal as a function of organic liquid dosage for the pure diesel binder and the emulsion binder using optimised agitation times in the agglomeration experiments.

It can be seen that the results presented in Figure 5.6 are similar to those presented in Chapter 4. Both binders exhibit an increase in yield as the organic liquid dosage is increased. Furthermore, a plateau in yield is observed, once again, for both binders which commences at the minimum dosage required to completely agglomerate all of the carbonaceous material in the feed. As consistent with the results presented in Chapter 4 for the same (high quality) feed, a dosage of 16 – 17 wt% of diesel was required to reach this plateau. The uniformity in the results for the pure diesel was not surprising as previous studies have shown that consistently good results can be achieved for a variety of mixing conditions using pure oil as mixing intensity and mixing duration are linked via an inverse relationship (Capes & Germain, 1982). The emulsion binder, however, now

required a dosage of only 5 – 6 wt% signifying that a 3-fold reduction in the amount of organic liquid required had been achieved.

This 3-fold reduction was a considerable improvement on the 2-fold reduction consistently achieved throughout the work presented in Chapter 4. It should be noted, however, that this result does not mean that the overall level of binder required to agglomerate the coal feed has been reduced as a result of the adjusted experimental conditions. Rather, these results indicated that more of the emulsion binder that is introduced into the process is now available for agglomeration. In other words, this result seemed to indicate that by limiting the level of agitation applied to the emulsion binder, the level of degradation has been reduced.

Although a 3-fold reduction represented a significant advance in the overall maximisation of the functionality of the emulsion, it was considered that the emulsion, in theory, still had a much greater potential. The substitution theory, as described in Chapter 4, Section 4.2, predicts that an emulsion binder with a dispersed, aqueous phase volume fraction of 0.85 could achieve a 7-fold reduction. Therefore, only half of the theoretical potential of the emulsion was being realised. At this stage, the factors which limited the performance of the binder were not known. However, the factor which was considered to be most likely to still have the greatest effect was emulsion stability, or lack thereof, and the resulting degradation. Therefore, as a first attempt to improve the stability of the emulsion, an investigation was carried out to determine the effect of mixing intensity during the preparation of the emulsion on its performance as a binder. This work was done in an effort to increase the ability of the emulsion to withstand the shear applied during the agglomeration process.

5.6 Influence of Mixing Intensity in Emulsion Preparation

The level of mixing applied during the emulsion preparation process may influence the performance of the emulsion as the level of mixing, in part, determines the stability of the emulsion. The level of mixing influences stability as it controls the internal droplet size within the emulsion and emulsions which have smaller droplets are generally more stable (Dunstan, et al., 2012). Therefore, it was thought that by increasing the mixing intensity applied during the preparation of the emulsion and thus, reducing the size of the internal droplets, the stability to the emulsion binder may be enhanced. It should be noted that the

need for small internal droplets is further accentuated in this application as the emulsion must be dispersed into small globules via the action of the impeller in order to be distributed among the solid particles. Figure 5.7 presents a schematic representation of two of these individual water-in-oil emulsion globules.

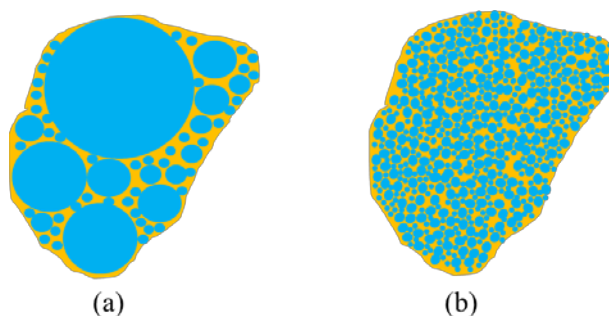


Figure 5.7: Schematic representation of two individual water-in-oil emulsion globules with a) internal droplets of a comparable to the globule size and b) internal droplets which are considerably smaller than the globule size.

Now, if the internal droplets are not sufficiently small, such as in Figure 5.7a, droplet cleavage may occur resulting in the release of the internal aqueous phase to the surrounding suspension. In this instance, the benefits gained through the creation of the emulsion structure would be nullified. However, if the droplets are sufficiently small, such as in Figure 5.7b, the likelihood of a large release from the internal, aqueous phase through droplet cleavage is greatly reduced. Therefore, a device that could impart high shear to the emulsion during the preparation process was sought.

5.6.1 Microniser

A highly specialised device was sourced from Quadro Engineering for the refinement of the internal droplets within the emulsion. The device, called a HV-Emulsifier, was selected as it had the ability to provide high shear homogenisation. Moreover, this device, which will be referred to as the microniser from here on in, could produce micronised emulsions without the need for subsequent high pressure processing. Figure 5.8 presents the microniser used in this work. The feed to the device consisted of an emulsion prepared using the methodology described in Chapter 4, Section 4.3.3. This emulsion was pumped from a 2 L feed tank using a Masterflex peristaltic pump and received in a separate tank after processing.



Figure 5.8: The device used to produce the micronised emulsion binder.

Figure 5.8 shows the control box, motor and the reactor head. The shearing device, located within the reactor head, has a maximum tip speed of 70 m/s at an operating frequency of 90 Hz. At these high shear rates heat accumulated relatively quickly and as such the flow rate of the emulsion had to be at least 4 L/min to prevent overheating. Overheating had to be avoided as it would have resulted in damage to both the microniser componentry and the emulsion binder.

Due to the high viscosity of the emulsion binder, unforeseen difficulties were encountered in meeting the required pumping rate. Therefore, initially, emulsions with lower dispersed, aqueous phase volume fractions of 0.50 and 0.70 were processed. At these volume fractions, the emulsion had a lower viscosity and, thus, could be pumped with relative ease at the required rate. It should be remembered, however, that the data presented in Figure 5.9 is intended to qualitatively represent the reductions which may be achieved using the microniser and does not quantitatively represent the more concentrated emulsion, which have a smaller initial internal droplet size.

Prior to the introduction of the micronized emulsion binder to the agglomeration process, a small study was carried out to investigate the effect of the operating frequency of the microniser on the droplet size within the emulsion. An emulsion was made with an aqueous, dispersed volume fraction of 0.50 and processed using the microniser at various

operating frequencies. The size distribution of the droplets within the processed emulsion was then analysed using a Mastersizer S (Malvern Instruments, Malvern, UK). The liquid medium used to dilute the emulsion and thus disperse and mobilise the internal water droplets was diesel. Figure 5.9 presents the effect of the operating frequency on the d_{50} of the droplets within the emulsion.

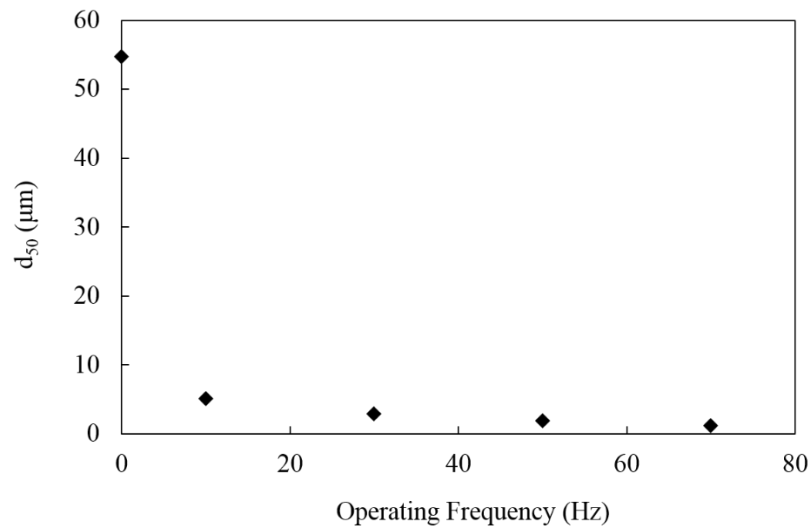


Figure 5.9: Effect of the operating frequency of the microniser on the d_{50} of the droplets within the emulsion.

It can be seen in Figure 5.9 that the emulsion with a dispersed phase volume fraction of 0.50 initially had an internal droplet d_{50} of 55 μm. However, even at low operating frequencies, this droplet size was quickly reduced to 5 μm. At the highest operating frequency tested, 70 Hz, the d_{50} of the droplets was only 1 μm. Therefore to produce an emulsion with smallest internal droplet d_{50} , and presumably the highest stability, high operating frequencies must be used.

5.6.2 Influence of Mixing Intensity on Performance of Emulsion

An emulsion with a dispersed phase volume fraction of 0.70 was processed at 70 Hz in the microniser for use as a binder in the agglomeration process. As noted, an emulsion with a volume fraction of 0.70 was tested because, at this composition, the emulsion could still be pumped at the required rate. Of course, an emulsion with a dispersed phase volume fraction of 0.70 is not technically a high internal phase emulsion and, in addition, can only theoretically achieve a maximum reduction of 3.3-fold.

Figure 5.10 presents the results of agglomeration experiments using the micronised emulsion binder. The results for the diesel binder and the standard emulsion binder with an aqueous volume fraction of 0.85 have been reproduced for inclusion in Figure 5.10. The results for the standard emulsion have been faded to grey to draw attention to the new results.

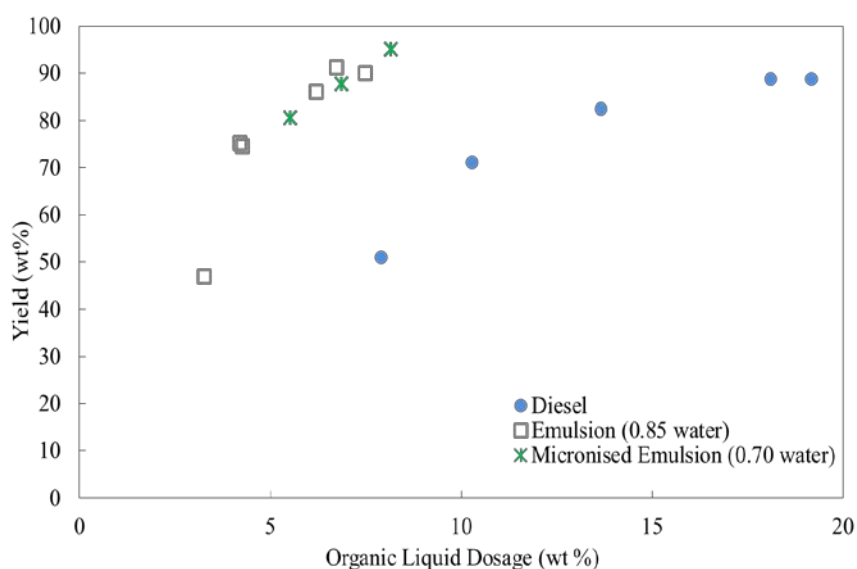


Figure 5.10: Yield of product coal as a function of organic liquid dosage for the pure diesel binder, a standard emulsion binder with an aqueous volume fraction of 0.85 and a micronised emulsion binder with an aqueous volume fraction of 0.70.

As can be seen in Figure 5.10 the performance of micronised emulsion binder has matched that of the emulsion prepared using the standard procedure and, thus, achieved a 3-fold reduction in the organic liquid dosage as compared to the benchmark diesel case. This consistency between the two data sets appeared to indicate that the size reduction of the internal droplets performed using the microniser had no effect on the performance of the emulsion as a binder. However, on the other hand, it can be said that an improvement in the performance of the emulsion binder had been achieved because a 3-fold reduction is effectively the theoretical maximum reduction achievable using an emulsion with a dispersed phase volume fraction of 0.70. Following on, if the assertion that the emulsion binder is degrading during the agglomeration process is valid, these results show that the micronised emulsion degrades to a lesser extent.

At the time, this result was encouraging as it once again indicated that the performance of the emulsion binder could be improved by improving the emulsion stability. However the use of the microniser unfortunately could not be pursued any further due to the operational limitations imposed by the emulsion viscosity and the flow rate requirements of the device. Therefore, another means by which the stability, and thus functionality, of the emulsion could be improved was required. This work is presented in the initial part of following chapter which focuses on improving the functionality of the emulsion via modifications to its composition.

5.7 Summary

The influence of mixing on the functionality of the emulsion was explored in this chapter. In the first instance, the influence of mixing time on the agglomeration process using the emulsion binder was investigated. As a result of these experiments a decrease in agglomerate size was found to occur at extended agitation times. To further clarify this finding, a comparison of the influence of mixing time on agglomerate size was performed between the emulsion and a pure diesel binder. It was found that a similar decrease in agglomerate size was not observed when using a pure oil and thus, it was concluded that the decrease was a result of emulsion degradation. The comparison between the agglomeration kinetics of the two binders also highlighted a variation in the mixing time required to achieve agglomeration. The emulsion binder required 40 s whereas the pure diesel required 120 s to reach the same agglomerated state. The application of these optimised mixing times resulted in an improvement in the performance of the emulsion binder which equated to a 3-fold reduction.

In the second phase of the work presented in this chapter the influence of mixing intensity during the preparation of the emulsion was investigated. This work was undertaken in an effort to improve the ability of the emulsion to withstand the mixing applied in the agglomeration process. It appeared that by increasing the level of mixing the emulsion was subjected to during preparation its stability and, thus performance improved.

The work in this chapter indicated that the mixing regimes used in the preparation of the emulsion and, in particular, the agglomeration process influence the functionality of the emulsion. Moreover, it appears that the functionality of the emulsion has been improved by limiting the level to which the emulsion degrades. Therefore, due to these

improvements, the following chapter revisits the influence of emulsion composition on functionality of the binder. It was considered that compositional changes would now have an effect on the performance of the emulsion, contrary to the results presented in Chapter 4, as the level of degradation had been significantly reduced.

Chapter 6

Maximising Binder Functionality through Composition

Contribution to the Research

Paper:

van Netten, K., Moreno-Atanasio, R., & Galvin, K. P. (2014). Fine Particle Beneficiation through Selective Agglomeration with an Emulsion Binder. *Industrial and Engineering Chemistry*, 53, 15747 - 15754.

Contribution:

Author	Primary Contribution
van Netten, K.	Collaborator in design of experimental program, carried out experimental program of work, data analysis, and lead author of paper
Moreno-Atanasio, R.	Supervisor and collaborator in preparation of paper
Galvin, K. P.	Co-supervisor, collaborator in design of experimental program, and co-author of paper

Paper:

van Netten, K., Moreno-Atanasio, R., & Galvin, K. P. (2016). Selective agglomeration of fine coal using a water-in-oil emulsion. *Chemical Engineering Research and Design*, 110, 54 - 61.

Contribution:

Author	Primary Contribution
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6.1 Introduction

The findings presented in Chapter 4 and Chapter 5 demonstrated that the emulsion had the ability to selectively agglomerate coal at a reduced organic liquid dosage. Throughout Chapter 4, a 2-fold reduction in the organic liquid dosage was consistently achieved and while the work in Chapter 5 led to a 3-fold reduction it was considered that the emulsion was still performing well below its potential. Therefore, the work in this chapter focused on maximising the functionality of the emulsion through modifications to its composition.

In the previous chapter it was found that the functionality and performance of the emulsion may be improved by limiting emulsion degradation during the agglomeration process. Emulsion degradation is undesirable as it negates the benefits gained through the creation of the emulsion structure and may occur if the stability of the emulsion is not sufficient to withstand the mixing within the turbulent, aqueous, environment of the agglomeration process. Therefore, initially in this chapter, a means of improving the stability of the emulsion and hence reducing degradation via a modification to the composition was investigated. This modification was the inclusion of electrolytes into the aqueous phase of the emulsion.

Following the changes made to improve the stability, the investigation into the effect of the dispersed phase volume fraction on the functionality of the emulsion was repeated. It was anticipated that the effect of modifying the dispersed phase on the functionality of the emulsion would now be apparent due to the reduced level of degradation.

Finally in this chapter, the influence of the composition of the continuous phase on the functionality of emulsion was explored in an effort to increase the functionality of the emulsion. In this final section the parameters under investigation were the emulsifier type and the oil type.

6.2 Experimental Methodology

The original components of the emulsion were tap water, diesel and the PIB emulsifier. This composition was used consistently throughout the work until this point. The work in this chapter considers the effects of modifications to this original composition on the functionality of the binder. In some cases sorbitan mono-oleate was used as the emulsifier, instead of the PIB emulsifier. Similarly, in some experiments kerosene was used to form the continuous, organic phase of the emulsion in the place of diesel. Tap water was still used as the aqueous phase however, as noted in the introduction, a salt was dissolved into the water prior to its inclusion into the emulsion.

6.2.1 Materials

Sorbitan mono-oleate (SMO), sourced from Sigma-Aldrich, was used without any further chemical or physical modification. Kerosene was sourced from Recochem Inc and was used without any chemical or physical modification. The density and viscosity of kerosene are 800 kg/m^3 and 0.0016 Pa s , respectively (Recochem, 2011). Sodium chloride salt was sourced from Cerebos Ltd and dissolved in tap water at a concentration of 3 wt%. The resulting aqueous salt solution was used to form the dispersed phase of the emulsion.

The coal feed used throughout the work in this chapter was sourced from the same batch used throughout the work in Chapter 4 and Chapter 5. This coal feed was used once again to provide consistency throughout all of the work to allow for comparisons between the new results and previously obtained results.

6.2.2 Preparation of High Internal Phase Emulsion

The experimental methodology for the preparation of the emulsion binder effectively remained the same as described in Section 4.3.3 in Chapter 4 but has been reproduced below.

To prepare the emulsion, the organic components, the continuous oil phase and the emulsifier, were placed into a stainless steel mixing bowl. The comparably large volume of water was then added in small increments under continuous mixing provided by a Russell Hobbs Electric Hand Mixer (350 W motor) set at maximum speed. To ensure phase inversion of the emulsion did not occur, the incremental volume of water was

limited to half of the initial volume of the organic phase. Furthermore, the incremental volume of water was completely incorporated into the organic phase prior to the addition of the next increment of water. An increment of water was deemed to be incorporated into the organic phase when water droplets were no longer visible on the surface of the hydrophobic emulsion. The total time taken to add the water was typically 360 s.

6.2.3 Selective Agglomeration

In general, the investigations in this phase of work involved modifications to the composition of the emulsion binder. As such, the experimental methodology for the agglomeration experiments remained unchanged from that presented for the Waring blender in Chapter 5, Section 5.3.1, and has not been presented again here.

6.3 Influence of Electrolyte Presence in Aqueous Phase

Tap water had been used to form the aqueous, dispersed phase of the emulsion binder in the experiments performed thus far. However, as the stability of the emulsion has proven to be an issue, the inclusion of electrolytes into the aqueous phase was investigated in the next stage of work. The use of an aqueous salt solution was considered, in the first instance, as a result of observations of the emulsion during storage.

During storage over relatively short periods of time, for example a few days, the emulsion exhibited signs of instability. The most prominent and immediate of these signs was a reduction in the emulsion viscosity. Galvin, et al. (2001) has shown that the viscosity of a high internal phase emulsion is inversely proportional to the internal droplet size and as such, the observed reduction in viscosity was presumed to occur as a result of growth of the internal droplets. Now, the inclusion of an aqueous salt in these internal droplets impedes this growth by retarding the rate of diffusion of water from the small to the large droplets (Ostwald ripening) as well as hindering the rate of droplet coalescence due to film rupture (Aronson & Petko, 1993; Gaitzch, Gabler, & Kraume, 2011). Therefore an emulsion binder was made with a 3 wt% aqueous sodium chloride solution as the dispersed phase and, subsequently, examined in the agglomeration process. Table 6.1 presents the composition of the emulsion used in this stage.

Table 6.1: The composition of the emulsion used in agglomeration experiments in which the effect of electrolyte presence in the dispersed, aqueous phase was investigated.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
3 wt% aqueous NaCl	Diesel	PIB emulsifier
0.84	0.08	0.08

As shown in Table 6.1, no modifications to the organic phase were made in this phase of work and as such it consisted of diesel and the PIB emulsifier.

Figure 6.1 presents the yield of product coal as a function of the organic liquid dosage for the agglomeration experiments using the 3wt% aqueous NaCl-in-diesel emulsion. The benchmark diesel case is presented along with the results from the previous chapter for the emulsion binder made with tap water. The results for the emulsion binder made with tap water have been faded to grey to draw attention to the new results and trend lines have been added to each data set.

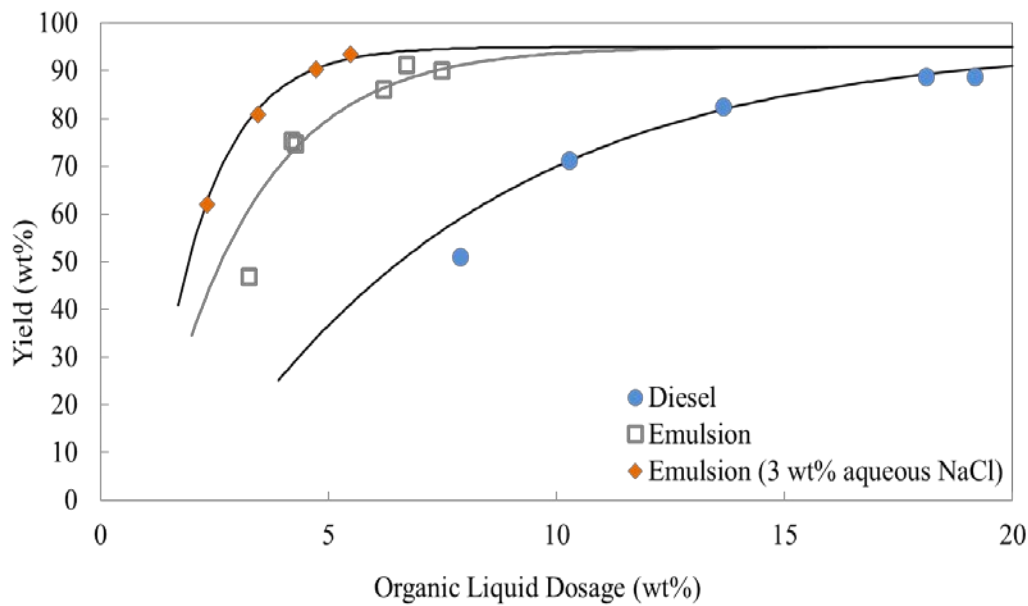


Figure 6.1: Yield of product coal as a function of organic liquid dosage for the pure diesel binder, a tap water-in-oil emulsion binder and a 3 wt% aqueous NaCl-in-oil emulsion binder.

Figure 6.1 shows that the inclusion of the salt into the dispersed, aqueous phase of the emulsion binder has led to an improvement in the performance of the emulsion binder.

That is, a reduced dosage of organic liquid is now required to achieve agglomeration, as indicated by the yield curve shifting to the left. This reduction is of the order of 4-fold, as compared to the benchmark diesel case, which is an improvement on the 3-fold reduction achieved by the emulsion binder made with tap water.

These results, therefore, suggest that by hindering the growth of the internal water droplets, the stability of the emulsion during dispersal within the agglomeration process has been improved. In addition, observations of the emulsion during storage indicated that the long-term stability had also been drastically improved as signs of degradation were no longer evident even after several months of storage.

6.3.1 Emulsion Stability

The introduction of salt to the internal, aqueous phase of the emulsion also afforded an opportunity to confirm the occurrence of emulsion degradation. That is, due to the presence of the salt the extent that the emulsion degraded could be measured by monitoring the change in conductivity of the external suspending liquid. If the emulsion did not degrade and the internal water droplets were encapsulated by oil, the dissolved salt would not add to the conductivity of the external suspending liquid. However, if the emulsion structure was indeed breaking down as suspected, the dissolved salt would be released and thus influence the conductivity of the suspending liquid. In these experiments, 8 g of emulsion (composition as described in Table 6.1) were dispersed in 500 ml of tap water using the Waring blender set at a speed of 22 000 rpm, effectively forming a water-in-oil-in-water emulsion. The conductivity of the suspension was measured as a function of agitation time

To simplify the measurements these experiments were carried out in the absence of the coal feed. These experimental conditions were considered sufficient at the time as the aim was to confirm the occurrence of degradation rather than provide a quantitative assessment. Figure 6.2 presents the conductivity of the suspending liquid as a function of agitation time. Also presented in the figure is the maximum limit of the conductivity which would result if all of the salt within the internal aqueous phase of the emulsion was released to the suspending liquid. It should be noted that the experimental curve begins at zero as each conductivity reading was calibrated to account for the conductivity of the tap water.

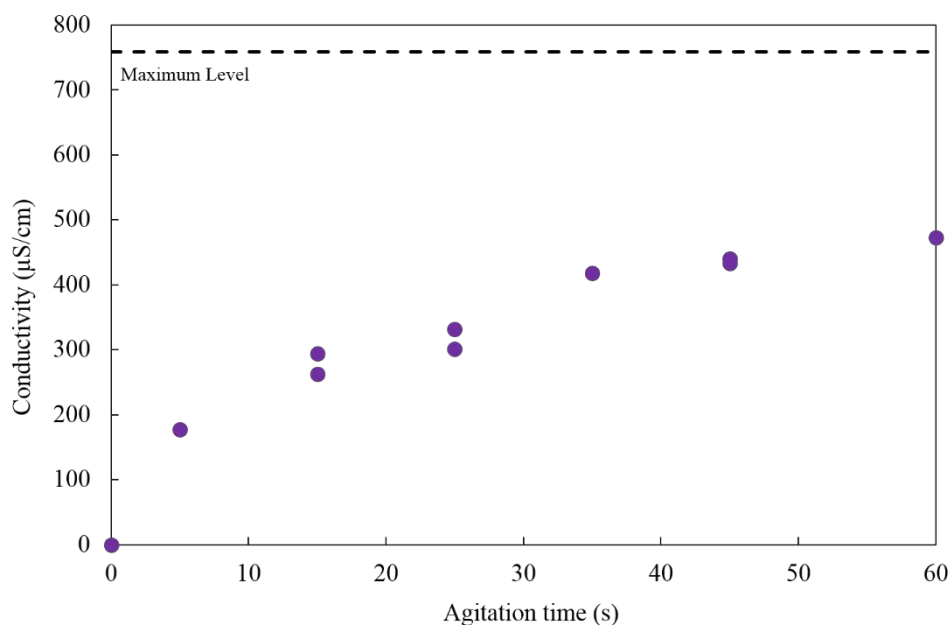


Figure 6.2: Conductivity of the suspending liquid as a function of agitation time.

The results in Figure 6.2 confirm that degradation of the emulsion occurs as the conductivity of the suspending liquid increases with time. This increase is initially quite rapid, with the conductivity rising to approximately 400 $\mu\text{S}/\text{cm}$ within 40 s. After this time, however the conductivity of the suspension tapers off to a constant level. Of course, it must be remembered that these results only apply in a qualitative sense. That is, as solid particles also interact with the emulsion binder in an agglomeration process the time scale would be different to that observed here.

6.4 Influence of Aqueous Phase Volume Fraction – Revisited

The experimental results presented in Chapter 4 indicated that the dispersed, aqueous phase volume fraction had no effect on the performance of the emulsion binder. At the time, it was hypothesised that the emulsion was degrading to a certain, constant level during the agglomeration process such that the effect of varying the composition was not apparent. Now, as the mixing time has been optimised such that emulsion degradation is limited and the inclusion of salt into the dispersed phase has improved the stability of the emulsion it seemed prudent to revisit the investigation into the influence of the dispersed, aqueous volume fraction. Therefore, emulsion binders with dispersed, aqueous phase volume fractions of 0.89 and 0.94 were tested. Table 6.2 presents the compositions of these higher volume fraction emulsion binders.

Table 6.2: The composition of the emulsions used in agglomeration experiments in which the influence of the dispersed, aqueous phase volume fraction was investigated.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
3 wt% aqueous NaCl	Diesel	PIB emulsifier
0.89	0.055	0.055
0.94	0.03	0.03

Figure 6.3 presents the yield of product coal as a function of organic liquid dosage for the higher volume fraction emulsion binders. Also presented in Figure 6.3 are the results from the previous section for the emulsion binder made from 3 wt% aqueous NaCl solution and with a dispersed phase volume fraction of 0.84. The results for the emulsion binder made with tap water and the benchmark diesel case have also been reproduced for comparison. The results which have been presented previously in this chapter have been faded to grey in the figure to draw attention to the most recent results.

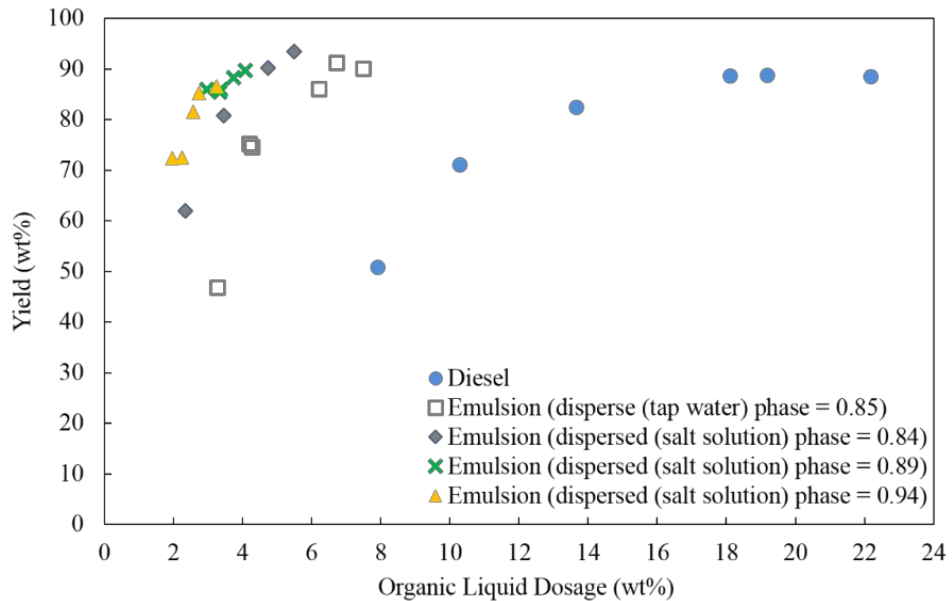


Figure 6.3: Yield of product coal as a function of organic liquid dosage for the pure diesel binder and various emulsion binders. The emulsions had dispersed phase volume fractions in the range of 0.84 – 0.94. In each case the dispersed phase consisted of either tap water or a 3 wt% aqueous NaCl solution.

Figure 6.3 shows that a reduced amount of organic liquid is required to achieve agglomeration when higher volume fraction emulsions are used, as indicated by the respective yield curves shifting further left along the horizontal axis. A 5-fold reduction, as compared to the benchmark diesel case, was realised through the use of the emulsion with a dispersed phase volume fraction of 0.89, while the emulsion with a dispersed phase volume fraction of 0.94 achieved the best result with a 6-fold reduction. When comparing these results to the 4-fold reduction achieved by the emulsion with a dispersed phase volume fraction of 0.84, it becomes apparent that the dispersed phase volume fraction does indeed have an effect on the performance of the emulsion binder. This was an important finding as it appeared to qualitatively confirm the initial hypothesis that the overall reduction in the organic liquid dosage is related to the extent that water takes the place of oil in filling the void spaces within the agglomerates.

The findings in this investigation were a significant milestone in the work thus far as they included the best reduction achieved to date and appeared to confirm the substitution theory detailed in the beginning of Chapter 4. However, the fact remained that the reductions achieved by the emulsion binders in this most recent work were still significantly less than predicted in the substitution theory. That is, the reductions in the organic liquid dosage achieved by the emulsions with dispersed phase volume fractions of 0.89 and 0.94 should have been 9-fold and 17-fold, respectively. Consequently, it may be considered that degradation of the emulsion is still occurring to a considerable extent and this break down is responsible for the lower than expected results. However, it may also be that the maximum theoretical reductions depicted in Figure 4.1 cannot be realised as other factors limit the functionality of the HIP emulsion as a binder.

At this point in the study, the factors which limited the functionality of the emulsion as a binder were not immediately apparent. Therefore, in the following stage of work, the influence of the emulsifier type was investigated in an attempt to elucidate the additional factors which affect the functionality of the emulsion binder.

6.5 Influence of Emulsifier Type

The only emulsifier used in the emulsion binders tested thus far in this work has been the PIB emulsifier. The PIB emulsifier was selected as it is an emulsifier with a low hydrophile-lipophile (HLB) value. A low HLB value means that it is soluble in the oil

phase and therefore, by Bancroft's rule, will form a W/O emulsion (Adamson & Gast, 1997; Bancroft, 1913). However, while the PIB emulsifier did allow for the successful creation of HIP W/O emulsions, it was not known whether it was the most suitable emulsifier for this original application. Furthermore, the cost of the PIB emulsifier, relative to diesel, is quite high (estimated to be 2-3 times dearer) thus providing further reason to explore other options.

Therefore, in this stage of the work, a series of experiments were undertaken using an emulsion binder made from a different emulsifier, sorbitan mono-oleate (SMO). SMO was selected as it satisfies the requirement of a low HLB value and is relatively inexpensive, that is, the price is comparable to the cost of diesel. Table 6.3 presents the composition of the emulsion binder used in this investigation.

Table 6.3: The composition of the emulsion binder used in agglomeration experiments in which the influence of the emulsifier type was investigated.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
3 wt% aqueous NaCl	Diesel	SMO
0.89	0.055	0.055

In the initial agglomeration experiment using the new emulsion, the agitation time employed matched that used in the previous experiments. However, it was noted that the colour change of the slurry, signifying the completion of the agglomeration process, occurred sooner than observed for the experiments using the PIB based emulsion binders. The PIB based emulsion binders required 40 s, whereas the SMO based emulsion binder appeared to need only 15 s. Therefore, in the interest of limiting emulsion degradation the agglomeration time was restricted to 15 s for the experiments using the SMO based emulsion binder.

Figure 6.4 presents the yield of product coal as a function of the organic liquid dosage for the experiments in which the emulsion binder made with SMO was used. Also presented in Figure 6.4 are the results from Figure 6.3 for the emulsion binder made with the PIB emulsifier and, also, with an aqueous phase volume fraction of 0.89. The benchmark diesel case is also presented for comparison.

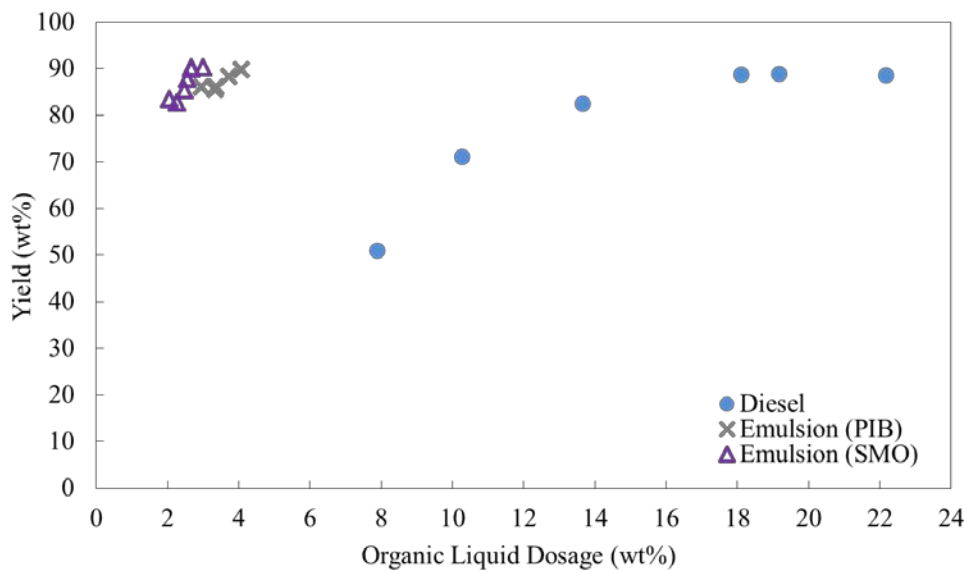


Figure 6.4: Yield of product coal as a function of organic liquid dosage for the pure diesel binder, an emulsion binder made from a PIB emulsifier and an emulsion binder made from a SMO emulsifier. The aqueous phase of both emulsion binders consisted of 3 wt% aqueous NaCl and had a volume fraction of 0.89.

Figure 6.4 shows a further decrease in the dosage of organic liquid required to achieve a given yield when using the SMO based emulsion binder. This decrease equates to a 7.5-fold reduction in the organic liquid dosage, as compared to the benchmark diesel case, which clearly surpasses even the best result achieved by the PIB based emulsion. As SMO has been shown, in the past, to provide lower stability for HIP aqueous salt-in-oil emulsions than PIB type emulsifiers, this was a surprising result (Rajapakse, 2007). It was assumed that an emulsion binder with a lower stability would break down more rapidly and, thus, result in lower yields for a given organic liquid dosage. Therefore, to confirm this assumption a small investigation into the stability of the SMO based emulsion was carried out. As similar to the experiments described in Section 6.3.1 for the PIB based emulsion, 8 g of emulsion were dispersed in 500 ml of tap water and the conductivity of the suspension was measured as a function of agitation time. The composition of the emulsion used in these experiments is presented in Table 6.4.

Table 6.4: The composition of the emulsion binder used in emulsion stability experiments.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
3 wt% aqueous NaCl	Diesel	SMO
0.84	0.08	0.08

As can be seen in the table, an emulsion with an aqueous phase volume fraction of 0.84 was used. This emulsion was used such that the results could be compared to those presented in Figure 6.2 for the emulsion binder made with the PIB emulsifier. Figure 6.5 presents the results for the SMO based emulsifier along with the results for the PIB emulsifier. Also presented in the figure is the maximum limit of the conductivity which would result if all of the salt within the internal aqueous phase of the emulsion was released to the suspending liquid. Once again, it should be noted that the experimental curve begins at zero as each conductivity reading was calibrated to account for the conductivity of the tap water.

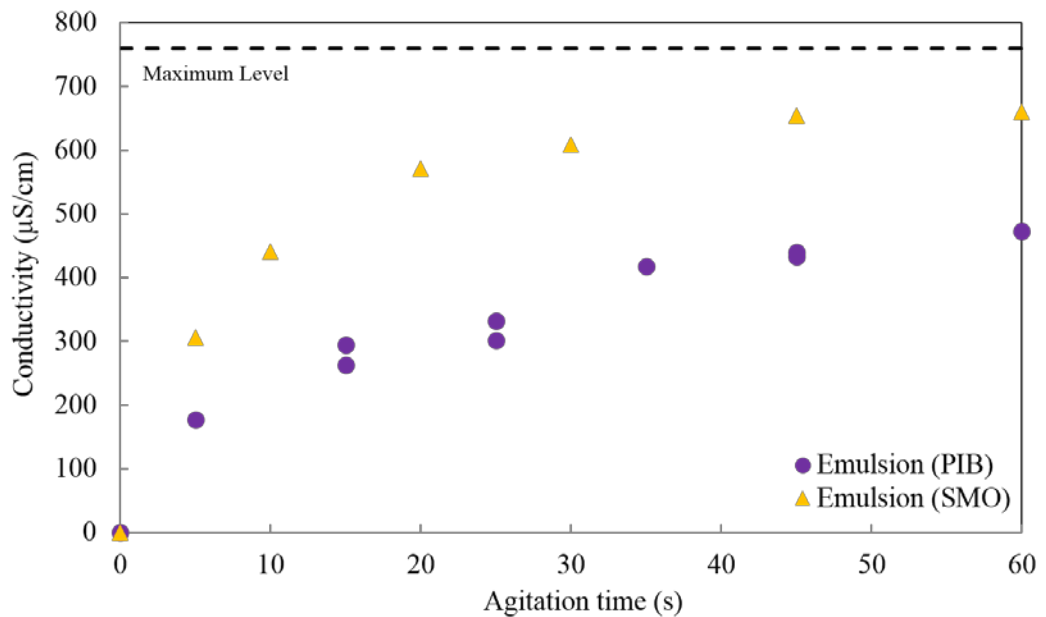


Figure 6.5: Conductivity of the suspending liquid as a function of agitation time for an emulsion binder made from a PIB emulsifier and for an emulsion binder made from a SMO emulsifier.

The results in Figure 6.5 show that the emulsion made from SMO also degrades in the turbulent, aqueous environments of the agglomeration process as the conductivity of the

suspending liquid increases with agitation time. This increase is followed by a plateau in conductivity similar to the results for the emulsion made with the PIB emulsifier. Now, by comparing the two curves it can be seen that the plateau for the SMO based emulsion occurs at a higher value, indicating that the emulsion degrades to a greater extent. Also, a comparison of the initial slopes of the two curves reveals that the SMO based emulsion breaks down more rapidly than the emulsion made with the PIB emulsifier. Of course, it must be remembered that these results can only be considered qualitatively due to the absence of the solid particles. Still, these results do seem to confirm that the SMO emulsifier results in an emulsion with a lower stability than the PIB emulsifier and this, once again, makes the performance improvement realised through the use of SMO surprising.

Therefore, to account for the superior performance of the SMO based emulsion attention was once again placed on the action of emulsion degradation. More specifically, it was considered that a balance must exist between the rate with which the emulsion degrades and the rate with which it achieves agglomeration and the result of this balance determines the extent of the reduction in the organic liquid dosage. That is, the longer the emulsion takes to achieve agglomeration, the greater the level of degradation and thus, the lower the reduction. In the case of the SMO based emulsion binder it seems that, even though the emulsion had a lower stability as compared to the PIB based emulsion, the increased speed with which it achieved agglomeration more than compensated for this and resulted in a greater reduction in the organic liquid dosage.

In an effort to explain the highly beneficial property of the SMO based emulsion to achieve agglomeration in a reduced amount of time, as compared to the PIB based emulsion, attention was drawn to the relative viscosities of the two emulsifiers. The viscosity of the PIB emulsifier is 2.5 Pa s, whereas the viscosity of the SMO emulsifier is less, in the range of 1.2 – 2 Pa s. Now, the viscosity of the emulsifier within a HIP emulsion is of consequence as it contributes to the overall viscosity of the continuous phase and the viscosity of the continuous phase affects the overall rheology of the emulsion. More specifically, the continuous phase viscosity affects the internal droplet size and the viscosity of the emulsion (Das et al., 1992). These parameters are important as they are both factors which may affect the behaviour of the emulsion within the turbulent, aqueous environment of the agglomeration process.

Therefore, to investigate this effect further, a series of experiments were carried out using an oil of lower viscosity to form the continuous phase of the emulsion. As similar to the effect of SMO, the use of a lower viscosity oil should lower the overall viscosity of the continuous phase thus resulting in a modification to the rheological properties of the emulsion. Prior to this investigation, however, a small series of experiments were carried out to determine the minimum time required to achieve agglomeration using the SMO based emulsion binder.

6.5.1 Minimisation of Agglomeration Time

The discovery of the reduced mixing time required when using the SMO binder served to instigate an interest in discovering the minimum operating, or residence, time required in the agglomeration process. A minimised residence time is favourable in an industrial setting as it reduces capital costs, through reduced unit size requirements, increases throughput capacity and reduces energy costs.

The residence time within the agglomeration process using the emulsion binder can be broken down into two primary stages: binder dispersion and particle/binder contact. Following on, it was considered that the residence time within the agglomeration process could be further reduced if the binder dispersion occurred prior to the addition of the fine particle slurry. The combination of two evenly dispersed suspensions would facilitate rapid contacting and, thus, fast agglomeration. It should be noted, however, that this configuration does not reduce the duration of mixing applied to the emulsion and thus was not expected to improve its functionality. Rather the aim of this work, as previously mentioned, was to maximise the efficiency of the agglomeration process with respect to residence time.

Therefore, a series of experiments was carried out to determine the minimum residence time required to achieve complete agglomeration of the fine coal particles using the SMO based emulsion binder. In each test, the emulsion binder, composition unchanged from that described in Table 6.3, was dispersed for 10 s in 250 mL of water. Following this, 250 mL of coal slurry with a pulp density of 20 wt% was added and the mixing was continued for a predetermined period of time, called the agglomeration time. The agglomeration time was varied between 2.5 – 10 s. It should be noted that the organic liquid dosage was held constant at 2.7 wt%, that is, the minimum dosage required to

achieve complete agglomeration of the coal feed under the condition of adequate agitation time. This dosage was determined from the results for the SMO based emulsion binder in Figure 6.4.

Figure 6.6 presents the results from these experiments and displays the yield of product coal as a function of the agglomeration time. It should be noted, once again, that the agglomeration time includes only the period in which the coal slurry was in contact with the pre-dispersed emulsion binder.

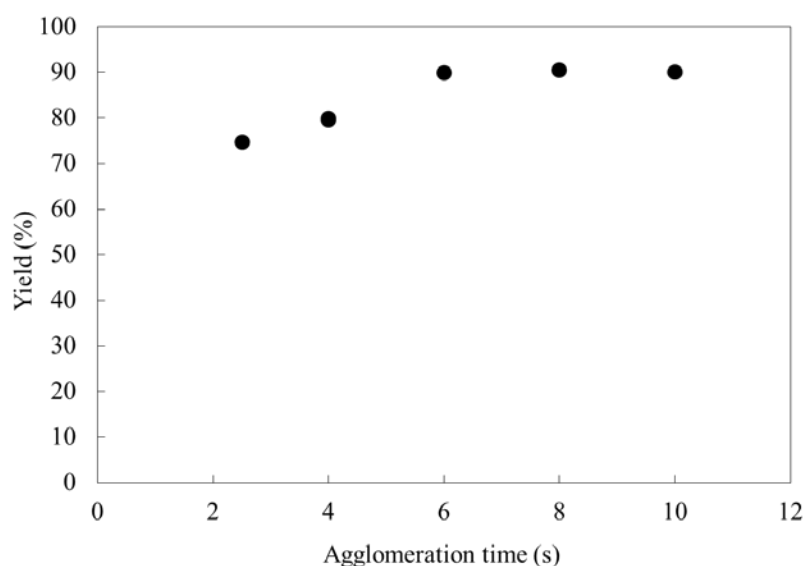


Figure 6.6: Yield of product coal as a function of agglomeration time at a constant organic liquid dosage using a SMO based emulsion binder.

As shown in Figure 6.6, a minimum of 6 s is required to completely agglomerate all of the carbonaceous material in the feed and thus achieve the maximum yield. Prior to this time, lower yields are achieved as there is insufficient contacting time and following this time a constant yield is achieved as the agglomeration is already complete.

An agglomeration time of 6 s was a considerable achievement in the development of the emulsion binder within the agglomeration process. This finding was especially important when the agglomeration time of 120 s required by pure diesel in this system was considered. Of course, the aforementioned time for the pure diesel included binder dispersion. However, as shown by Bensley, et al., (1977), pre-dispersion of pure oil can, at most, halve the agglomeration time required in the process.

6.6 Influence of Continuous Phase Oil Type

The previous series of experiments illustrated the influence of the properties of the continuous phase on the functionality of the emulsion binder within the agglomeration process. This investigation was continued in this stage of work through a study on the influence of the continuous phase oil type on the functionality of the emulsion as a binder. More specifically, this investigation focussed on the influence of a less viscous continuous oil phase. Therefore, kerosene, with a viscosity of 0.0016 Pa s, was introduced to replace diesel, which had a viscosity of 0.0025 Pa s, as the continuous oil phase of the emulsion.

Now, at this point it was acknowledged that a comparison between an SMO/kerosene emulsion binder and a pure diesel binder (the benchmark used up until this point) may no longer be valid due to the absence of diesel within the emulsion binder. Consequently, it seemed necessary to re-establish the benchmark case using a pure kerosene binder despite the fact that oils of different viscosities and densities have been shown to achieve similar yields for a given organic liquid dosage (Capes & Germain, 1982). Therefore, agglomeration experiments were conducted using a pure kerosene binder and the results from which are presented in Figure 6.7. Figure 6.7 presents the yield as a function of organic liquid dosage for the pure kerosene binder and the pure diesel binder, the previous benchmark case.

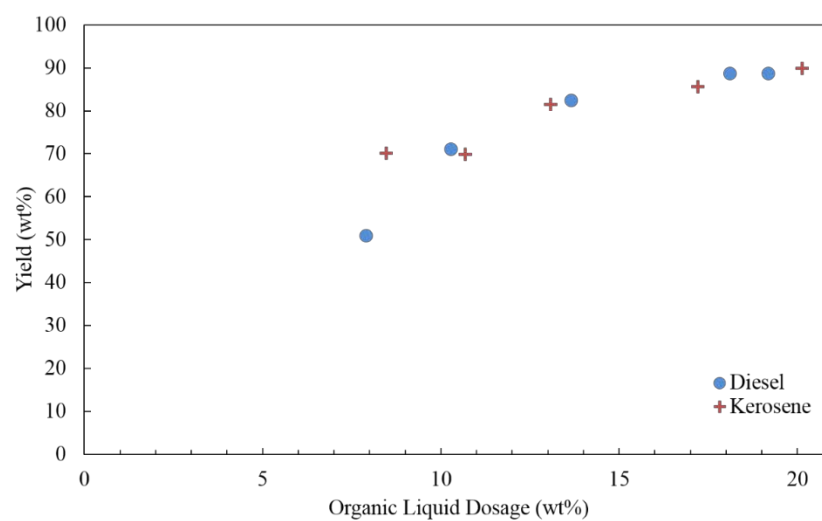


Figure 6.7: Yield of product coal as a function of organic liquid dosage for the pure diesel binder and a pure kerosene binder.

As shown in Figure 6.7 there is effectively no difference in the performance of the pure kerosene binder and the pure diesel binder. The results for the two binders exhibit excellent agreement and confirm the aforementioned result from Capes and Germain (1982) that under the appropriate conditions, different oils, especially light oils as used here, can achieve similar yields for a given organic liquid dosage. Therefore, the use of the diesel benchmark for evaluation of the new emulsion binder is valid.

A series of experiments was carried out using an emulsion binder made from kerosene, SMO and a 3 wt% aqueous NaCl solution. Of course, the use of the aqueous salt solution as the internal phase and SMO as the emulsifier was continued in the interest of producing an emulsion binder which possessed the greatest functionality within the agglomeration process. For the same reason, the emulsion binder used in these experiments had a dispersed, aqueous phase volume fraction of 0.95. Table 6.5 presents the composition of the emulsion used throughout this investigation.

Table 6.5: The composition of the emulsion binder used in agglomeration experiments in which the influence of the continuous phase oil type was investigated.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
3 wt% aqueous NaCl	Kerosene	SMO
0.95	0.025	0.025

As expected the introduction of a less viscous component to the continuous phase of the emulsion once again resulted in a reduction in the agitation time required to achieve agglomeration. After only 7 s of agitation, including binder dispersion, the colour change of the slurry was observed to be complete. As such, the agitation time used in these experiments was 7 s, which can be compared to the time required in the previous experiments using the diesel/SMO based emulsion which was 15 s.

Now, to evaluate the effect of the reduced mixing time required to achieve agglomeration Figure 6.8 presents the yield of product coal as a function of organic liquid dosage for the SMO/kerosene based emulsion binder. Also presented is the data from Figure 6.4 for the SMO/diesel based emulsion which has been faded to grey to draw attention to the newest results. Also included in the figure is the benchmark diesel case.

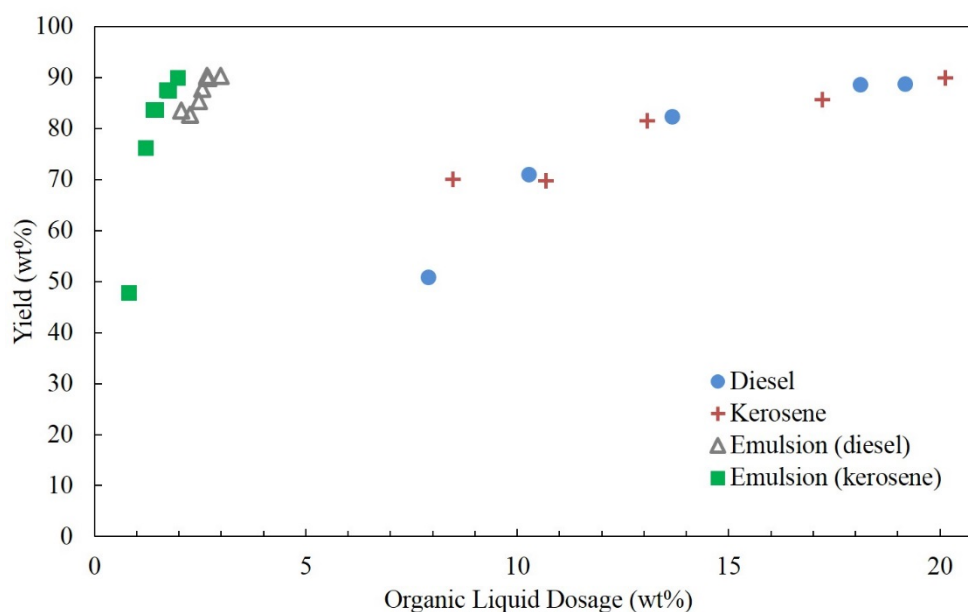


Figure 6.8: Yield as a function of organic liquid dosage for the pure diesel binder, the pure kerosene binder, a 3wt% aqueous NaCl-in-diesel emulsion binder and a 3wt% aqueous NaCl-in-kerosene emulsion binder. The dispersed, aqueous phase of the diesel based emulsion binder is 0.89 and is 0.95 for the kerosene based emulsion binder.

It is clear in Figure 6.8 that a considerable improvement has been made in the performance of the emulsion binder. Through the use of the SMO/kerosene based emulsion binder complete agglomeration of the coal feed was achieved at an organic liquid dosage of only 1.7 wt%. Now, by comparing this value with the dosage required when pure diesel is used, 17 wt%, it is evident that a 10-fold reduction in the organic liquid requirement has been realised. It should be noted, that the data for the diesel binder was used for the performance comparison rather than the pure kerosene binder to maintain continuity with the other results presented in this thesis. Furthermore, it was shown in Figure 6.7 that the performance of the pure kerosene binder matched that of the pure diesel binder, making them effectively interchangeable for the purpose of a performance comparison with the emulsion binder.

As this 10-fold reduction was a significant improvement on the 7.5-fold reduction achieved using the SMO/diesel based emulsion, these findings appeared to confirm that an emulsion which can achieve agglomeration in a shorter period of time experiences degradation to a lesser extent. Moreover, these findings appeared to confirm the

conclusion made at the end of the previous section that the functionality of the emulsion is greatly influenced by its rheology.

In an effort to elucidate the relationship between the rheology of the emulsion and its functionality, the rheological behaviour of two different emulsions was examined and compared to their performance as binders. Now, as this investigation represented only a limited examination of a very complex area of study, *i.e.* HIP emulsion rheology and, was secondary to the main investigation of this thesis, the complete set of results and the discussion were not included in the main body of text. Rather, the results were included as Appendix E. To summarise, however, in the investigation the relationship between the overall emulsion viscosity and the shear rate was measured and compared for a SMO/kerosene based emulsion and a PIB/diesel based emulsion. The former emulsion included the less viscous continuous phase components studied in this work and the latter included the more viscous continuous phase components which have been studied. The results indicated that the SMO/kerosene based emulsion had a higher overall viscosity at low shear rates and, as such, indicated that a decrease in the viscosity of the continuous phase increased the overall viscosity of the emulsion. To explain this observation it was considered that the reduced viscosity of the continuous phase facilitated the formation of smaller internal droplets within the emulsion as this would, in turn, increase the overall viscosity of the emulsion (Galvin et al., 2001).

Now, as the SMO/kerosene based emulsion displayed the best functionality these results also indicated that the use of a lower viscosity continuous phase creates an emulsion which is more suitable for use as a binder. This increased suitability has been considered to relate to the reduced internal droplet diameter and the increased overall emulsion viscosity. The reduced droplet diameter would improve the functionality of the emulsion binder as it would improve short term stability. Also, the increased overall viscosity may improve functionality by helping to keep the binder intact and also potentially improve the ‘sticking’ or collection efficiency of the emulsion globules such that agglomeration is achieved in a shorter time period. Once again, though, this was a limited study and future work would be beneficial to investigate, in detail, the relationship between the rheology of the emulsion and its functionality in the agglomeration process. Future work could also examine the behaviour of a complex non-Newtonian fluid such as the HIP emulsion in a high shear, three phase system.

While the 10-fold reduction was a remarkable achievement it was acknowledged that it was still below that predicted by the substitution theory detailed in Chapter 4. This theory predicted that an emulsion with a dispersed, aqueous phase volume fraction of 0.95 would achieve a 20-fold reduction in the organic liquid dosage. Now, prior to this result it was considered that the emulsion was performing below the predicted level because of emulsion degradation. However, as the mixing time required when using the SMO/kerosene emulsion was only 7 s, it was considered that emulsion degradation would now be extremely limited or even non-existent and as such would not be constraining the functionality of the emulsion to such a substantial level. So, to explain the most recent results it was considered that, contrary to the assumption made in the development of the substitution theory, the emulsion does not agglomerate fine particles in the exact same manner as pure oil. The substantial difference between the emulsion and pure oil in the time required to achieve agglomeration also supported this conclusion.

Therefore, the following phase of work, which is presented in the next chapter, was concerned with detailing the functionality of the emulsion binder and comparing it to a pure oil binder. Prior to this work, however, a small investigation was carried out to re-evaluate the minimum agglomeration time required to achieve agglomeration using the SMO/kerosene based emulsion binder.

6.6.1 Minimisation of the Agglomeration Time

Using the SMO/kerosene based emulsion binder a total agitation time of only 7 s was required to disperse the binder and agglomerate the fine coal. Now, as it was shown in the previous section that this residence time could be minimised by dispersing the emulsion binder prior to its introduction to the coal slurry, a small number of experiments were carried out to determine this minimum agglomeration time. In these experiments, the emulsion binder was dispersed for 4 s in 250 ml of water prior to the addition of 250 ml of 20 wt% coal slurry. It was found that an agglomeration time of only 3 s was required to achieve the maximum yield at an organic liquid dosage of 1.7 wt%. This 3 s residence time achieved by the SMO/kerosene based emulsion binder was half that required for the SMO/diesel based emulsion binder and presumably at least 10 times less than required for a pure oil binder.

6.7 Summary

An extensive series of agglomeration experiments was carried out in the work presented in this chapter. The work was conducted in a number of stages, each of which involved a modification to the composition of the emulsion and a subsequent evaluation of the effect on the functionality of the emulsion. These modifications included: the replacement of the tap water in the dispersed phase of the emulsion with a 3 wt% aqueous salt solution; the replacement of the PIB emulsifier with SMO; and the replacement of diesel in the continuous phase of the emulsion with kerosene. The salt solution was introduced as a means of enhancing the stability of the emulsion by impeding the growth of the internal droplets within the emulsion. The SMO emulsifier was investigated to elucidate the effect of the various components of the emulsion on its functionality as a binder and the kerosene was introduced as a result of the findings from the SMO based emulsion binder. Table 6.6 presents a summary of the modifications made to the composition of the emulsion binder. The highlighted cells in the table illustrate the emulsion component which was modified in each stage. Also presented in Table 6.6 is the reduction in the organic liquid dosage achieved by each of the various emulsion binders as compared to the benchmark diesel case.

Table 6.6: A summary of the emulsion binder composition modifications and the subsequent reduction in the organic liquid dosage achieved by each of the binders. The reduction is relative to the organic liquid dosage required when a pure diesel binder is used. The cells highlighted with grey represent the component of the emulsion modified in each stage.

<i>Aqueous Phase</i>		<i>Organic Phase</i>				<i>Reduction</i>
Dispersed Water	Volume Frac.	Continuous Oil	Volume Frac.	Emul -sifier	Volume Frac.	
Tap water	0.84	Diesel	0.08	PIB	0.08	3-fold
3 wt% aqueous NaCl	0.84	Diesel	0.08	PIB	0.08	4-fold
3 wt% aqueous NaCl	0.89	Diesel	0.055	PIB	0.055	5-fold
3 wt% aqueous NaCl	0.94	Diesel	0.03	PIB	0.03	6-fold
3 wt% aqueous NaCl	0.89	Diesel	0.055	SMO	0.055	7.5-fold
3 wt% aqueous NaCl	0.95	Kerosene	0.025	SMO	0.025	10-fold

Furthermore, Figure 6.9 presents the yield of product coal as a function of organic liquid dosage for each of the emulsion binders presented in Table 6.6. Also presented in the figure are the results for the benchmark diesel case. All but the most recent result, for the 3 wt% aqueous NaCl-in-kerosene emulsion binder, have been faded to grey.

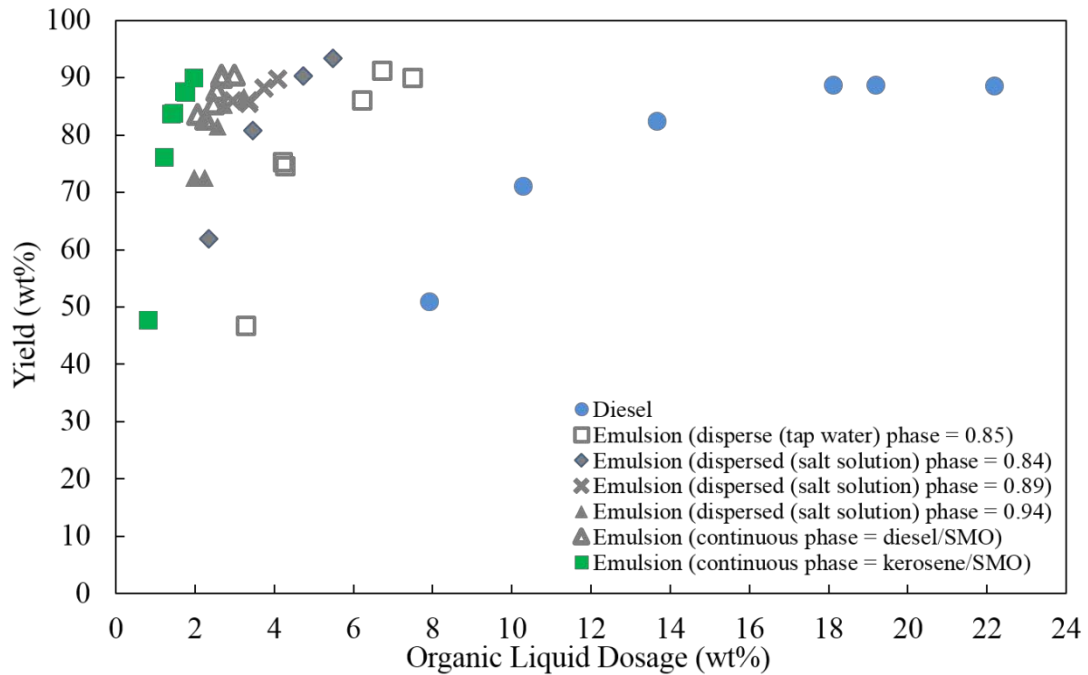


Figure 6.9: Yield of product coal as a function of organic liquid dosage for the pure diesel binder and a variety of emulsion binders.

As can be seen in Figure 6.9, each of the emulsion binder composition modifications led to a step change in the organic liquid dosage required to achieve agglomeration. That is, for each subsequent modification there is a perceivable decrease in the dosage at which the plateau in yield occurs. In each case, these reductions in the organic liquid dosage were found to be the result of a reduction in the level of degradation the emulsion experienced during the agglomeration process. The highlight of the work is the result for the 3 wt% aqueous NaCl-in-kerosene emulsion binder which achieved a 10-fold reduction as compared to the benchmark diesel case. This emulsion achieved agglomeration in only 3 s and thus experienced the lowest level of degradation which resulted from mixing in the turbulent, aqueous environment of the agglomeration process.

In general the findings presented thus far have indicated that the manner in which the emulsion achieves agglomerates is somewhat different to that of a pure oil. Therefore, the next phase of this work, which is presented in the following chapter, was used to detail and summarise the functionality of the emulsion binder and compare it to a pure oil binder.

Chapter 7

On the Functionality of the Binder

Contribution to the Research

The table below indicates the contribution of each person to the research.

Contributor	Primary Contribution
van Netten, K.	Collaborator in design of experimental program of work, carried out experimental program of work, and data analysis
Galvin, K. P.	Co-supervisor, collaborator in design of experimental program of work, proof reading of thesis chapter
Moreno-Atanasio, R.	Supervisor, proof reading of thesis chapter

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Roberto Moreno-Atanasio

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Kim van Netten

7.1 Introduction

In Chapter 6 it was established that significant binder performance can be achieved by preparing an emulsion from an organic phase consisting of kerosene and SMO, and an aqueous phase consisting of 3 wt% NaCl solution, with the aqueous, dispersed phase volume fraction set at 0.95. The use of this emulsion led to a 10-fold reduction in the organic liquid dosage required to achieve agglomeration. While this result was significant, the performance of the binder was still below the 20-fold level expected on the basis of the elementary substitution theory described in Chapter 4. Moreover, as the agglomeration time had been reduced to only 7 s and the stability of the emulsion had been greatly improved, it was considered that the substantial difference between the achieved reduction and the predicted reduction could no longer be attributed to emulsion degradation.

This chapter, therefore, explores the functionality of the emulsion binder in order to build an improved understanding of the apparent discrepancy between its actual performance and its anticipated performance, dictated by its dispersed phase volume fraction. As a basis for the investigation it was considered that the space-filling benefit generated by the internal water droplets of the emulsion applies to the portion of the binder within the void spaces of the agglomerates but not to the portion of the binder which spreads over the surface of the particles. In other words, it has been considered that a thin film forms over the surface of the hydrophobic particles and, due to the tendency for oil to spread over the surface of coal in an aqueous environment, would involve only the pure organic phase. The consequence of this proposal is that the performance of the emulsion will be dependent on the distribution, in particular the film thickness of organic liquid within the agglomerate and how it compares with the distribution in an agglomerate made from pure oil. In other words the dosage required to achieve agglomeration should vary with the specific surface area of the hydrophobic particles.

This chapter commences with a general discussion of binder functionality in the formation of agglomerates. Following this, the results from an investigation into the influence of the specific hydrophobic surface area of the coal feed on the organic liquid dosage required to achieve agglomeration are presented. This work then leads to a simple

theory for describing the binder consumption in the context of its functionality, with direct reference to the reagent consumption required in conventional oil agglomeration.

7.2 Binder Functionality

Figure 7.1 presents the proposed distribution of the organic liquid in the formation of an agglomerate made from three particles. As discussed in the introduction, the binder has been divided into two separate portions to illustrate its two separate roles: liquid film formation and space-filling. The liquid film is shown to have a thickness of δ (m).

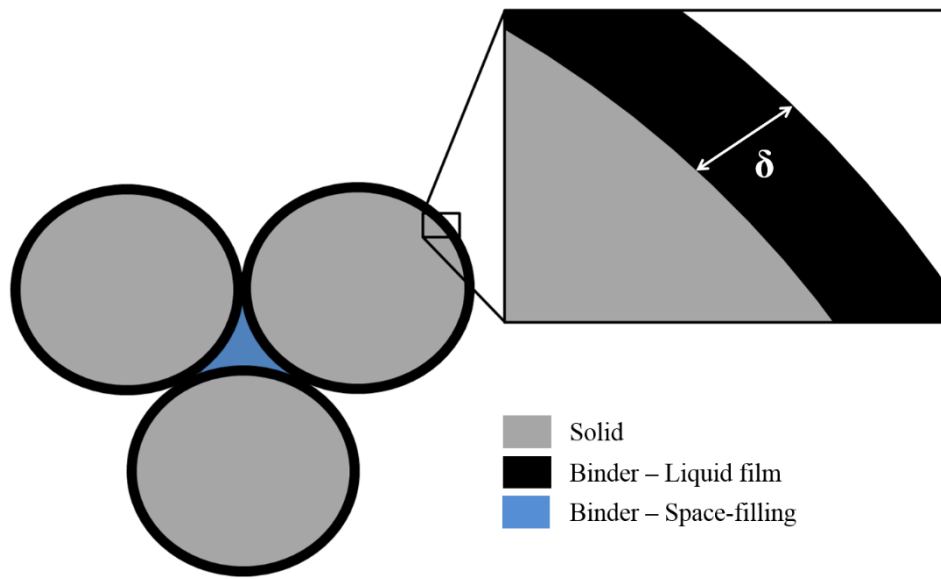


Figure 7.1: Schematic of three agglomerated particles showing the distribution of the binder. A portion of the binder forms a film of thickness δ over the surface of the particles and the remainder of the binder fills the void space within the agglomerate.

By assuming complete saturation of the void space an analytical expression for the specific volume of organic liquid required to achieve agglomeration, v_{oil} ($\text{m}^3/\text{m}^3_{\text{coal}}$) can be written as the simple sum of two independent volumes:

$$v_{oil} = \delta SA + v_{void} \quad (7.1)$$

where the former term on the right-hand relates to the formation of a film of thickness δ over a specific surface area of SA ($\text{m}^2/\text{m}^3_{\text{coal}}$) and the latter term, v_{void} ($\text{m}^3/\text{m}^3_{\text{coal}}$) relates to the specific volume of the saturated void space within the agglomerates. Now, it should be highlighted that the binder volumes in Equation 7.1 have been defined such that they

reflect the volume of organic liquid. Therefore, when using the emulsion v_{void} should be much smaller in magnitude than when using pure oil binder due to the space-filling capacity of the dispersed water droplets.

Following on, by considering the form of Equation 7.1, it may be noted that the latter term on the right hand side becomes constant if it is assumed that the volume of binder required to fill the void space within the agglomerates is independent of the specific surface area, or d_{32} , of the particles. In other words, if it is assumed that the particles always pack in effectively the same way the voidage will be constant provided that the relative proportions of particles are the same. Figure 7.2 further illustrates this concept.

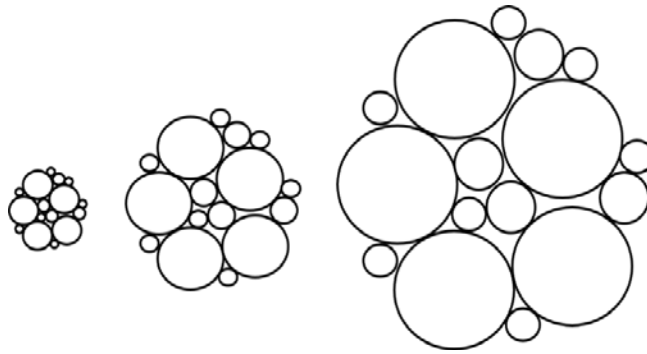


Figure 7.2: Illustration of self-similarity in packing of particles with the same distribution over three different scales.

This assumption was considered reasonable because the size range of coal feeds cover a number of orders of magnitude such that a self-similar packing structure would be created all the way down to a given lower limit. It has been, of course, acknowledged that this assumption would not be completely valid and that packing problems offer much greater levels of complexity than implied by this discussion. However, it has been considered that the variation in packing which may occur would not be consequential to the macroscopic parameters being studied in this work.

Now, the assumption discussed above is important because it means that the volume of organic liquid required to achieve agglomeration as a function of the specific surface area can be described by a straight line. Moreover, Equation 7.1 illustrates that information about the liquid distribution within agglomerates can be extracted from experimental results of this nature. That is, by investigating the relationship between the specific

surface area of a feed and the specific volume of organic liquid required to achieve agglomeration, the film thickness and the volume of the voids within the agglomerates can be back-calculated from the gradient and the y-intercept, respectively. Therefore, in this phase of work an investigation into the influence of the specific surface area on the specific organic liquid volume required to achieve agglomeration was carried out for both the emulsion binder and a pure kerosene binder. It was anticipated that by developing a linear equation for both binders the values of δ and v_{void} could be compared and used to develop a relative description of the liquid distribution within the agglomerates. The experimental results are presented following the description of the experimental methodology.

7.3 Experimental Methodology

To explore the functionality of the emulsion binder and a pure oil binder in the formation of agglomerates this phase of work investigated the influence of the specific surface area of the feed solids on the organic liquid dosage required to achieve agglomeration.

7.3.1 Materials

The emulsion binder used in the experiments described in this chapter was prepared using a 3 wt% aqueous NaCl solution, kerosene and sorbitan mono-oleate (SMO). The details of these materials have been presented previously and thus will not be presented again here.

Eight different coals sourced from the various regions throughout Australia were used in this phase of experiments. The coals were selected such that feeds with a wide range of Sauter mean diameters, d_{32} (m), and thus specific surface areas could be examined. Table 7.1 presents the Sauter mean diameter of the each coal sample.

Table 7.1: Sauter mean diameter, d_{32} , of the eight different coal feeds used to investigate the influence of the specific hydrophobic surface area of the feed on the binder dosage required to achieve agglomeration.

Feed	d_{32} (μm)	Specific Surface Area $\text{m}^2 / \text{m}^3_{\text{coal}}$
1	9.1	660928
2	10.9	551188
3	13.9	430725
4	26.4	227212
5	17.6	340909
6	63.5	94429
7	25.4	236220
8	182.0	32967

It should be noted that all of the feeds used in these experiments contained both hydrophobic material, *i.e.* coal, and hydrophilic material, *i.e.* mineral matter. However, the values presented in Table 7.1 are representative of only the hydrophobic, recoverable portion of the feed. This basis was selected as the binder is active on only hydrophobic particles and thus only these particles contribute to the active surface area to be agglomerated. In other words, the mineral matter was considered to be an inactive component in the process. The process by which these values were obtained is outlined in Appendix C.

7.3.2 Preparation of High Internal Phase Emulsion

The method by which the emulsion was prepared has been presented previously in Chapter 6 in Section 6.2.2 and thus will not be presented again here. The composition of the emulsion was not modified throughout this chapter and is presented in Table 7.2.

Table 7.2: Composition of the emulsion used to investigate the influence of the specific hydrophobic surface area of the feed on the binder dosage required to achieve agglomeration.

<i>Aqueous Phase Volume Fraction</i>	<i>Organic Phase Volume Fraction</i>	
3 wt% aqueous NaCl	Kerosene	SMO emulsifier
0.95	0.025	0.025

7.3.3 Selective Agglomeration

Selective agglomeration experiments were carried out for the eight different feeds using both a pure kerosene binder and the emulsion binder. The methodology used in these experiments remained unchanged from that used in the previous chapters and will not be presented again here. It should be noted, however, that as a result of the work in Chapter 6, the agitation time used for the emulsion binder was only 7 s.

7.4 Influence of the Specific Hydrophobic Solid Surface Area on Dosage Required to Achieve Agglomeration

It has been evident throughout this thesis that the organic liquid dosage used in an agglomeration experiment defines the product structure and the yield. Moreover, it has been shown that for a given coal feed there is a certain minimum dosage which is required to achieve complete agglomeration of the hydrophobic material in the feed. In a graphical sense, this value is the point at which the curve of product yield as a function of organic liquid dosage reaches a plateau. Now, this dosage is important as it can be considered as the point at which there is sufficient binder to completely agglomerate all of the hydrophobic material in the feed. In other words, it is at this dosage that the void space within the agglomerates is saturated and there is a thin film of oil over the surface of the hydrophobic particles, *i.e.* the state which was used to develop Equation 7.1. Therefore, in order to investigate the influence of the specific surface area of a feed on the specific volume of organic liquid required to achieve agglomeration, the dosage required to achieve agglomeration for each coal feed had to be first established.

To establish the dosage required to achieve agglomeration for each coal feed, a series of experiments was carried out in which the organic liquid dosage was varied. From these results, the dosage required to achieve agglomeration was extracted and used to build the data set required to examine the relationship between specific binder volume required to achieve agglomeration and specific surface area of the feed.

This initial work involved a considerable number of experiments which were similar in nature to each other and to the work presented previously in this thesis. As such, they have not been included in the main body of this thesis and hence have been compiled in

Appendix D. Presented below, however, is one example for each binder to illustrate the process by which the required values were established.

7.4.1 Data Analysis Method

A standardised analysis was developed to determine the dosage at the commencement of the plateau in the yield-dosage curve for the kerosene binder and the emulsion binder. Interestingly, a different method was required for each binder. In the case of the emulsion, it was found that the best fit for the data was a positive gradient straight line commencing from the origin to the point at which the maximum yield was achieved, followed by a horizontal line at maximum yield. Figure 7.3 presents an example plot for the emulsion binder with the analysis method applied.

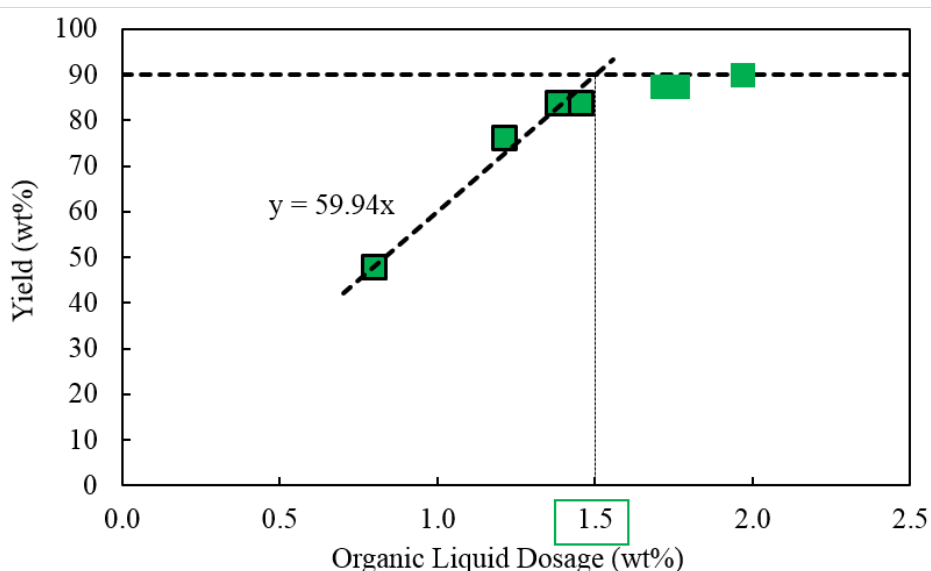


Figure 7.3: Yield as a function of organic liquid dosage example plot for the emulsion binder with the curve fit analysis applied.

As can be seen a straight line has been fitted to the data prior to the commencement of the plateau in yield. The data points included in the curve fit have been outlined in bold. A straight, horizontal line has also been fitted to the data to indicate the maximum yield recoverable from this feed. In this case the maximum yield is 90 wt% as the feed had an ash content of 10%. The dosage required to achieve agglomeration was then considered to be the point at which the positive gradient straight line from the origin intersected the horizontal maximum yield line. In this example, the dosage was $90/59.94 = 1.5$ wt%. As

can be seen in this figure, this dosage is effectively at the commencement of the plateau and thus after the significant increases in yield which occur at lower binder levels.

As mentioned above, in the case of the kerosene binder it was found that the best fit for the data was different from the emulsion. It was found that the best fit was first order type curve which related the yield, Y (wt%), with the dosage, D (wt%), in the following manner,

$$Y = Y_{max}(1 - e^{-kD})$$

where Y_{max} is the maximum yield for a given feed and k is a first order coefficient which is also feed dependent. Figure 7.4 presents an example plot for the kerosene binder with the analysis method applied. In this example the maximum yield was 44 wt% and $k = 0.23$.

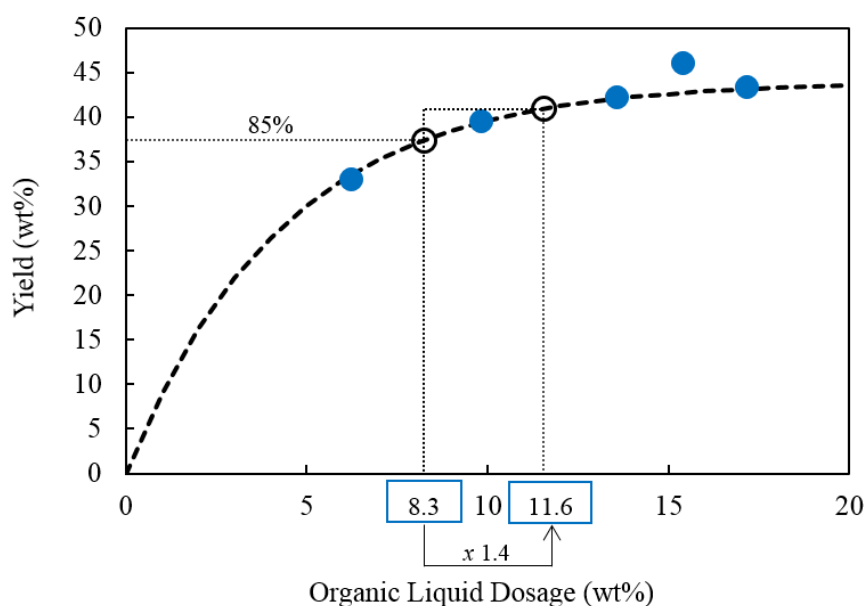


Figure 7.4: Yield as a function of organic liquid dosage example plot for the kerosene binder with the curve fit analysis applied. The two open circles indicate the points along the curve which the analysis was based around.

As can be seen in the figure, the first order curve provides a good fit. Construction lines can also be seen on the figure which indicate the method by which the dosage required to achieve agglomeration, *i.e.* the dosage at the start of the plateau was calculated. As indicated by the construction lines, the dosage at 85% of the maximum yield was

determined which was, in this case, 8.3 wt%. The dosage value at 85% of the maximum yield value was then multiplied by 1.4 to provide the dosage at the start of the plateau which was 11.6 wt%. The two points on the curve which were used in the analysis method are indicated by the open circles in Figure 7.4. The open circle on the right hand side, which indicates the dosage required to achieve agglomeration, can be seen to sit after the main changes in curvature of the data but prior to the levelling out of the data.

As can be seen in Figure 7.3 and Figure 7.4 the two different analysis methods provide good fits with the data in each case and therefore provide a standardised method of evaluating the dosage at agglomeration for a given feed and binder. Also, as a result of the application of the two different methods it may be tentatively concluded that a different mechanism of agglomeration exists for the two types of binders. This conclusion is of course also supported by the significant difference in time required to achieve agglomeration. However, at this stage it is difficult to suggest how the mechanism of agglomeration using the emulsion binder differs from the well-understood process using a pure oil. As such future work is required in this area which involves a fundamental investigation into the mechanism of agglomeration when using the emulsion binder.

7.4.2 Influence of Specific Surface Area

Figure 7.5 presents the influence of the specific hydrophobic surface area of the feed on the dosage, or specific volume of organic liquid, required to achieve agglomeration. It should be noted that the dosage values are presented on a volumetric basis, consistent with Equation 7.1. The density of coal used in the conversion calculation was 1350 kg/m^3 . Also, the method by which the specific surface area was calculated from the Sauter mean diameter of each feed is presented in Appendix C.

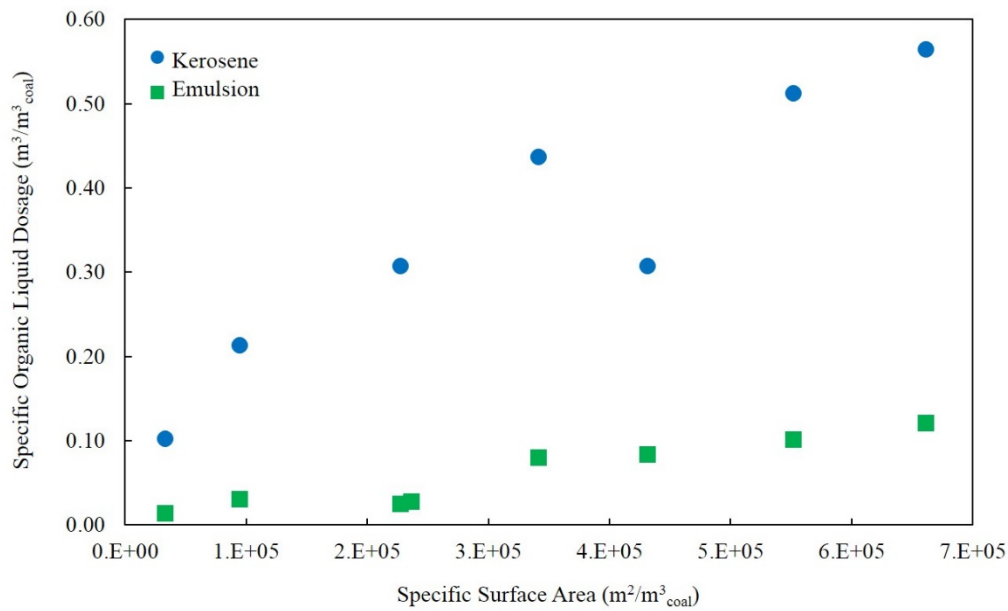


Figure 7.5: Organic liquid dosage required to achieve agglomeration as a function of the specific hydrophobic surface area for the emulsion and a pure kerosene binder.

Figure 7.5 shows that the volume of organic liquid required to achieve agglomeration increases as the specific hydrophobic surface area of the feed increases. Furthermore, it can be seen that this increase is linear for each binder and as such, is consistent with that predicted by Equation 7.1. This linearity and consistency in the data is also noteworthy considering that a broad range of coals was used to build the data set. Following on, Figure 7.6 presents the data for both the emulsion and the kerosene binder fitted with linear trendlines. Also presented on the plot are the linear equations for each binder and inserts to illustrate the resulting organic liquid distribution for each binder.

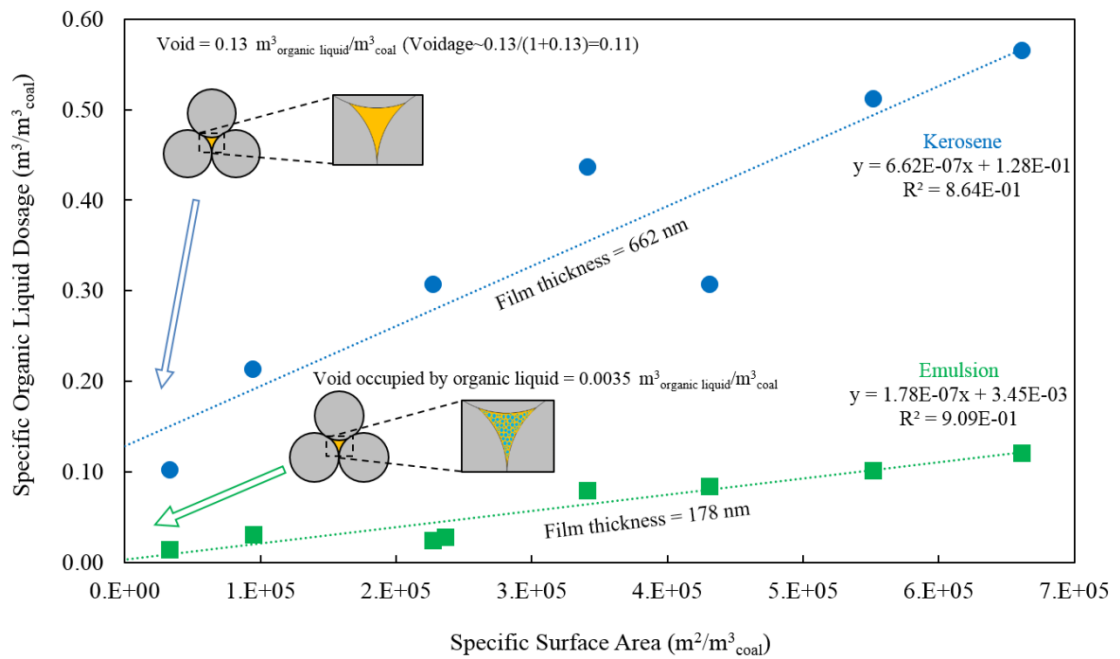


Figure 7.6: Organic liquid dosage required to achieve agglomeration as a function of the specific hydrophobic surface area for the emulsion and a pure kerosene binder. Linear trendlines are fitted to each data set and the corresponding linear functions and R^2 values are displayed. Inserts illustrate the resulting organic liquid distribution for each binder.

Considering initially the y-intercept for the kerosene data it can be seen that the specific volume of organic liquid required to fill the void space within the agglomerated material is $0.13 \text{ m}^3/\text{m}^3_{\text{coal}}$, as depicted in the upper left insert. Moreover, by assuming complete saturation of the void space this value indicates that the voidage within the agglomerated material is 0.11. Considering now the y-intercept for the emulsion data it can be seen that the volume of organic liquid required to fill this void space, which is assumed to be constant, is $0.0035 \text{ m}^3/\text{m}^3_{\text{coal}}$, as depicted in the lower left insert. As expected, the volume required when using the emulsion is significantly less than when using pure kerosene due to the presence of the dispersed water droplets. Indeed, the difference between two intercepts is equal to the specific volume of the dispersed water droplets within the void space. Therefore, these results indicate that the assumption made about the space-filling nature of the water droplets within the void space was reasonable.

Considering now the organic film thickness for each binder it can be seen that an organic film of thickness 178 nm is formed when using the emulsion binder while the film formed when using the kerosene binder is thicker and equal to 662 nm. This result indicates that

the organic liquid can spread more thinly when provided by the emulsion binder. This enhanced spreading may be due to the presence of the emulsifier which reduces the interfacial tension between the constituents of the system. It is also interesting to compare these results to work by Macaulay (2001) in which the adhesion and rheology of a highly concentrated W/O emulsion was investigated. In this work it found that the thickness of the organic layer which forms between a smooth glass surface and the bulk of an emulsion under shear is between 20 – 30 nm, depending on the type of oil used (Macaulay, 2001). These values compare well with the results observed here, especially when considering the porosity of coal which would increase the apparent film thickness.

Taken as a whole, these results indicate that the substitution theory is appropriate to describe the distribution of the organic phase within the void spaces of the agglomerated material. However, the thin film of organic liquid which forms over the surface of the agglomerated particles also adds to the organic liquid requirement. Therefore, these results indicate that the reduction which may be achieved is a function not only of the dispersed phase of the emulsion but also of the surface area of the feed. That is, the reduction which may be achieved will be determined by the extent to which the volume of the organic liquid in the film contributes to the overall volume of organic liquid required to achieve agglomeration.

To illustrate the influence of the specific surface area on the reduction, Figure 7.7 presents the experimental data and the linear fits for the two binders with construction lines indicating the reduction level. It should be noted the y-intercept of the emulsion trendline has been constrained for this figure such that it is exactly 20 times less than the y-intercept for the kerosene binder. This constraint was considered reasonable as the forced intercept of the emulsion trendline is within one standard deviation of the natural intercept and better conforms to the substitution theory, *i.e.* an emulsion with an aqueous phase content of 0.95 should result in a 20-fold reduction in the volume organic liquid required to fill the void space. The data for the high quality feed which achieved a 10-fold reduction is also indicated on the figure.

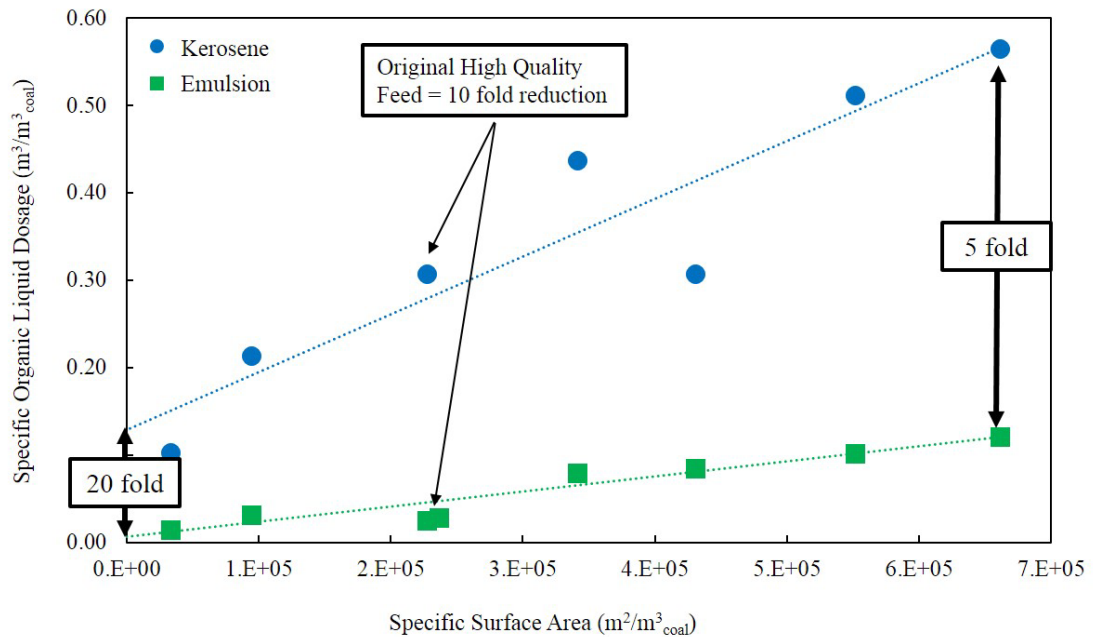


Figure 7.7: Organic liquid dosage required to achieve agglomeration as a function of the specific hydrophobic surface area for the emulsion and a pure kerosene binder. Linear trendlines are fitted to each data set. The y-intercept of the emulsion trendline was constrained to be 20x less than the y-intercept for the kerosene binder. Construction lines and inserts indicate that the reduction in organic liquid which results from the use of the emulsion is a function of the specific surface area.

As depicted in Figure 7.7, in the theoretical case when there is no surface area, the reduction will be equivalent to that predicted by the substitution theory. However, as the surface area increases, a certain amount of organic liquid is also required to form a thin film in which the dispersed water droplets do not play a significant space-filling role. This requirement means that the reduction decreases as the specific surface area increases. Therefore, in a qualitative sense it can be concluded that for feeds with relatively large particles and, therefore, small specific surface areas, the reduction which may be achieved using the emulsion will be closer to that predicted by the substitution theory. However for relatively fine feeds, with large specific surface areas, the reduction will be considerably lower than that predicted by the substitution theory.

As a final note, it should be acknowledged that linear models were used to fit the data for both binders due to the theory presented at the start of the chapter and as there was no

indication that a more complicated function would be more appropriate. However, it has been noted as a result of this work that another possible fit for the pure kerosene data may be a first order reaction type curve. If this type of curve were appropriate, the initial steep section would indicate that agglomerates made from coarser feeds have thicker films of oil. Then, the flatter section of the curve would indicate that agglomerates made from finer feeds have a thinner films of oil. This may very well be the case if the size distribution becomes wider for the finer feeds and the ultra-fine particles pack in between the coarser particles. Moreover, it could be expected that the packing in the pure oil based agglomerates would be more orderly than in the emulsion based agglomerates due to the much longer mixing time required to form the agglomerates using the pure oil binder.

7.5 Summary

The functionality of the emulsion binder was explored in this chapter in an attempt to provide an explanation for the 10-fold reduction achieved in the previous chapter. An analytical expression was developed for the dosage required to achieve agglomeration, based on the specific surface area of the feed, agglomerate void volume and film thickness. Using this expression and the experimental results from an investigation into the influence of the specific hydrophobic surface area of the feed on the organic liquid dosage required to achieve agglomeration, the organic liquid required to form a thin film over the surface of the particles and fill the void space was quantified and compared for each binder. From these values a relative description of the liquid distribution with the agglomerates made from each binder was developed. It was found that while the substitution theory was appropriate to describe the distribution of the organic phase within the void spaces of the agglomerated material, it did not adequately account for the distribution of the organic liquid over the surface of the particles. Therefore, the results in this chapter show that the reduction which may be achieved is a function not only of the dispersed phase of the emulsion but also of the surface area of the feed.

Chapter 8

Potential Application

Contribution to the Research

Paper:

van Netten, K., Ernst, T., Moreno-Atanasio, R., & Galvin, K. P. (2016). Fast and Selective Fine Coal Agglomeration Using an Economic Binder. *Proceedings, 16th Australian Coal Preparation Society Conference, Wollongong. Accepted*

Contribution:

Author	Primary Contribution
van Netten, K.	Collaborator in design of experimental program, trained and supervised T. Ernst, collaborator in data analysis, and lead author of paper
Ernst, T.	Carried out experimental program of work and collaborator in data analysis.
Moreno-Atanasio, R.	Supervisor and collaborator in preparation of paper
Galvin, K. P.	Co-supervisor and collaborator in design of experimental program, and collaborator in preparation of paper

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Roberto Moreno-Atanasio

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Kim van Netten

8.1 Introduction

The aim of the work in this thesis was to maximise binder functionality in the process of selective agglomeration to allow for the effective treatment of a mixture of coal and mineral particles. As illustrated in the preceding chapters, the result of this work has been the successful development of a fast and selective agglomeration process with a greatly reduced organic liquid reagent requirement. Therefore, this chapter discusses the potential application of this work in an industrial setting.

Presented initially in this chapter is a consideration of the product quality required in coal processing applications. Therefore, an investigation into the ash% and moisture of the agglomerated product is presented. Following this, the results from an investigation into the application of the emulsion binder to a coarse coal feed are presented.

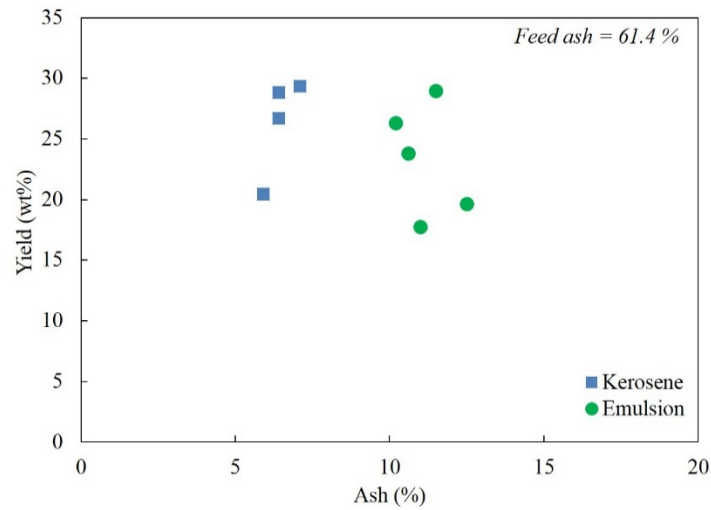
8.2 Coal Processing

8.2.1 Product Quality

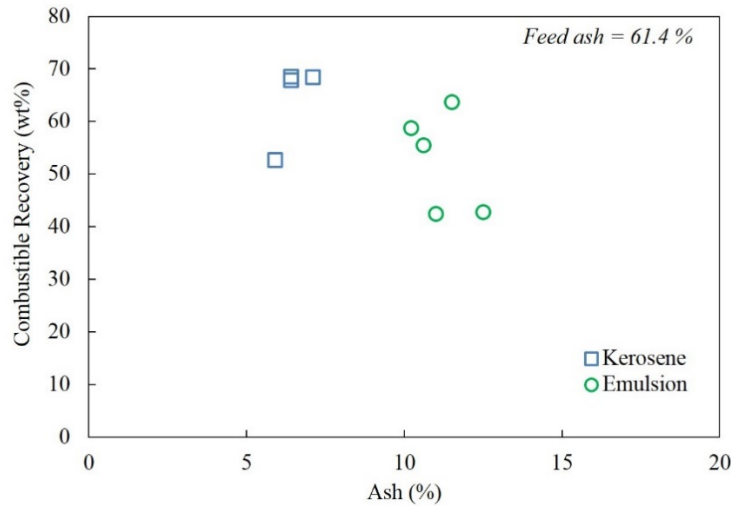
For a coal product to be saleable it must meet requirements, often stipulated in a contract, of a low level of mineral matter (ash%) and low % moisture in the product. Therefore, in this section, the ability of the emulsion binder to produce a low ash% and low moisture product was investigated

The selectivity of the emulsion binder was investigated at the commencement of this work, the results from which were presented in Chapter 4. At that time, it was found that the selectivity of the emulsion was excellent as it produced a low ash product. However, since that investigation both the process of agglomeration and the composition of the emulsion has changed substantially. Therefore, the selectivity of the emulsion was re-examined here to confirm the ability of the emulsion to produce a low ash product. The experimental methodology and the composition of the emulsion binder used was unchanged from the preceding chapter. Experiments were also carried out using a pure kerosene binder for comparison. The coal feed which was used in this investigation had a $d_{50} = 17 \mu\text{m}$ and an ash% of 61.4%. Due to the high level of mineral matter and the substantial amount of ultra-fine material this coal feed would be considered difficult to process in an industrial setting.

Figure 8.1a presents the product yield as a function of the ash% for both the emulsion binder and a pure kerosene binder. Following on, Figure 8.1b presents the combustible recovery as a function of ash% for both binders. The ash analysis on the agglomerated samples was carried out externally by ALS global and the raw data can be found in Appendix B. The method by which the combustible recovery was calculated is also presented in Appendix B.



(a)



(b)

Figure 8.1: a) Yield and b) combustible recovery as a function of the ash% for the emulsion and pure kerosene.

Figure 8.1 clearly illustrates that the ash content of the agglomerated product is, in general, slightly higher for the emulsion binder than the pure kerosene binder for a comparable yield or combustible recovery. When using pure kerosene, the ash content is consistently in the range of 6 – 7%. However, when using the emulsion binder the ash% is in the range of 10 – 11%. Now, while this ash% is still in the acceptable range it is noted that in Chapter 4, the selectivity of the emulsion binder and a pure oil binder were shown to be almost identical with similar product ashes. Therefore, it appears that through the development of the emulsion throughout this work its selectivity has been slightly diminished.

The reduced selectivity noted above may be the result of the increased speed with which the emulsion achieves agglomeration. That is, as the emulsion only requires 7 s, it may be that mineral particles become entrapped into the fast forming agglomerates. On the other hand, the increased ash% of the emulsion based agglomerates may be the result of the increased tendency for the emulsion to collect composite particles. That is, a particle that is part mineral matter and part coal may be collected by the emulsion but not by pure oil. The recovery of composite particles is not necessarily required in a coal processing application, however this attribute would be highly beneficial in other applications in which the valuable material is finely disseminated. Future work into the selectivity of the emulsion is required to explore this aspect and further detail the selectivity of the emulsion. It should be noted, however, that the product ash% achieved by the emulsion is well within the acceptable range.

Another parameter of concern in a saleable coal product is the moisture content. As the presence of moisture reduces the calorific value of coal and increases transportation requirements, it must be reduced to an acceptably low level. Coarse coal can be dewatered with relative ease, whereas fine coal often presents a more difficult task. In many cases agglomeration and flocculation processes are applied to the fine particles to facilitate dewatering. Size enlargement processes such as these assist dewatering by reducing the surface area of the solid material and improving permeability.

Through the use of a Buchner funnel filtration system it was found that the product coal agglomerates formed from the emulsion binder could be dewatered to 25 – 30 wt% moisture. Now, it should be noted that this value includes the free surface moisture and the moisture trapped within the emulsion binder which holds the agglomerates together. Moreover, it is estimated that the water within the emulsion binder accounts for approximately 60 – 70 % of the overall moisture content. The presence of this additional moisture, which would otherwise be absent in agglomerates made from a pure oil binder, is clearly not ideal; however the overall moisture content of the product coal is within the acceptable limits. In addition, it should be noted that the presence of the organic liquid within the emulsion increases the calorific value of the coal.

8.2.2 Coarse Particles

The coal feeds examined thus far in this work would all be classified as fine or ultra-fine feeds due to the small size of the particles. Fine coal feeds were studied exclusively as

selective agglomeration has been shown in the past to be most effective on feeds which are $< 500 \mu\text{m}$. However, the ability to process and recover coal over a wider size range is highly desirable. Operating over a wider size range is desirable as it reduces the number of unit operations required and thus reduces the overall complexity of a processing plant.

Therefore, in this work a new feed was introduced which contained coal and mineral particles in the range of 0 – 2 mm. The size distribution of this feed was measured using laser diffraction in a Mastersizer 3000 and is presented in Figure 8.2. Water was used as the dispersing medium during the laser analysis. To facilitate the submersion of the dry coal in the dispersant, the particles were wetted using a 0.025 wt% dri-decon detergent solution. As can be seen the feed contained a substantial portion of both fine and coarse particles.

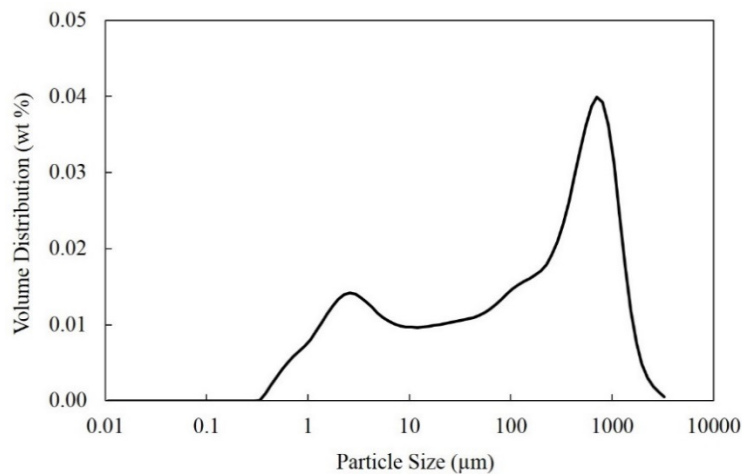


Figure 8.2: Size distribution of the feed used in the investigation into agglomeration of coarse particles.

Agglomeration experiments were carried out using both the emulsion binder and a pure kerosene binder. The composition of the emulsion binder remained unchanged and was 0.025 SMO, 0.025 kerosene and 0.95 3wt% NaCl solution. The agitation time using the emulsion was 7 s and the agitation time used for the kerosene was 120 s. At the completion of mixing the agglomerated slurry was not poured over a screen as was done previously due to the presence of the coarse mineral particles which could also potentially be retained on the screen. Rather, to achieve a separation, the agglomerates were scooped off the top of the agglomerated slurry. This method was possible as the agglomerates are sufficiently buoyant to float and the coarse mineral particles quickly sink to the bottom of the vessel. The product agglomerates were then placed on a screen (aperture = $250 \mu\text{m}$) to remove any finely dispersed mineral matter that was entrained with the bulk of the agglomerated

material. Figure 8.3 presents a) the coarse coal feed slurry and b) the agglomerated slurry prior to the agglomerates being scooped off the top. In both cases, coarse particles can be seen settled at the base of the jug, however, in Figure 8.3b there is a distinct lack of dark, coarse particles.



Figure 8.3: a) Coarse coal feed slurry and b) agglomerated coal slurry

Figure 8.4 now presents the yield of product coal as a function of the organic liquid dosage for the two binders. As noted above, the product yield is defined as the material which may be scooped off the top of the agglomerated slurry and subsequently retained on a 250 μm screen.

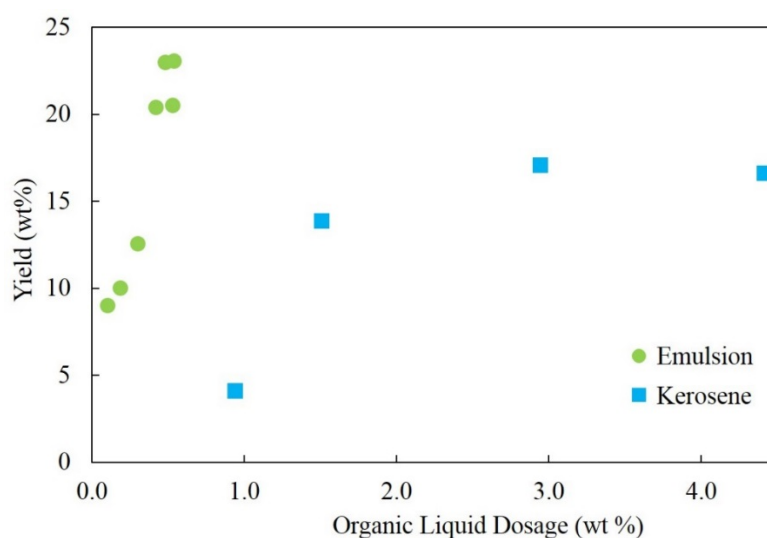


Figure 8.4: Yield of product coal as a function of organic liquid dosage for a pure kerosene binder and an emulsion binder. The emulsion binder had a dispersed, aqueous phase volume fraction of 0.95.

As can be seen in Figure 8.4, the general trend for the two binders is consistent with that observed previously. The yield increases with increases in the organic liquid dosage until a plateau in yield is reached. As discussed previously, this plateau is observed because complete agglomeration of the carbonaceous material has been achieved. Now, these results are interesting because it can be seen that the emulsion not only achieves agglomeration at a lower organic liquid dosage than the pure kerosene but also achieves a higher product yield. When using the emulsion binder a yield of 24 wt% was achieved at a dosage of 0.5 wt%. However when using the kerosene the maximum yield which could be achieved was 15 wt%.

To explain the superior performance of the emulsion on this feed attention was drawn to size distribution of the product material. It was considered that the emulsion binder had an enhanced capacity for agglomerating coarse particles. Therefore, the size distribution of the individual particles which formed the agglomerated product material for each binder was measured. Laser diffraction using the Mastersizer 3000 was used to perform this measurement. To ensure that the particles were no longer agglomerated during the size analysis, the product was dried to constant mass in the oven such that the binder was evaporated. It should be noted that the emulsion based agglomerates no longer maintained their structure when dry.

The results from the size distribution analysis illustrated that the product material collected by the emulsion had a d_{90} of 638 while the d_{90} for the product material collected by the kerosene was only 428 μm . Therefore, the results appeared to confirm that the emulsion does have the ability to agglomerate coarser particles, thus explaining the higher yield observed in Figure 8.4. Now, it should be noted that these results do not necessarily indicate that the kerosene did not agglomerate the large particles. However, they indicate that the agglomerates made from the emulsion binder, even when including coarse particles, had sufficient buoyancy to be recovered via the method used in this study. This enhanced buoyancy would be highly beneficial in an industrial gravity/density separation process such as a reflux classifier, a modified flotation process, a hydrocyclone, or a fluidised bed.

To further consider the ability of the emulsion to collect particles over a broad size range, the size distribution of the product and reject samples from the experiment which attained highest yield (dosage = 0.5 wt%) were screened into nine different size fractions. Figure 8.5 presents the a) yield and b) combustible recovery as a function of size and Figure 8.6 presents an image and the ash content of each of the samples in the nine size fractions for the product and reject material. The same information for a representative feed sample screened into the same size fractions is also presented.

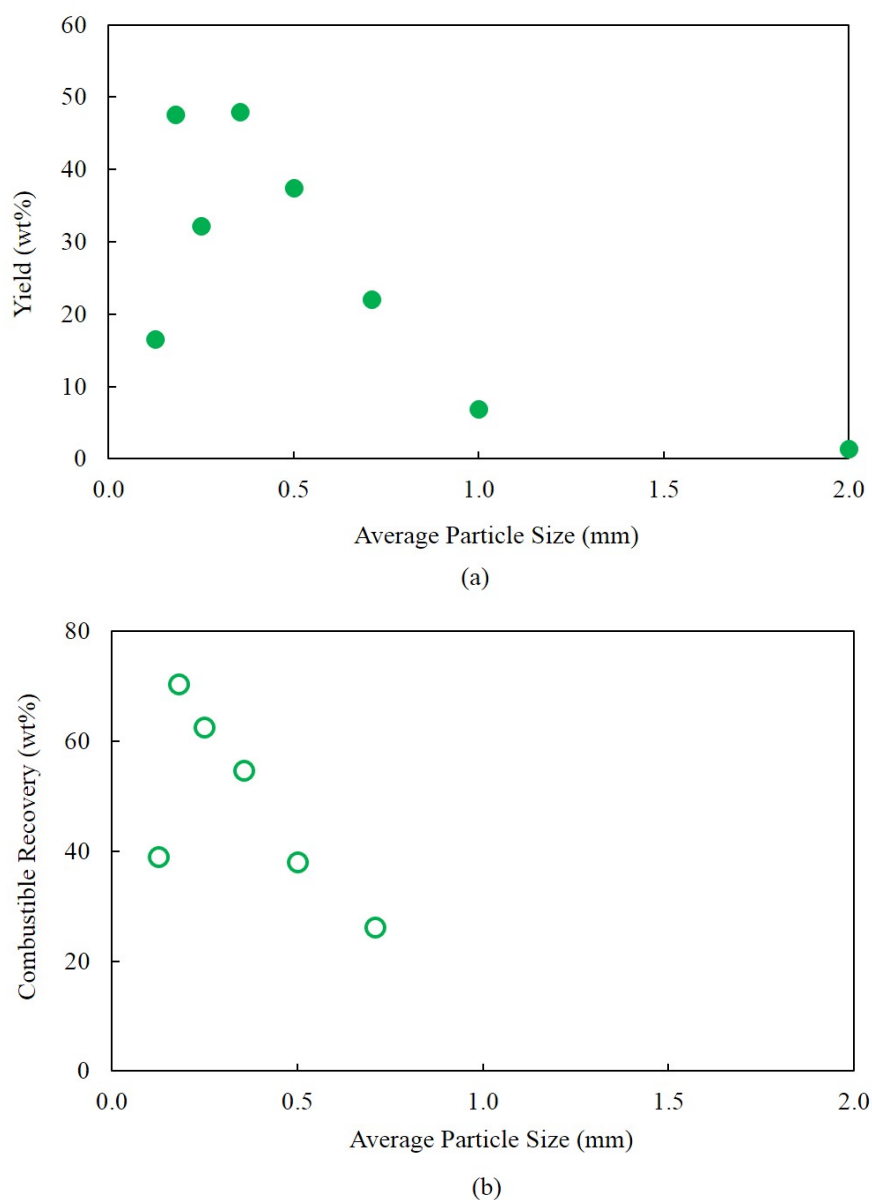


Figure 8.5: a) Yield and b) combustible recovery as a function of particle size for the emulsion binder


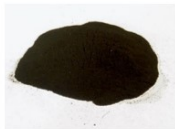


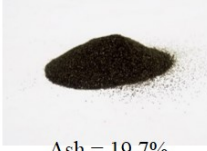
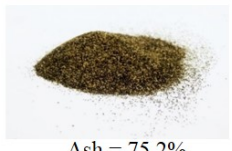


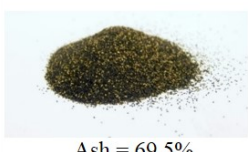




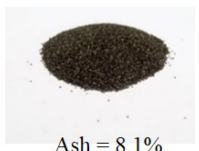
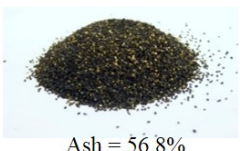
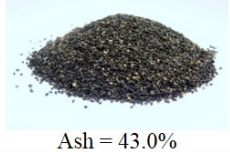
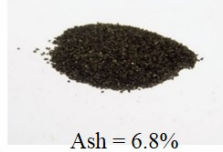
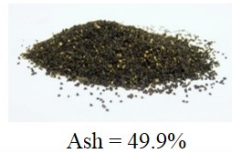
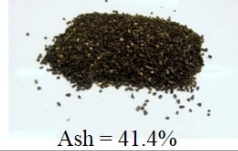

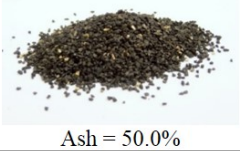
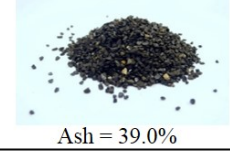
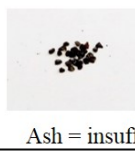
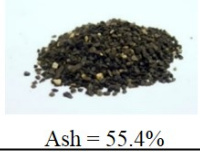

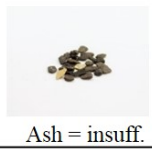
Size Fraction (mm)	Feed	Product	Reject
- 0.125	 Ash = 75.0%	 Ash = 29.3%	 Ash = 82.3%
+ 0.125 - 0.180	 Ash = 51.7%	 Ash = 19.7%	 Ash = 75.2%
+0.180 – 0.250	 Ash = 49.5%	 Ash = 17.1%	 Ash = 69.5%
+0.250 – 0.355	 Ash = 46.6%	 Ash = 12.4%	 Ash = 63.7%
+0.355 – 0.500	 Ash = 45.9%	 Ash = 8.1%	 Ash = 56.8%
+ 0.500 – 0.710	 Ash = 43.0%	 Ash = 6.8%	 Ash = 49.9%
+ 0.710 – 1.000	 Ash = 41.4%	 Ash = insuff.	 Ash = 50.0%
+ 1.000 – 2.000	 Ash = 39.0%	 Ash = insuff.	 Ash = 55.4%
+ 2.000	 Ash = 36.3%		 Ash = insuff.

Figure 8.6: Ash% and image of the feed, product and reject samples sized into nine different size fractions from an experiment using the emulsion binder at a dosage sufficient for maximum recovery

Figure 8.5 indicates reasonable yields and combustible recoveries were achieved by the emulsion binder up to a particle size of 1 mm with low yields and combustible recoveries for particles greater than 1 mm. Moreover, it can be seen that in general combustible recovery decreases as particle size increases. This decrease may signify a reduced collection efficiency for the larger particles. It should be noted that the combustible recovery data for the size fractions greater than 1 mm is missing from Figure 8.5b as ash analysis could not be performed on the small mass which was collected. It may also be observed that the ultra-fine, -0.125 mm fraction experienced an unusually low yield. This low yield may be due to the very high mineral matter content of the feed in this size fraction. The high ash content of the reject material in the -0.125 mm size fraction also indicates that to achieve even higher combustible recoveries, it would be necessary to recover particles of high incremental ash, thus further increasing the product ash.

Finally, it is interesting to note the colour of the feed and product materials in Figure 8.6. In particular, the shiny black quality of the product coal extracted from the mixed quality feed samples. The -0.125 mm is especially impressive as a pure black product was extracted from the dirty grey-brown feed.

8.4 Summary

The work in this chapter indicates agglomeration using the emulsion binder can produce a saleable product from fine coal and may be able to treat particles coarser than possible when using pure oil. In the first section it was shown that the product quality of the coal agglomerates formed using the emulsion binder was sufficient to meet industry standards. The ash% of the product coal was shown to be in the range of 10 – 11% and the product moisture after the application of filtration was in the range of 25 – 30 wt%. The application of the emulsion binder to a coal feed which contained both coarse and fine coal particles also proved to be successful. The emulsion was shown to have the ability to form buoyant agglomerates from particles in the range of 0 – 1 mm.

Chapter 9

Conclusions and Recommendations

9.1 Conclusion

This study was concerned with improving the process of selective agglomeration by maximising the functionality of the liquid binder. A new type of binder, a high internal phase water-in-oil emulsion, was introduced to selectively agglomerate coal from an aqueous mixture of coal and mineral particles. A HIP water-in-oil emulsion was selected for use as it appeared to be an economical alternative to the pure oils which are traditionally used to separate aqueous mixtures of hydrophobic and hydrophilic particles.

The aim of this work was to maximise the functionality of the emulsion binder such that it produced a high quality, agglomerated product at substantially reduced organic liquid dosage. It was considered that the emulsion was capable of a 10 – 20 fold reduction in the organic liquid dosage required to achieve agglomeration, as compared to pure oil. This reduction value was, however, based on the assumption that the emulsion was as effective as pure oil in agglomerating fine coal.

To determine the reductions that were possible in practice, the results for the emulsion binder were compared to a benchmark case in which pure diesel was used. The effects of emulsion composition, mixing regimes and emulsion stability on the functionality of the emulsion were studied. The selectivity of the emulsion was also studied and compared to a pure diesel binder benchmark.

In the earliest work using the emulsion binder the ability of the emulsion to agglomerate coal in a similar manner to a pure diesel binder was investigated. A series of experiments was carried out to determine the influence of the organic liquid dosage on yield for the emulsion binder and a pure diesel binder. It was found that an emulsion with a dispersed, aqueous phase volume fraction of 0.85 exhibited a similar ability to selectively recover fine coal as pure diesel. It was also shown that the use of the emulsion resulted in a 2-fold reduction in the organic liquid dosage required to achieve agglomeration, as compared to using pure diesel.

Modifications to the aqueous phase volume fraction and emulsifier concentration within the organic phase of the emulsion appeared to have no influence on the functionality of the emulsion as a 2-fold reduction was consistently achieved in the early work. Due to this consistency, it was considered that the emulsion was experiencing degradation in the turbulent, aqueous environment of the agglomeration process.

The influence of mixing regimes on the functionality of the emulsion was investigated subsequently. A series of experiments was carried out which studied the influence of mixing duration on the size distribution of the agglomerated sample. It was found that the emulsion binder required only 40 s to completely agglomerate all of the carbonaceous material in the feed into large, discrete agglomerates. Whereas, the pure diesel binder required 120 s to reach the same agglomerated state. Moreover, the results for the emulsion highlighted a decrease in agglomerate size at extended agitation times, > 45 s. A comparison between the emulsion and a pure diesel binder on the influence of mixing time on agglomerate size illustrated that a similar decrease in agglomerate size was not observed when using a pure oil. Therefore it was concluded that the decrease in agglomerate size for the emulsion binder was the result of emulsion degradation. These results were significant because in the early work the operating conditions which were appropriate for the diesel binder were applied directly to the emulsion binder in the interest of a fair comparison.

To reduce the apparent level of emulsion degradation, the agitation time was restricted to 40 s when using the emulsion binder and the influence of the organic liquid dosage on yield was re-established. It was found that a 3-fold reduction, as compared to the pure diesel benchmark, was now achieved. Therefore, these results appeared to confirm that the functionality and performance of the emulsion was linked to its stability.

In the second phase of work into the influence of mixing regimes on the functionality of the emulsion, the influence of the mixing intensity applied during the preparation of the emulsion was studied. This work was undertaken in an effort to improve the ability of the emulsion to withstand the mixing applied in the agglomeration process. A high shear homogenising device, a microniser, was introduced for use in the preparation of the emulsion. This device worked by reducing the diameter of the internal dispersed droplets of the emulsion. Agglomeration experiments using the 'micronised' emulsion indicated that by increasing the level of mixing the emulsion was subjected to during preparation its stability and thus performance improved. The use of the microniser, however, could not be pursued further due to the operational limitations imposed by the emulsion viscosity and the flow rate requirements of the device.

The influence of compositional changes on the functionality of the emulsion was revisited in the following stage of work. It was considered that compositional changes would have

an effect on the functionality of the emulsion, contrary to the results from the early investigations, as the level of degradation had been significantly reduced. An extensive program of work was carried out in a number of stages. Each stage involved a modification in the composition of the emulsion and a subsequent evaluation of the effect on the functionality of the emulsion. The modifications included: the replacement of the tap water in the dispersed phase of the emulsion with a 3 wt% aqueous salt solution; the replacement of the PIB emulsifier with SMO; and the replacement of diesel in the continuous phase of the emulsion with kerosene. The salt solution was introduced as a means of enhancing the stability of the emulsion by impeding the growth of the internal droplets within the emulsion. The SMO emulsifier was investigated to elucidate the effect of the various components of the emulsion on its functionality as a binder. Finally, the kerosene was introduced as a result of the findings from the SMO based emulsion binder which indicated that the viscosity of the continuous phase affected the performance of the emulsion.

The evaluation of each modification was performed by re-establishing the influence of the organic liquid dosage on the product yield for the emulsion and comparing this result to the benchmark, diesel case. Figure 9.1 presents a summary of all of the findings in the investigation into the influence of emulsion composition on its functionality. The product yield is presented as a function of the organic liquid dosage for each data set. All but the best result, which was for the 3 wt% aqueous NaCl-in-kerosene emulsion binder, have been faded to grey. Also presented in the figure are the results for the benchmark diesel case.

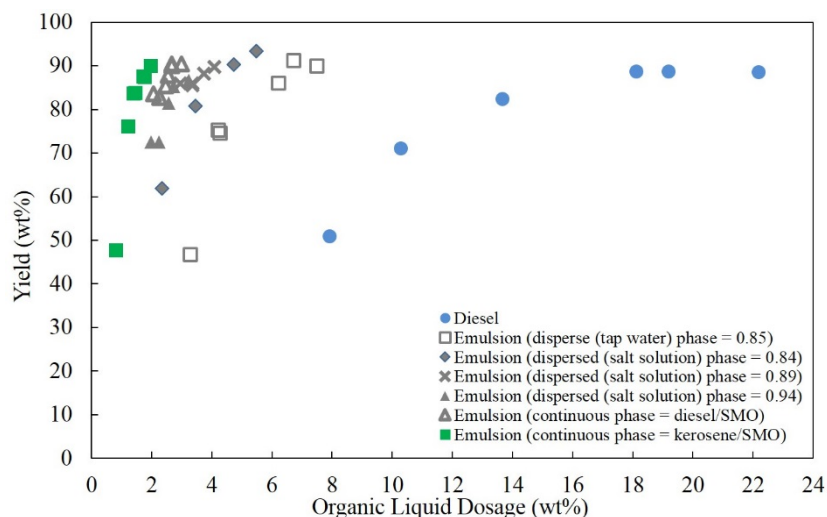


Figure 9.1: Summary of the product yield as a function of the organic liquid dosage for a pure diesel binder and a variety of emulsion binders. The aqueous phase of the emulsion binder varies between 0.84 – 0.95 and the continuous phase consists of PIB emulsifier and diesel unless noted otherwise.

As can be seen in Figure 9.1, each of the emulsion binder composition modifications led to a step change reduction in the organic liquid dosage required to achieve agglomeration. In each case, the change in the organic liquid dosage appeared to be the result of a reduction in the level of degradation the emulsion experienced during the agglomeration process. The highlight of this work is the result for the 3 wt% aqueous NaCl-in-kerosene emulsion binder which achieved a 10-fold reduction as compared to the benchmark diesel case. This emulsion achieved agglomeration in only 7 s, or 3 s if the emulsion was pre-dispersed, and thus experienced the lowest level of degradation which resulted from mixing in the turbulent, aqueous environment of the agglomeration process.

The functionality of the emulsion binder was studied in the following phase of work. The functionality of the emulsion binder was explored in an attempt to provide an explanation for the 10-fold reduction achieved. An analytical expression was developed for the dosage required to achieve agglomeration, based on the specific surface area of the feed, agglomerate void volume and film thickness. Using this expression and the experimental results from an investigation into the influence of the specific hydrophobic surface area of the feed on the organic liquid dosage required to achieve agglomeration, the organic liquid distribution within agglomerates was quantified and compared for each binder. It was found that the substitution theory was appropriate to describe the distribution of the organic phase within the void spaces of the agglomerated material. However, the results

also indicated that a thin film of organic liquid forms over the surface of the agglomerated particles, adding to the organic liquid requirement. Therefore, it was concluded that the reduction which may be achieved is a function not only of the dispersed phase of the emulsion but also of the surface area of the feed.

Overall, the work in this study has resulted in the development of a rapid agglomeration process with reduced organic reagent requirements.

9.2 Recommendations

This study was the first to use a high internal phase water-in-oil emulsion to agglomerate fine particles in suspension. Benefits which arose due to the use of this new type of binder included a significant reduction in the residence time and a substantially reduced organic reagent requirement. However, it was also made clear throughout the thesis, that the use of the emulsion binder added levels of complexity to the agglomeration process that are not present when using a traditional binder, such as oil. Therefore, there is still a considerable amount of work which can be done in this area. Several recommendations for future work are suggested:

1. The description of the functionality of the emulsion developed in Chapter 7 was specific to coal. Further investigations using more homogenous and non-porous materials would provide further insight. The study of a variety of materials may provide an improved understanding of the general functionality of the emulsion.
2. Throughout this thesis, indications were given that the rheology of the emulsion affects its functionality. Therefore, further improvements may be realised by investigating the relationship between the rheology of the emulsion and its functionality in the agglomeration process. Future work could also examine the behaviour of a complex non-Newtonian fluid such as the HIP emulsion in a high shear, three phase system.
3. The results in Chapter 7 provided a preliminary indication that the mechanism of agglomeration using the emulsion binder may differ to that of a pure oil binder. Therefore, a fundamental investigation into the mechanism of agglomeration when using the emulsion binder is required in future work.
4. This work has indicated that agglomeration using the emulsion binder may be viable for industrial applications in fine coal processing. Therefore, future work is required to develop this process from the lab-scale demonstrated in this work to a continuous, steady state process. This work would initially involve a small lab-scale continuous unit, followed by a pilot scale unit and then to full plant trials. The application of this work in an industrial setting would also necessitate a more detailed investigation into the product quality produced by the emulsion binder. This investigation would involve a detailed examination of the selectivity of the emulsion and moisture content of the product material.

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APPENDIX A: Raw Data

This appendix contains the raw data for all of the agglomeration experiments. In any given experiment the typical data which was recorded was the date, run number, mixing speed (rpm), mixing time (s), screen aperture size (μm), product mass (g), reject mass (g) slurry mass (g), binder type and the organic liquid content of the binder (vol. frac). Following an experiment the data which was typically calculated included total solids (g), solids concentration (%), yield (wt%) and organic liquid dosage (wt%). Table A.1 and Table A.2 present example sets of raw data followed by the corresponding calculations for a pure diesel binder and the emulsion binder. It should be noted that in the case of the emulsion binder, the composition of the emulsion is also recorded.

Table A.1 Example data set for an agglomeration experiment using a pure oil binder

Binder Type	Diesel
Organic Liquid Content (vol. frac)	1
Screen (μm)	500
Mixing Speed (r/min)	2000
Mixing Time (s)	600

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
6/07/12	0	39.5	1990.7	203.1	24.2	227.3	11.4	89.4	17.4

Table A.2 Example data set for an agglomeration experiment using the emulsion binder

Binder Type	Emulsion
Organic Liquid Content (vol. frac)	0.15
Screen (μm)	500
Mixing Speed (r/min)	2000
Mixing Time (s)	600

Emulsion Component	Material	Volume Fraction
Oil	Diesel	0.075
Emulsifier	PIB	0.075
Water	Tap water	0.85

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (wt%)	Yield (wt%)	Organic Liquid Dosage (wt%)
9/07/12	3	62.3	1829.4	152.5	100.8	253.3	13.8	60.2	3.7

Sample Calculations

Sample calculations are performed using the data in Table A.2

Total Solids

$$\text{Total Solids (g)} = \text{Overflow (g)} + \text{Underflow (g)}$$

$$\begin{aligned}\text{Total solids} &= 152.5 + 100.8 \\ &= 253.3 \text{ g}\end{aligned}$$

Solids Concentration

$$\text{Solids Concentration (wt\%)} = \frac{\text{Total Solids (g)}}{\text{Slurry Mass (g)}} \times 100\%$$

$$\begin{aligned}\text{Solids Concentration} &= \frac{253.3}{1829.4} \times 100 \\ &= 13.8 \text{ wt\%}\end{aligned}$$

Yield

$$\text{Yield (wt\%)} = \frac{\text{Overflow (g)}}{\text{Total Solids (g)}} \times 100\%$$

$$\begin{aligned}\text{Yield} &= \frac{152.5}{253.3} \times 100 \\ &= 60.2 \text{ wt\%}\end{aligned}$$

Organic Liquid Dosage

$$\text{Organic Liquid Dosage (wt\%)} = \frac{\text{Binder Mass} \times \text{Organic Liquid Content}}{\text{Total Solids}} \times 100\%$$

$$\begin{aligned}\text{Organic Liquid Dosage} &= \frac{62.3 \times 0.15}{253.3} \times 100\% \\ &= 3.7 \text{ wt\%}\end{aligned}$$

These calculations were repeated to produce the results presented in this appendix and throughout the thesis.

The headings used to organise the raw data below reflect the organisation of the data in the main thesis.

Fine Coal Recovery

Agglomeration experiments were carried out using a pure diesel binder and an emulsion binder and the results are presented in Table A.3 and Table A.4 respectively.

Table A.3 Raw and Calculated Data for Agglomeration Experiments using a Pure Diesel Binder

Binder Type	Diesel
Organic Liquid Content (vol. frac)	1
Screen (μm)	500
Mixing Speed (r/min)	2000
Mixing Time (s)	600

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
6/07/12	0	39.5	1990.7	203.1	24.2	227.3	11.4	89.4	17.4
9/07/12	1	30.8	1866.6	194.7	30.2	224.9	12.0	86.6	13.7
9/07/12	2	23.2	1842.2	180.4	53.4	233.8	12.7	77.2	9.9
9/07/12	4	14.5	1849.6	126.5	111.6	238.1	12.9	53.1	6.1
13/07/12	9	18.8	not rec.	166.9	74.0	240.9		69.3	7.8
13/07/12	10	26.5	1898	195.8	46.2	242	12.8	80.9	11.0
31/07/12	23	11.9	1891	96.6	158.7	255.3	13.5	37.8	4.7

Table A.4 Raw and Calculated Data for Agglomeration Experiments using the Emulsion Binder

Binder Type	Emulsion
Organic Liquid Content (vol. frac)	0.15
Screen (μm)	500
Mixing Speed (r/min)	2000
Mixing Time (s)	600

Emulsion Component	Material	Volume Fraction
Oil	Diesel	0.08
Emulsifier	PIB	0.08
Water	Tap water	0.85

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
6/07/12		90.4	2376.3	190.8	68.7	259.5	10.9	73.5	5.4
9/07/12	3	62.3	1829.4	152.5	100.2	252.7	13.8	60.3	3.8
11/07/12	7	152.7	2079.6	236.3	7.8	244.1	11.7	96.8	9.6
11/07/12	8	133.2	1966.3	245.5	9.7	255.2	13.0	96.2	8.0
18/07/12	13	111	1921.6	219.5	38.7	258.2	13.4	85.0	6.6

Maximising the Functionality of the Emulsion through Composition Modifications

Internal Aqueous Phase Volume Fraction

Agglomeration experiments were carried out using emulsion binders with varying internal phase volume fractions and the results are presented in Table A.5, Table A.6 and Table A.7.

Table A.5 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder with an Internal Phase Volume Fraction of 0.90

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.10	Oil	Diesel	0.05
Screen (μm)	500	Emulsifier	PIB	0.05
Mixing Speed (r/min)	2000	Water	Tap water	0.90
Mixing Time (s)	600			

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield (wt%)	Organic Liquid Dosage (wt%)
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
26/07/12	19	100.0	1889.1	146.7	111.7	258.4	13.7	56.8	3.9
26/07/12	20	159.9	1987.6	215.92	30.2	246.1	12.4	87.7	6.5
27/07/12	21	128.6	1926.7	187.84	70.6	258.4	13.4	72.7	5.0

Table A.6 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder with an Internal Phase Volume Fraction of 0.93

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.07	Oil	Diesel	0.04
Screen (μm)	500	Emulsifier	PIB	0.04
Mixing Speed (r/min)	2000	Water	Tap water	0.93
Mixing Time (s)	600			

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
2/08/2012	26	217.5	2066.1	213.8	34.2	248.0	12.0	86.2	6.2
2/08/2012	27	170.2	2139	171.2	72.9	244.1	11.4	70.1	5.0

Table A.7 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder with an Internal Phase Volume Fraction of 0.67

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.33	Oil	Diesel	0.17
Screen (μm)	500	Emulsifier	PIB	0.17
Mixing Speed (r/min)	2000	Water	Tap water	0.67
Mixing Time (s)	600			

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
2/08/12	28	65.1	1910.6	228.2	18.1	246.3	12.9	92.7	8.6

Organic Phase Composition

Agglomeration experiments were carried out using emulsion binders with varying organic phase compositions and the results are presented in Table A.8 and Table A.9.

Table A.8 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder with a PIB volume fraction of 0.045

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.15	Oil	Diesel	0.105
Screen (μm)	500	Emulsifier	PIB	0.045
Mixing Speed (r/min)	2000	Water	Tap water	0.85
Mixing Time (s)	600			

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
13/07/12	11	117.2	1923.3	233.3	24.1	257.4	13.4	90.6	7.1
16/07/12	12	96.2	1904.7	196.0	52.1	248.1	13.0	79.0	6.0
18/07/12	14	63.9	1975.3	145.9	112.6	258.5	13.1	56.4	3.8
18/07/12	15	51.4	2022.8	77.3	182.7	260.0	12.9	29.7	3.1
20/07/12	16	77.4	1892.7	170.5	63.4	233.9	12.4	72.9	5.1

Table A.9 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder with a PIB volume fraction of 0.105

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.15	Oil	Diesel	0.045
Screen (μm)	500	Emulsifier	PIB	0.105
Mixing Speed (r/min)	2000	Water	Tap water	0.85
Mixing Time (s)	600			

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
20/07/12	17	107.0	2041.9	221.3	58.3	279.6	13.7	79.1	5.9
20/07/12	18	123.9	2154	232.3	35.6	267.9	12.4	86.7	7.2

Influence of Mixing on Agglomeration Process

Emulsion Binder

Agglomeration experiments were carried out using an emulsion binder and varying mixing times and the results are presented in Table A.10. It should be noted that the agglomerated material was not screened in this case.

Table A.10 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder and varying mixing times

Binder Type	Emulsion
Organic Liquid Content (vol. frac)	0.150
Mixing Speed (r/min)	20000
Organic Liquid Dosage (wt%)	8.0

Date	Run	Mixing Time (s)	Slurry (g)	Total Solids (g)	Solids Concentration (%)	d_{43}^* (μm)
12/04/13	109	10	664.0	10.0	1.5	203.2
12/04/13	111	15	659.6	10.4	1.6	232.7
12/04/13	112	20	675.3	8.8	1.3	292.5
12/04/13	113	25	689.2	8.8	1.3	336.8
12/04/13	114	30	669.3	9.6	1.4	391.2
12/04/13	115	35	672.1	8.3	1.2	427.4
12/04/13	116	45	625.5	9.0	1.4	399.2
12/04/13	117	60	670.6	9.2	1.4	336.0
12/04/13	118	90	669.5	12.9	1.9	295.1
12/04/13	119	120	669.5	9.6	1.4	313.78

*measured using the Mastersizer 2000

Binder Comparison

Agglomeration experiments were carried out using an emulsion binder and a pure diesel binder, both with varying mixing times, and the results are presented in Table A.11 and Table A.12, respectively. It should be noted that the agglomerated material was classified over 2 different screens with apertures 150 μm and 355 μm . In instances in which a measurement was not taken 'n.a' appears in the table.

Table A.11 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder and varying mixing times.

Binder Type	Emulsion
Organic Liquid Content (vol. frac)	0.15
Mixing Speed (r/min)	20000
Organic Liquid Dosage (wt%)	8

Date	Run	Mixing Time (s)	Slurry (g)	Total Solids (g)	Solids Conc. (%)	-150 μm (wt%)	-355 μm +150 (wt%)	+355 μm (wt%)
20/10/13	feed	0	-	55.0	-	60.7	39.4	0.0
20/10/13	302	10	496	57.1	11.5	52.7	26.7	20.6
21/10/13	303	20	494	59.0	11.9	36.4	22.2	41.4
21/10/13	304	30	502	52.7	10.5	16.1	5.7	78.1
22/10/13	305	40	485	54.1	11.2	10.5	4.0	85.5
22/10/13	306	60	498	53.7	10.8	8.5	27.8	63.7
11/11/13	307	100	465	53.4	11.5	n.a	n.a	61.2

Table A.12 Raw and Calculated Data for Agglomeration Experiments using a Pure Diesel Binder and varying mixing times.

Binder Type	Diesel
Organic Liquid Content (vol. frac)	1
Mixing Speed (r/min)	20000
Organic Liquid Dosage (wt%)	16

Date	Run	Mixing Time (s)	Slurry (g)	Total Solids (g)	Solids Conc. (%)	-150 μm (wt%)	-355 μm +150 (wt%)	+355 μm (wt%)
20/10/13	feed	0	-	55.0	-	60.7	39.4	0.0
4/11/13	286	10	462	42.0	9.1	n.a	n.a	0.0
29/10/13	281	20	418	35.9	8.6	32.7	62.0	5.3
7/11/13	299	40	493	57.2	11.6	21.8	64.3	13.8
29/10/13	284	60	418	41.6	10.0	13.2	66.1	20.7
7/11/13	295	70	468	54.5	11.6	n.a	n.a	47.9
7/11/13	293	90	460	56.8	12.3	9.6	26.8	63.6
7/11/13	289	105	566	53.7	9.5	n.a	n.a	70.7
29/10/13	283	120	438	41.2	9.4	7.7	11.0	81.3
7/11/13	291	140	490	58.7	12.0	n.a	n.a	82.6

Improved Mixing Time

Agglomeration experiments were carried out using a pure diesel binder and an emulsion binder and the results are presented in Table A.13 and Table A.14 respectively.

Table A.13 Raw and Calculated Data for Agglomeration Experiments using a Pure Diesel Binder in the new mixing device

Binder Type	Diesel
Organic Liquid Content (vol. frac)	1.00
Screen (μm)	355
Mixing Speed (r/min)	20000
Mixing Time (s)	120

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
9/05/13	160	6.5	461.0	30.1	3.8	33.9	7.4	88.8	19.2
9/05/13	161	4.97	487.5	30.0	6.4	36.4	7.5	82.4	13.7
9/05/13	162	3.7	453.5	25.6	10.4	36.0	7.9	71.1	10.3
9/05/13	163	3.01	505.8	19.4	18.7	38.1	7.5	50.9	7.9
25/07/13	217	8.98	420.3	44.0	5.6	49.6	11.8	88.7	18.1

Table A.14 Raw and Calculated Data for Agglomeration Experiments using the Emulsion Binder with a reduced mixing time

Binder Type	Emulsion
Organic Liquid Content (vol. frac)	0.15
Screen (μm)	355
Mixing Speed (r/min)	20000
Mixing Time (s)	40

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
8/05/13	154	10.31	470.4	28.3	9.3	37.6	8.0	75.3	4.20
8/05/13	155	12.33	465	33.0	11.2	44.2	9.5	74.6	4.27
8/05/13	156	14.55	456	30.9	5.0	35.9	7.9	86.1	6.21
8/05/13	157	17.08	470	35.5	3.4	38.9	8.3	91.3	6.72
8/05/13	158	19.13	464.2	35.2	3.9	39.1	8.4	90.0	7.48
8/05/13	159	8.67	443.3	19.0	21.6	40.6	9.2	46.8	3.27

Microniser

The Mastersizer was used to measure the dispersed droplet size of emulsions produced using the microniser at different operating frequencies. The results from the analysis are presented in Table A.15.

Table A.15 Raw data from the analysis of the micronised emulsion

Binder Type	Emulsion
Organic Liquid Content (vol. frac)	0.50

Date	Frequency (hz)	d50 (µm)
20/06/2013	0	54.7
20/06/2013	10	5.2
20/06/2013	30	2.9
20/06/2013	50	1.9
20/06/2013	70	1.2

Agglomeration experiments were carried out using a micronised emulsion binder and the results are presented in Table A.16.

Table A.16 Raw and Calculated Data for Agglomeration Experiments using a Micronised Emulsion Binder

Binder Type	Emulsion
Organic Liquid Content (vol. frac)	0.70
Screen (µm)	355
Mixing Speed (r/min)	20000
Mixing Time (s)	40

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
11/07/13	205	9.19	419.9	31.0	1.6	32.6	7.8	95.1	8.17
10/07/13	206	7.92	398	29.3	4.1	33.4	8.4	87.7	6.88
12/07/13	207	6.28	387.1	26.5	6.4	32.9	8.5	80.5	5.53

Influence of Electrolyte Presence in Aqueous Phase

Agglomeration experiments were carried out using an emulsion binder and the results are presented in Table A.17.

Table A.17 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder made from a 3 wt% aqueous NaCl solution

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.16	Oil	Diesel	0.08
Screen (μm)	250	Emulsifier	PIB	0.08
Mixing Speed (r/min)	20000	Water	3 wt% Aqueous NaCl	0.84
Mixing Time (s)	40			

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
31/07/13	230	12.6	430.6	33.3	3.6	36.9	8.6	90.3	4.73
31/07/13	231	15.56	462.3	36.7	2.6	39.3	8.5	93.4	5.49
31/07/13	232	10.04	482.3	32.5	7.7	40.2	8.3	80.8	3.46
31/07/13	233	6.96	448.5	25.5	15.7	41.2	9.2	61.9	2.34

Emulsion Stability

The breakdown of the emulsion was examined by mixing the emulsion in tap water and examining the conductivity of the solution as a function of mixing time. The raw and calculated data is presented in Table A.18.

Table A.18 Raw and Calculated Data for Emulsion Breakdown Experiments

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.16	Oil	Diesel	0.08
Mixing Speed (r/min)	20000	Emulsifier	PIB	0.08
Volume (ml)	500	Water	3 wt% Aqueous NaCl	0.84

Date	Time (s)	Binder (g)	Cond ₀ (μS)	Cond _a (μS)	Cond ₂ (μS)	Cond _{avg} (μS)	ΔCond (Cond _{av} - Cond ₀) (μS)	Normalised Cond. (μS)
28/02/14	5	7.39	222	383	402	393	171	177.1
28/02/14	15	9.73	220	541	566	554	334	263.1
28/02/14	15	7.8	220	506	532	519	299	294.2
28/02/14	25	9.79	220	574	635	605	385	301.4
28/02/14	25	7.81	220	531	584	584	53	331.7
28/02/14	35	7.79	222	632	660	660	28	417.7
28/02/14	45	7.78	191	630		630	439	433.1
28/02/14	45	8.2	195	606	615	611	416	440.0
28/02/14	60	8.04	198	627	644	636	438	472.5

Sample Calculations for Conductivity Data

The base conductivity, $Cond_0$, measurement represents the background conductivity of the tap water used to suspend the emulsion. Two conductivity measurements were taken, $Cond_1$ and $Cond_2$, and the average of these two measurements was considered to be the conductivity of the suspension. The change in conductivity, $\Delta Cond$, was then found using $Cond_{avg} - Cond_0$, as shown in Table A.18. The $\Delta Cond$ value was then normalised to a constant salt concentration. This normalisation was required as slightly different amounts of emulsion were used in each experiment. Therefore all of the conductivity measurements were normalised to a constant mass (7.7 g) of emulsion.

Influence of Aqueous Phase Volume Fraction – Revisited

Agglomeration experiments were carried out using emulsion binders with varying internal phase volume fractions and the results are presented in Table A.19, and Table A.20.

Table A.19 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder with a dispersed volume fraction of 0.89

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.11	Oil	Diesel	0.06
Screen (μm)	250	Emulsifier	PIB	0.06
Mixing Speed (r/min)	20000	Water	3 wt% Aqueous NaCl	0.89
Mixing Time (s)	40			

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
2/08/13	237	21.58	394.6	44.7	5.1	49.8	12.6	89.8	4.08
5/08/13	244	20.92	430.0	46.5	6.2	52.7	12.3	88.2	3.73
9/08/13	245	17.89	429.6	43.1	7.0	50.1	11.7	86.0	3.36
9/08/13	246	18.66	433.6	44.9	7.6	52.5	12.1	85.5	3.35
12/08/13	247	15.93	478.5	43.5	7.1	50.6	10.6	86.0	85.5

Table A.20 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder with a dispersed volume fraction of 0.94

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.06	Oil	Diesel	0.03
Screen (µm)	250	Emulsifier	PIB	0.03
Mixing Speed (r/min)	20000	Water	3 wt% Aqueous NaCl	0.94
Mixing Time (s)	40			

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
5/08/13	238	20.23	480.2	38.5	14.6	53.2	11.1	72.5	1.97
6/08/13	240	22.38	468.1	37.4	14.2	51.6	11.0	72.5	2.25
6/08/13	241	27.6	416.7	44.6	7.7	52.3	12.5	85.3	2.74
8/08/13	242	25.58	454.6	41.9	9.5	51.4	11.3	81.5	2.58
6/08/13	243	30.04	470.1	41.6	6.4	48.0	10.2	86.7	3.24

Influence of Emulsifier Type

Agglomeration experiments were carried out using an emulsion binder made with SMO as the emulsifier and the results are presented in Table A.21.

Table A.21 Raw and Calculated Data for Agglomeration Experiments using an Emulsion Binder made with SMO

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.11	Oil	Diesel	0.06
Screen (µm)	250	Emulsifier	SMO	0.06
Mixing Speed (r/min)	20000	Water	3 wt% Aqueous NaCl	0.89
Mixing Time (s)	15			

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
2/12/13	315	15.3	478	49.9	5.3	55.2	11.5	90.4	2.66
2/12/13	316	14.5	478	48.1	8.2	56.3	11.8	85.4	2.47
2/12/13	317	13.1	484	45.9	9.6	55.5	11.5	82.7	2.27
18/12/13	325	17.2	433	49.7	5.3	55.0	12.7	90.4	2.99
18/12/13	326	15.4	450	50.3	7.0	57.3	12.7	87.8	2.56
19/12/13	327	12.7	475	49.3	9.7	59.0	12.4	83.6	2.06
19/12/13	328	16.0	366	51.5	59.0	110.5	30.2	46.6	2.66

The breakdown of the emulsion was examined for the SMO based binder by mixing the emulsion in tap water and examining the conductivity of the solution as a function of mixing time. The raw and calculated data is presented in Table A.22

Table A.22 Raw and Calculated Data for Emulsion Breakdown Experiments using the SMO based binder

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.16	Oil	Diesel	0.08
Mixing Speed (r/min)	20000	Emulsifier	SMO	0.08
Volume (ml)	500	Water	3 wt% Aqueous NaCl	0.84

Date	Time	Binder	Condo	Conda	Cond2	Conda _{avg}	Δ Cond (Conda _{av} - Condo)	Normalised Cond.
	(s)	(g)	(μ S)	(μ S)	(μ S)	(μ S)	(μ S)	(μ S)
4/03/14	5	8.2	203	509	543	526	323	306
4/03/14	10	8.2	213	664	695	680	467	441
4/03/14	20	7.91	215	790	804	797	582	571
4/03/14	30	8.06	210	838	846	842	632	608
4/03/14	45	8.11	210	888	901	895	685	655
4/03/14	60	7.74	207	863	869	866	659	661

Minimisation of Agglomeration Time

Agglomeration experiments were carried out using an emulsion binder made with SMO to examine the influence of mixing time on yield if the binder is pre-dispersed. The raw and calculated data is presented in Table A.23.

Table A.23 Raw and Calculated Data for Minimisation of Agglomeration Time Experiments

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.11	Oil	Diesel	0.06
Screen (μ m)	250	Emulsifier	SMO	0.06
Mixing Speed (r/min)	20000	Water	3 wt% Aqueous NaCl	0.89
Organic Liquid Dosage (wt%)	2.7			
Emulsion Pre-Disperse Time (s)	10			

Date	Run	Agglomeration Time	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield
		(s)	(g)	(g)	(g)	(g)	(%)	(wt%)
19/12/13	328	10	366	51.5	5.7	57.2	15.6	90.0
19/12/13	329	6	386	49.8	5.6	55.4	14.4	89.9
14/01/14	331	8	388	33.5	3.5	37.0	9.5	90.5
14/01/14	333	4	461	29.3	7.5	36.8	8.0	79.6
14/01/14	334	2.5	459	27.1	9.2	36.3	7.9	74.7

Influence of Continuous Phase Oil Type

Agglomeration experiments were carried out using pure kerosene and an emulsion binder made with kerosene. The raw and calculated data is presented in Table A.24 and Table A.25.

Table A.24 Raw and Calculated Data for Agglomeration Experiments for a Pure Kerosene Binder

Binder Type		Kerosene							
Organic Liquid Content (vol. frac)		1.0							
Screen (μm)		250							
Mixing Speed (r/min)		20000							
Mixing Time (s)		120							

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
14/07/14	385	8.1	452.1	50.7	11.5	62.2	13.8	81.5	13.1
14/07/14	386	10.4	480.0	51.9	8.7	60.6	12.6	85.6	17.2
14/07/14	387	6.2	561.9	40.7	17.6	58.3	10.4	69.8	10.7
16/07/14	389	5.2	498.8	42.7	18.2	60.9	12.2	70.1	8.5
16/07/14	390	12.4	465.8	55.2	6.2	61.4	13.2	89.9	20.1

Table A.25 Raw and Calculated Data for Agglomeration Experiments for a Kerosene based Emulsion Binder

Binder Type		Emulsion	
Organic Liquid Content (vol. frac)		n	
Screen (μm)		250	
Mixing Speed (r/min)		20000	
Mixing Time (s)		7	

Emulsion Component	Material	Volume Fraction
Oil	Kerosene	0.03
Emulsifier	SMO	0.03
Water	3 wt% Aqueous NaCl	0.95

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
11/07/14	379	10.1	462.4	30.1	32.9	63.0	13.6	47.8	0.80
11/07/14	380	15.3	474.1	48.1	15.0	63.1	13.3	76.2	1.21
11/07/14	381	18.2	438.4	52.2	10.1	62.3	14.2	83.8	1.46
11/07/14	382	20.5	518.1	61.9	12.0	73.9	14.3	83.8	1.38
11/07/14	383	22.6	475.8	56.1	8.0	64.1	13.5	87.5	1.76
11/07/14	384	21.6	401.3	55.8	7.9	63.7	15.9	87.6	1.71
15/07/14	388	23.4	482.0	53.4	5.9	59.3	12.3	90.1	1.97

On the Functionality of the Binder

The raw and calculated data for the eight different coals examined in the investigation into the functionality of the binder are presented in Table A.26 – A.40. Results for both the pure kerosene binder and the emulsion binder are presented below. The mixing speed used for each binder was 120 s and 7 s, respectively. The composition of the emulsion remained unchanged from that shown in Table A.25.

Table A.26 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for Coal 1

Binder Type	Kerosene
Screen (µm)	150

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
22/07/14	399	2.8	476.6	8.3	20.0	28.3	5.9	29.3	9.9
22/07/14	400	1.8	476.6	5.3	20.6	25.9	5.4	20.5	6.9
22/07/14	401	3.9	477.7	7.3	19.2	26.5	5.5	27.5	14.8
22/07/14	402	3.3	462.5	8.3	20.5	28.8	6.2	28.8	11.4

Table A.27 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 1

Binder Type	Emulsion
Screen (µm)	150

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
23/07/14	410	8.0	462.5	4.7	25.3	30.0	6.5	15.7	1.3
23/07/14	419	12.5	485.0	7.6	21.3	28.9	6.0	26.3	2.1
4/08/14	442	12.6	481.7	8.4	20.6	29.0	6.0	29.0	2.3
4/08/14	444	11.5	458.9	7.6	24.3	31.9	7.0	23.8	1.9
7/10/15	559	13.2	384.0	7.4	20.5	27.9	7.3	26.5	2.4

Table A.28 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for Coal 2

Binder Type	Kerosene
Screen (μm)	150

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
1/08/14	430	4.3	421.5	8.8	18.2	27.0	6.4	32.6	15.9
1/08/14	431	3.1	526.0	9.3	19.4	28.7	5.5	32.4	10.7
14/08/14	451	1.9	467.4	6.6	22.7	29.3	6.3	22.5	6.4

Table A.29 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 2

Binder Type	Emulsion
Screen (μm)	150

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
23/07/14	418	12.5	483.8	8.8	21.5	30.3	6.3	29.0	2.0
4/08/14	439	10.9	439.5	8.1	17.5	25.6	5.8	31.6	2.2
4/08/14	440	11.9	458.1	9.7	20.6	30.3	6.6	32.0	2.1
4/08/14	441	12.9	559.0	9.8	25.0	34.8	6.2	28.2	1.9

Table A.30 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for Coal 3 [Experiments were carried out by masters student, Wenfei Zhang]

Binder Type	Kerosene
Screen (μm)	250

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
22/10/14	8	6.9	439.6	19.3	5.1	24.4	5.6	79.1	28.3
22/10/14	9	6.1	431.2	20.5	4.5	25	5.8	82.0	24.4
22/10/14	10	4.9	422.1	19.8	5.1	24.9	5.9	79.5	19.5
22/10/14	11	3.5	430.1	18.4	6.4	24.8	5.8	74.2	14.3

Table A.31 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 3 [Experiments were carried out by masters student, Wenfei Zhang]

Binder Type	Emulsion
Screen (μm)	250

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
15/10/14	4	10.5	455.8	9.5	18.1	27.6	6.1	34.4	1.9
15/10/14	5	14.8	474.6	12.5	12.5	25.0	5.3	50.0	3.0
15/10/14	6	20.2	452.2	18.6	6.6	25.2	5.6	73.8	4.0
26/08/15	33	24.48	460.7	21.3	13.6	34.9	7.6	61.0	3.4
27/08/15	34	33.44	475.9	26.4	7.6	34.0	7.1	77.6	4.7

Table A.32 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for Coal 4

Binder Type	Kerosene
Screen (μm)	250

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
14/07/14	385	8.1	452.1	50.7	11.5	62.2	13.8	81.5	13.1
14/07/14	386	10.4	480.0	51.9	8.7	60.6	12.6	85.6	17.2
14/07/14	387	6.2	561.9	40.7	17.6	58.3	10.4	69.8	10.7
16/07/14	389	5.2	498.8	42.7	18.2	60.9	12.2	70.1	8.5
16/07/14	390	12.4	465.8	55.2	6.2	61.4	13.2	89.9	20.1

Table A.33 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 4

Binder Type	Emulsion
Screen (μm)	250

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
11/07/14	379	10.1	462.4	30.1	32.9	63.0	13.6	47.8	0.80
11/07/14	380	15.3	474.1	48.1	15.0	63.1	13.3	76.2	1.21
11/07/14	381	18.2	438.4	52.2	10.1	62.3	14.2	83.8	1.46
11/07/14	382	20.5	518.1	61.9	12.0	73.9	14.3	83.8	1.38
11/07/14	383	22.6	475.8	56.1	8.0	64.1	13.5	87.5	1.76
11/07/14	384	21.6	401.3	55.8	7.9	63.7	15.9	87.6	1.71
15/07/14	388	23.4	482.0	53.4	5.9	59.3	12.3	90.1	1.97

Table A.34 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for Coal 5

Binder Type	Kerosene
Screen (μm)	250

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
12/10/15	564	6.4	532	19.9	27.1	47.0	8.8	42.3	13.6
12/10/15	565	4.4	565	17.7	27.0	44.7	7.9	39.6	9.8
12/10/15	566	2.7	488	14.4	29.1	43.5	8.9	33.1	6.2
13/10/15	568	6.7	487	20.0	23.3	43.3	8.9	46.2	15.4
14/10/15	573	7.2	475	18.2	23.7	41.9	8.8	43.4	17.2

Table A.35 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 5

Binder Type	Emulsion
Screen (μm)	250

Date	Run	Binder (g)	Slurry (g)	Prod. (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
23/09/15	544	20.0	513.0	20.4	23.8	44.2	8.6	46.2	2.2
23/09/15	545	15.7	510.0	14.7	30.7	45.4	8.9	32.4	1.7
23/09/15	546	11.9	519.0	10.1	34.9	45.0	8.7	22.4	1.3
29/09/15	548	10.0	494.7	8.6	35.9	44.5	9.0	19.3	1.1
29/09/15	549	22.1	518.0	21.1	25.3	46.4	9.0	45.5	2.4
29/09/15	551	12.5	520.0	11.1	33.6	44.7	8.6	24.8	1.4

Table A.36 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for Coal 6 [Experiments were carried out by honours student, Tom Ernst]

Binder Type	Kerosene
Screen (μm)	250

Date	Run	Binder (g)	Overflow (g)	Underflow (g)	Heavy (g)	Total Solids (g)	Yield (wt%)	Organic Liquid Dosage (wt%)
14/04/15	8	4.94	18.6	48.3	45	111.9	16.6	4.4
14/04/15	10	3.29	19.1	42.2	50.5	111.8	17.1	2.9
14/04/15	11	1.65	15.2	43	51.3	109.5	13.9	1.5
14/04/15	507	0.94	4.3	10	90.2	104.5	4.1	0.9

Table A.37 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 6 [Experiments were carried out by honours student, Tom Ernst]

Binder Type	Emulsion
Screen (µm)	250

Date	Run	Binder (g)	Prod. (g)	Light (g)	Heavy (g)	Total Solids (g)	Yield (wt%)	Organic Liquid Dosage (wt%)
7/04/15	1	2.0	8.0	7.9	72.9	88.8	9.0	0.10
7/04/15	3	9.5	24.1	5.2	75.5	104.8	23.0	0.48
7/04/15	4	8.3	18.7	5.9	66.9	91.5	20.4	0.42
7/04/15	5	6.0	11.5	7.7	72.3	91.5	12.6	0.30
7/04/15	6	3.6	9.7	6.5	80.4	96.6	10.0	0.18
7/04/15	7	10.5	22.1	2.1	83.5	107.7	20.5	0.53
7/04/15	9	10.7	25.7	5.6	80.1	111.4	23.1	0.54

Table A.38 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 7 [Experiments were carried out by honours student, Tom Ernst]

Binder Type	Emulsion
Screen (µm)	250

Date	Run	Binder (g)	Prod (g)	Light (g)	Heavy (g)	Total Solids (g)	Yield (wt%)	Organic Liquid Dosage (wt%)
11/07/15	E2R1	21.2	54.2	11.2	43.6	109.0	49.7	1.0
11/07/15	E2R2	17.1	50.8	9.2	50.6	110.6	45.9	0.8
11/07/15	E2R3	12.7	34.0	20.0	54.6	108.6	31.3	0.6
11/07/15	E2R4	8.4	19.8	21.6	64.7	106.1	18.7	0.4
11/07/15	E2R5	25.5	59.1	8.4	43.7	111.2	53.1	1.1
11/07/15	E2R6	24.2	44.2	5.8	31.0	81.0	54.6	1.5

Table A.39 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for Coal 8

Binder Type	Kerosene
Screen (µm)	355

Date	Run	Binder (g)	Slurry (g)	Prod (g)	Rej. (g)	Total Solids (g)	Solids Conc. (%)	Yield (wt%)	Organic Liquid Dosage (wt%)
12/10/15	567	1.0	369	24.4	7.9	32.3	8.8	75.5	3.2
13/10/15	569	2.8	398	30.8	1.4	32.2	8.1	95.7	8.5
13/10/15	570	1.7	394	28.3	4.6	32.9	8.4	86.0	5.2
13/10/15	571	2.3	416	29.2	3.8	33.0	7.9	88.5	7.0

Table A.40 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for Coal 8

Binder Type	Emulsion
Screen (μm)	355

Date	Run	Binder	Slurry	Prod.	Rej.	Total Solids	Solids Conc.	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(%)	(wt%)	(wt%)
12/09/14	459	9.9	394.7	52.7	2.0	54.7	13.9	96.3	1.0
15/09/14	461	9.6	415.3	52.9	3.2	56.1	13.5	94.3	0.9
15/09/214	462	7.7	441.1	44.4	8.3	52.7	11.9	84.3	0.8

Coarse Particles

Agglomeration experiments were carried on a feed containing fine and coarse particles. The raw and calculated data is presented in Table A.41 and Table A.42.

Table A.41 Raw and Calculated Data for Agglomeration Experiments for a Kerosene Binder for a feed containing coarse particles

Binder Type	Kerosene
Organic Liquid Content (vol. frac)	1.0
Screen (μm)	250
Mixing Speed (r/min)	20000
Mixing Time (s)	120

Date	Run	Binder	Overflow	Underflow	Heavy	Total Solids	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(wt%)	(wt%)
14/04/15	8	4.9	18.6	48.3	45.0	111.9	16.6	4.4
14/04/15	10	3.3	19.1	42.2	50.5	111.8	17.1	2.9
14/04/15	11	1.7	15.2	43.0	51.3	109.5	13.9	1.5
28/05/15	507	0.9	4.3	10.0	90.2	104.5	4.1	0.9

Table A.42 Raw and Calculated Data for Agglomeration Experiments for the Emulsion Binder for a feed containing coarse particles

Binder Type	Emulsion	Emulsion Component	Material	Volume Fraction
Organic Liquid Content (vol. frac)	0.05	Oil	Kerosene	0.03
Screen (µm)	250	Emulsifier	SMO	0.03
Mixing Speed (r/min)	20000		3 wt% Aqueous	
Mixing Time (s)	7	Water	NaCl	0.95

Date	Run	Binder	Overflow	Underflow	Heavy	Total Solids	Yield	Organic Liquid Dosage
		(g)	(g)	(g)	(g)	(g)	(wt%)	(wt%)
30/03/15	1	2.0	8	7.9	72.9	88.8	9.0	0.10
30/03/15	3	9.5	24.1	5.2	75.5	104.8	23.0	0.48
30/03/15	4	8.3	18.7	5.9	66.9	91.5	20.4	0.42
7/04/15	5	6.0	11.5	7.7	72.3	91.5	12.6	0.30
7/04/15	6	3.6	9.7	6.5	80.4	96.6	10.0	0.18
7/04/15	7	10.5	22.1	2.1	83.5	107.7	20.5	0.53
7/04/15	9	10.7	25.7	5.6	80.1	111.4	23.1	0.54

APPENDIX B: Ash Analysis Data

Initial investigation into selectivity



**THE UNIVERSITY OF
NEWCASTLE**

**REPORT: 20014194
DATE: 8/8/2013**

**REPORTED TO: Jamie Dickinson
FOR: 23 ashes for Kim van
Netten**

www.alsglobal.com

Table B.1: Ash Results from ALS Global



REPORT No. 20014194
ML13095691
Page 2

Sample Details	C4426	C4427	C4428	C4429
Mass (g)	8.7	13.1	8.3	12.3
Ash %	8.1	86.0	8.1	86.7

All results reported to air dried basis

Sample Details	C4430	C4431	C4432	C4433
Mass (g)	2.8	17.9	6.0	15.2
Ash %	8.2	65.5	7.8	76.1

All results reported to air dried basis

Sample Details	C4434	C4435	C4436	C4437
Mass (g)	7.6	13.0	8.0	10.2
Ash %	8.0	83.8	8.1	86.1

All results reported to air dried basis

Sample Details	C4438	C4439	C4440	C4441
Mass (g)	7.4	11.0	7.5	11.0
Ash %	7.8	83.8	7.6	85.7

All results reported to air dried basis

Sample Details	C4442	C4443	C4444	C4445
Mass (g)	7.3	11.6	5.7	15.2
Ash %	8.0	85.3	7.4	76.0

All results reported to air dried basis

Sample Details	C4446	C4447	C4448
Mass (g)	7.4	13.1	19.5
Ash %	7.7	84.1	57.5

All results reported to air dried basis

Table B.2: Raw data for the investigation into selectivity for the emulsion binder and a pure diesel binder.

ASH NO.		ASH (%)				MASS				CALCULATED - TWO PROD. FORMULA
PRO D.*	REJ.	PROD.	REJ.	BINDER	DOSAGE	PROD.	REJ.	YIELD	FEED ASH	COMBUSTIBLE RECOVERY
(%)	(%)	(%)	(%)	-	(wt%)	(g)	(g)	(wt%)	(%)	(%)
4448		57.5		-	-	-	-	-	-	-
4438	4439	7.8	83.8	DIESEL	9.9	7	14.7	32.3	57.5	75.07
4440	4441	7.6	85.7	DIESEL	13.6	7.7	15.3	33.5	57.5	78.50
4442	4443	8.0	85.3	DIESEL	17.1	7.7	14.5	34.7	57.5	77.85
4444	4445	7.4	76.0	DIESEL	7.9	5.8	15.2	27.6	57.5	58.76
4446	4447	7.7	84.1	DIESEL	14.0	7	13	35.0	57.5	75.61
4426	4427	8.1	86.0	EMULSION	6.0	7.2	12.9	35.8	57.5	79.11
4428	4429	8.1	86.7	EMULSION	7.4	7.2	12.0	37.5	57.5	80.33
4432	4433	7.8	76.1	EMULSION	4.5	5.3	14.9	26.4	57.5	59.08
4434	4435	8.0	83.8	EMULSION	5.3	7.3	17.1	35.7	57.5	75.11
4436	4437	8.1	86.1	EMULSION	6.3	7.6	14.2	34.9	57.5	79.29
4430	4431	8.2	65.5	EMULSION	2.9	2.4	7.8	11.9	57.5	30.16

*REJ. = Reject, PROD. = Product

Calculation of Combustible Recovery

The two product formula was used to calculate the combustible recovery, *i.e.* the recovery of the carbonaceous, valuable material. The two product formula is derived from a mass balance around a two component system which, in this case, consists of coal and mineral matter. Generally the two-product formula calculates the recovery of the valuable component based on assays of that material in each stream. However, as the assay values presented in table above are relative to the unwanted, mineral matter component, the formula was slightly modified to account for this.

$$R = \frac{(100-a_p)(a_R - a_F)}{(100-a_F)(a_R - a_p)} \times 100\%$$

Subsequent investigation into selectivity

This sections presents the raw data for the investigation into selectivity presented in Chapter 8.

Table B.3: Ash Results from ALS Global

ACIRL Quality Testing Services Pty

Ltd (ABN 66 003 451 876)



2 Spit Island Close, Mayfield West NSW 2304 Phone : (02) 4014 2600 Fax: (02) 4014 2699

Origin: Newcastle Institute for Energy and Resources.
University of Newcastle

Description: samples received for Prep and /or Ash

Report To: Kim van Netten

Sample ID	ASH (%ad)
C5390	61.4
C5391	7.1
C5392	83.0
C5393	5.9
C5394	76.7
C5395	6.4
C5396	82.8
C5397	6.4
C5398	83.1
C5403	11.0
C5404	72.8
C5405	12.5
C5406	72.8
C5413	10.2
C5414	78.7
C5415	11.5
C5416	80.6
C5417	10.6
C5418	77.4

Table B.4: Raw data for the investigation into selectivity for the emulsion binder and a pure kerosene binder.

ASH NO.		ASH (%)				MASS				*CALCULATED TWO PROD. FORMULA
PROD.*	REJ.	PROD.	REJ.	BINDER	DOSAGE	PROD.	REJ.	YIELD	FEED ASH	COMBUSTIBLE RECOVERY
(%)	(%)	(%)	(%)	-	(wt%)	(g)	(g)	(wt%)	(%)	(%)
c5390		61.4		-						
c5391	c5392	7.1	83	KEROSENE	9.89	8.3	20	29.3	61.4	68.49
c5393	c5394	5.9	76.7	KEROSENE	6.87	5.3	20.6	20.5	61.4	52.68
c5395	c5396	6.4	82.8	KEROSENE	14.83	7	19.2	26.7	61.4	67.92
c5397	c5398	6.4	83.1	KEROSENE	11.39	8.3	20.5	28.8	61.4	68.60
c5403	c5404	11	72.8	EMULSION	1.07	5.7	26.4	17.8	61.4	42.53
c5405	c5406	12.5	72.8	EMULSION	1.23	5.4	22.1	19.6	61.4	42.86
c5413	c5414	10.2	78.7	EMULSION	2.08	7.6	21.3	26.3	61.4	58.75
c5415	c5416	11.5	80.6	EMULSION	2.29	8.4	20.6	29.0	61.4	63.71
c5417	c5418	10.6	77.4	EMULSION	1.90	7.6	24.3	23.8	61.4	55.47

*REJ. = Reject, PROD. = Product

APPENDIX C: Hydrophobic Feed Characterisation

The mineral matter within a feed is generally not collected by hydrophobic binders and thus does not form part of product agglomerates. Therefore, during the investigation into the functionality of the binder within an agglomerate (Chapter 7) it became necessary to characterise the feed in terms of only the recoverable, and thus hydrophobic, particles. This section outlines the method by which this characterisation was achieved.

Experimental Methodology

In order to define the Sauter mean diameter, and thus the specific hydrophobic surface area of the coal feeds, a sample of each was agglomerated using pure kerosene. In each case, an aqueous sample of the feed was dispersed using the Waring blender at 22 000 rpm. Pure kerosene was then added at a dosage which would result in the maximum yield. This dosage was established for each coal via a series of experiments which investigated the influence of dosage on yield. The agitation was continued for 120 s. The agglomerated product was then dried in an oven (110 °C) to constant mass such that all of the kerosene binder had evaporated. As a result the product coal was no longer agglomerated and thus the size distribution was representative of the hydrophobic particles in the feed.

The size distribution of the product coal was then analysed using laser diffraction in the Mastersizer 3000. To ensure complete submersion of the coal into the dispersion medium (water), the particles were initially wet in a small volume of 0.025 wt% Dri-Decon solution (Decon Laboratories Ltd, 2012). Dri-Decon is a surfactant and was used to facilitate the wetting of the dry coal. The small coal slurry was then added to 800 ml of tap water and analysed.

Size Distribution Results

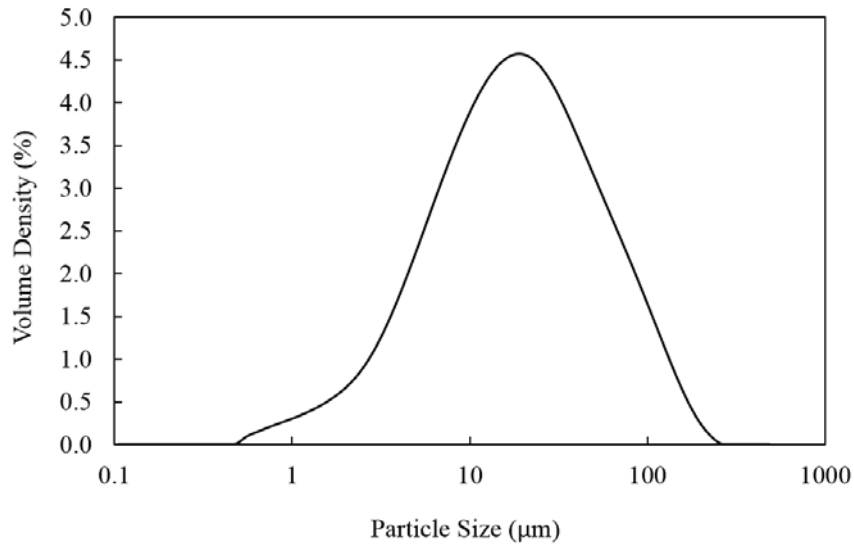


Figure C.1: Size distribution of coal 1

Table C.1: Size distribution data of coal 1

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.11	0.0	0.93	0.3	8.14	3.4	71.31	2.4
0.12	0.0	1.06	0.3	9.25	3.7	81.02	2.1
0.14	0.0	1.20	0.4	10.51	4.0	92.05	1.8
0.16	0.0	1.36	0.4	11.94	4.2	104.58	1.5
0.18	0.0	1.55	0.5	13.56	4.4	118.82	1.2
0.20	0.0	1.76	0.6	15.41	4.5	135.00	1.0
0.23	0.0	2.00	0.7	17.51	4.6	153.38	0.7
0.26	0.0	2.27	0.8	19.89	4.6	174.27	0.4
0.29	0.0	2.58	0.9	22.60	4.5	197.99	0.2
0.33	0.0	2.93	1.1	25.68	4.4	224.95	0.1
0.38	0.0	3.33	1.3	29.18	4.2	255.58	0.0
0.43	0.0	3.78	1.6	33.15	4.0	290.39	0.0
0.49	0.0	4.30	1.9	37.66	3.7	329.93	0.0
0.56	0.1	4.89	2.2	42.79	3.5	374.85	0.0
0.63	0.1	5.55	2.5	48.62	3.2	425.89	0.0
0.72	0.2	6.31	2.8	55.24	2.9	483.88	0.0
0.82	0.2	7.16	3.1	62.76	2.7		

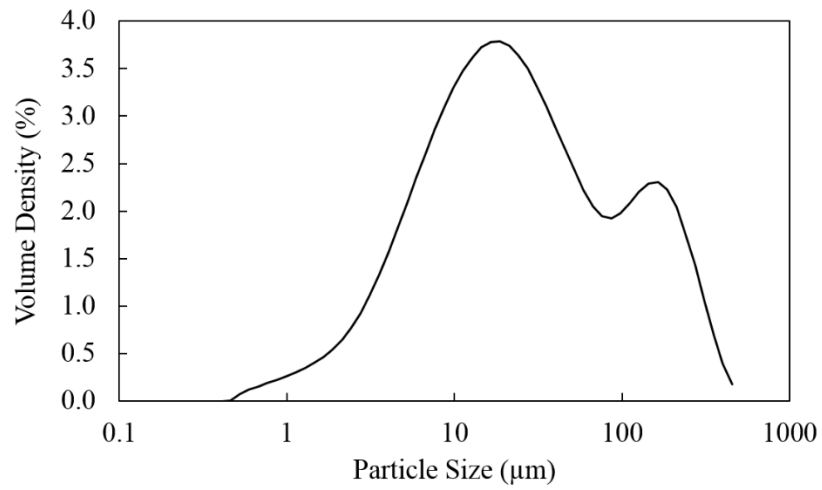


Figure C.2: Size distribution of coal 2

Table C.2: Size distribution data of coal 2

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.11	0.0	0.93	0.2	8.14	2.9	71.31	2.0
0.12	0.0	1.06	0.3	9.25	3.1	81.02	1.9
0.14	0.0	1.20	0.3	10.51	3.3	92.05	1.9
0.16	0.0	1.36	0.3	11.94	3.5	104.58	2.0
0.18	0.0	1.55	0.4	13.56	3.6	118.82	2.1
0.20	0.0	1.76	0.5	15.41	3.7	135.00	2.2
0.23	0.0	2.00	0.5	17.51	3.8	153.38	2.3
0.26	0.0	2.27	0.6	19.89	3.8	174.27	2.3
0.29	0.0	2.58	0.8	22.60	3.7	197.99	2.2
0.33	0.0	2.93	0.9	25.68	3.6	224.95	2.0
0.38	0.0	3.33	1.1	29.18	3.5	255.58	1.8
0.43	0.0	3.78	1.3	33.15	3.3	290.39	1.4
0.49	0.0	4.30	1.6	37.66	3.1	329.93	1.1
0.56	0.1	4.89	1.8	42.79	2.9	374.85	0.7
0.63	0.1	5.55	2.1	48.62	2.7	425.89	0.4
0.72	0.2	6.31	2.4	55.24	2.4	483.88	0.2
0.82	0.2	7.16	2.6	62.76	2.2		

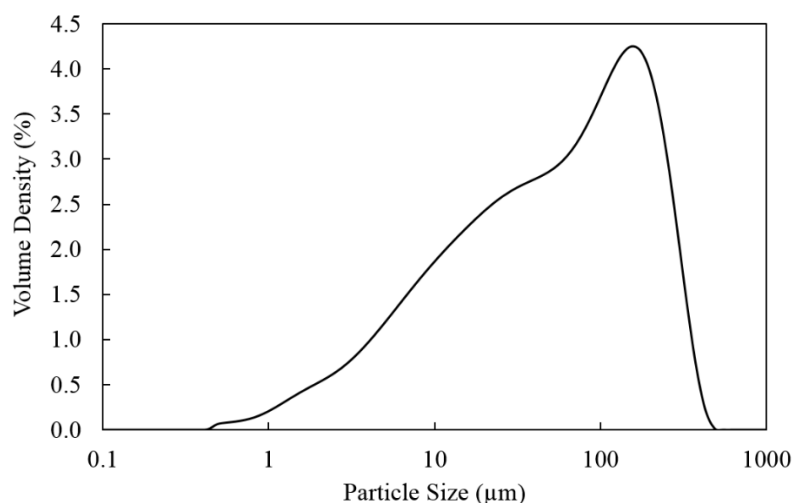


Figure C.3: Size distribution of coal 3

Table C.3: Size distribution data of coal 3

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.01	0.0	0.26	0.0	6.31	1.4	153.38	4.3
0.01	0.0	0.29	0.0	7.16	1.5	174.27	4.2
0.01	0.0	0.33	0.0	8.14	1.7	197.99	4.0
0.02	0.0	0.38	0.0	9.25	1.8	224.95	3.6
0.02	0.0	0.43	0.0	10.51	1.9	255.58	2.9
0.02	0.0	0.49	0.1	11.94	2.0	290.39	2.2
0.02	0.0	0.56	0.1	13.56	2.1	329.93	1.4
0.03	0.0	0.63	0.1	15.41	2.2	374.85	0.7
0.03	0.0	0.72	0.1	17.51	2.3	425.89	0.2
0.03	0.0	0.82	0.1	19.89	2.4	483.88	0.0
0.04	0.0	0.93	0.2	22.60	2.5	549.77	0.0
0.04	0.0	1.06	0.2	25.68	2.6	624.62	0.0
0.05	0.0	1.20	0.3	29.18	2.7	709.68	0.0
0.06	0.0	1.36	0.4	33.15	2.7	806.31	0.0
0.06	0.0	1.55	0.4	37.66	2.8	916.10	0.0
0.07	0.0	1.76	0.5	42.79	2.8	1040.83	0.0
0.08	0.0	2.00	0.5	48.62	2.9	1182.56	0.0
0.09	0.0	2.27	0.6	55.24	2.9	1343.58	0.0
0.11	0.0	2.58	0.6	62.76	3.0	1526.52	0.0
0.12	0.0	2.93	0.7	71.31	3.2	1734.38	0.0
0.14	0.0	3.33	0.8	81.02	3.3	1970.54	0.0
0.16	0.0	3.78	0.9	92.05	3.6	2238.85	0.0
0.18	0.0	4.30	1.0	104.58	3.8	2543.70	0.0
0.20	0.0	4.89	1.2	118.82	4.0	2890.06	0.0
0.23	0.0	5.55	1.3	135.00	4.2	3283.58	0.0

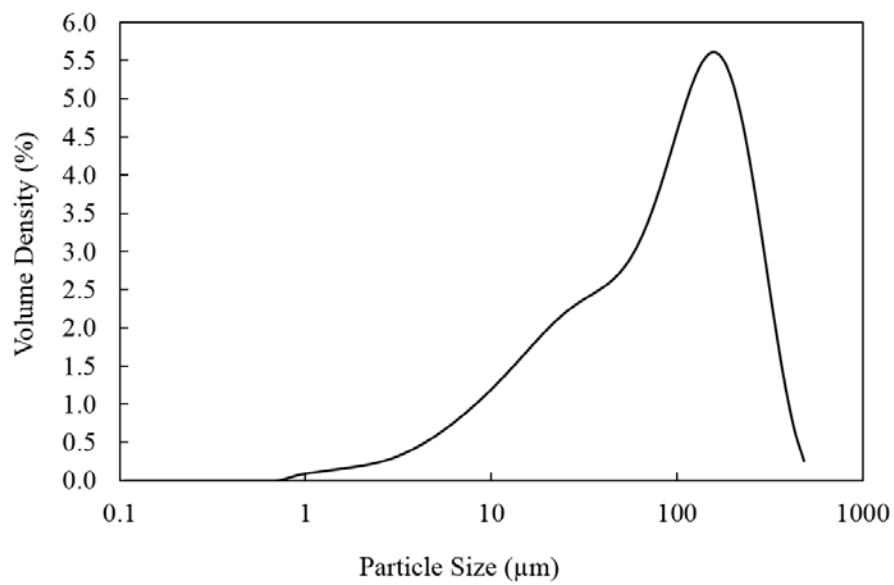


Figure C.4: Size distribution of coal 4

Table C.4: Size distribution data of coal 4

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.11	0.0	0.93	0.1	8.14	1.0	71.31	3.4
0.12	0.0	1.06	0.1	9.25	1.1	81.02	3.8
0.14	0.0	1.20	0.1	10.51	1.2	92.05	4.3
0.16	0.0	1.36	0.1	11.94	1.4	104.58	4.7
0.18	0.0	1.55	0.2	13.56	1.5	118.82	5.1
0.20	0.0	1.76	0.2	15.41	1.7	135.00	5.5
0.23	0.0	2.00	0.2	17.51	1.8	153.38	5.6
0.26	0.0	2.27	0.2	19.89	2.0	174.27	5.5
0.29	0.0	2.58	0.3	22.60	2.1	197.99	5.2
0.33	0.0	2.93	0.3	25.68	2.2	224.95	4.7
0.38	0.0	3.33	0.3	29.18	2.3	255.58	4.0
0.43	0.0	3.78	0.4	33.15	2.4	290.39	3.1
0.49	0.0	4.30	0.5	37.66	2.5	329.93	2.2
0.56	0.0	4.89	0.6	42.79	2.6	374.85	1.4
0.63	0.0	5.55	0.7	48.62	2.7	425.89	0.7
0.72	0.0	6.31	0.8	55.24	2.9	483.88	0.3
0.82	0.0	7.16	0.9	62.76	3.1		

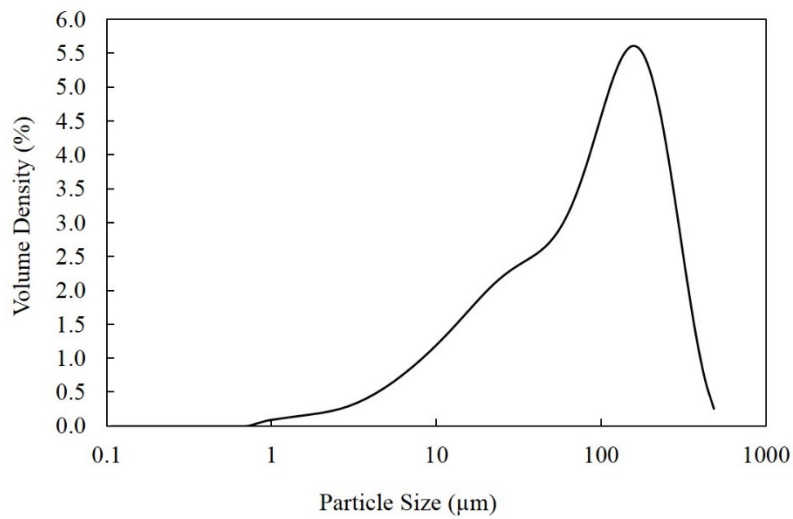


Figure C.5: Size distribution of coal 5

Table C.5: Size distribution data of coal 5

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.01	0.0	0.26	0.0	6.31	1.2	153.38	4.7
0.01	0.0	0.29	0.0	7.16	1.4	174.27	4.5
0.01	0.0	0.33	0.0	8.14	1.5	197.99	4.1
0.02	0.0	0.38	0.0	9.25	1.7	224.95	3.4
0.02	0.0	0.43	0.0	10.51	1.9	255.58	2.6
0.02	0.0	0.49	0.0	11.94	2.0	290.39	1.6
0.02	0.0	0.56	0.0	13.56	2.2	329.93	0.8
0.03	0.0	0.63	0.0	15.41	2.4	374.85	0.1
0.03	0.0	0.72	0.1	17.51	2.6	425.89	0.0
0.03	0.0	0.82	0.1	19.89	2.7	483.88	0.0
0.04	0.0	0.93	0.1	22.60	2.9	549.77	0.0
0.04	0.0	1.06	0.2	25.68	3.0	624.62	0.0
0.05	0.0	1.20	0.2	29.18	3.0	709.68	0.0
0.06	0.0	1.36	0.2	33.15	3.0	806.31	0.0
0.06	0.0	1.55	0.3	37.66	3.0	916.10	0.0
0.07	0.0	1.76	0.3	42.79	3.0	1040.83	0.0
0.08	0.0	2.00	0.3	48.62	3.0	1182.56	0.0
0.09	0.0	2.27	0.4	55.24	3.1	1343.58	0.0
0.11	0.0	2.58	0.5	62.76	3.1	1526.52	0.0
0.12	0.0	2.93	0.5	71.31	3.3	1734.38	0.0
0.14	0.0	3.33	0.6	81.02	3.5	1970.54	0.0
0.16	0.0	3.78	0.7	92.05	3.8	2238.85	0.0
0.18	0.0	4.30	0.8	104.58	4.1	2543.70	0.0
0.20	0.0	4.89	1.0	118.82	4.4	2890.06	0.0
0.23	0.0	5.55	1.1	135.00	4.6	3283.58	0.0

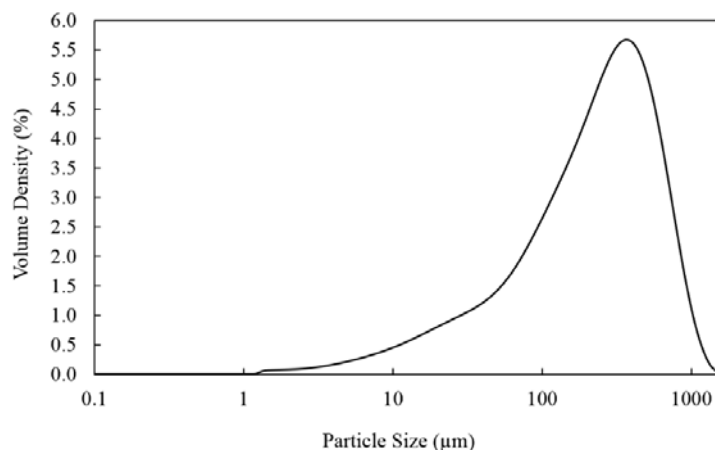


Figure C.6: Size distribution of coal 6

Table C.6: Size distribution data of coal 6

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.01	0.0	0.26	0.0	6.31	0.3	153.38	3.6
0.01	0.0	0.29	0.0	7.16	0.3	174.27	4.0
0.01	0.0	0.33	0.0	8.14	0.4	197.99	4.3
0.02	0.0	0.38	0.0	9.25	0.4	224.95	4.7
0.02	0.0	0.43	0.0	10.51	0.5	255.58	5.1
0.02	0.0	0.49	0.0	11.94	0.5	290.39	5.4
0.02	0.0	0.56	0.0	13.56	0.6	329.93	5.6
0.03	0.0	0.63	0.0	15.41	0.7	374.85	5.7
0.03	0.0	0.72	0.0	17.51	0.7	425.89	5.6
0.03	0.0	0.82	0.0	19.89	0.8	483.88	5.2
0.04	0.0	0.93	0.0	22.60	0.9	549.77	4.7
0.04	0.0	1.06	0.0	25.68	0.9	624.62	4.0
0.05	0.0	1.20	0.0	29.18	1.0	709.68	3.2
0.06	0.0	1.36	0.1	33.15	1.1	806.31	2.4
0.06	0.0	1.55	0.1	37.66	1.2	916.10	1.6
0.07	0.0	1.76	0.1	42.79	1.3	1040.83	0.9
0.08	0.0	2.00	0.1	48.62	1.4	1182.56	0.4
0.09	0.0	2.27	0.1	55.24	1.5	1343.58	0.1
0.11	0.0	2.58	0.1	62.76	1.7	1526.52	0.0
0.12	0.0	2.93	0.1	71.31	1.9	1734.38	0.0
0.14	0.0	3.33	0.1	81.02	2.2	1970.54	0.0
0.16	0.0	3.78	0.2	92.05	2.5	2238.85	0.0
0.18	0.0	4.30	0.2	104.58	2.7	2543.70	0.0
0.20	0.0	4.89	0.2	118.82	3.0	2890.06	0.0
0.23	0.0	5.55	0.2	135.00	3.3	3283.58	0.0

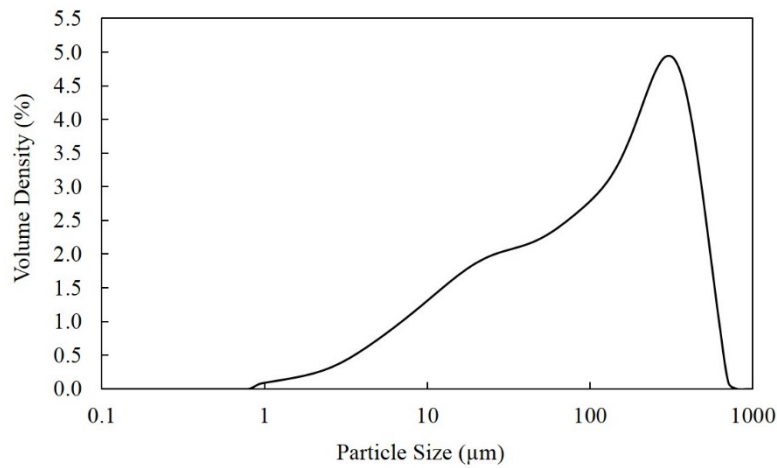


Figure C.7: Size distribution of coal 7

Table C.7: Size distribution data of coal 7

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.01	0.0	0.26	0.0	6.31	0.9	153.38	3.4
0.01	0.0	0.29	0.0	7.16	1.0	174.27	3.7
0.01	0.0	0.33	0.0	8.14	1.1	197.99	4.0
0.02	0.0	0.38	0.0	9.25	1.2	224.95	4.4
0.02	0.0	0.43	0.0	10.51	1.4	255.58	4.7
0.02	0.0	0.49	0.0	11.94	1.5	290.39	4.9
0.02	0.0	0.56	0.0	13.56	1.6	329.93	4.9
0.03	0.0	0.63	0.0	15.41	1.7	374.85	4.6
0.03	0.0	0.72	0.0	17.51	1.8	425.89	3.9
0.03	0.0	0.82	0.0	19.89	1.9	483.88	3.0
0.04	0.0	0.93	0.1	22.60	1.9	549.77	2.0
0.04	0.0	1.06	0.1	25.68	2.0	624.62	1.0
0.05	0.0	1.20	0.1	29.18	2.0	709.68	0.1
0.06	0.0	1.36	0.1	33.15	2.1	806.31	0.0
0.06	0.0	1.55	0.2	37.66	2.1	916.10	0.0
0.07	0.0	1.76	0.2	42.79	2.2	1040.83	0.0
0.08	0.0	2.00	0.2	48.62	2.2	1182.56	0.0
0.09	0.0	2.27	0.3	55.24	2.3	1343.58	0.0
0.11	0.0	2.58	0.3	62.76	2.4	1526.52	0.0
0.12	0.0	2.93	0.4	71.31	2.5	1734.38	0.0
0.14	0.0	3.33	0.5	81.02	2.6	1970.54	0.0
0.16	0.0	3.78	0.5	92.05	2.7	2238.85	0.0
0.18	0.0	4.30	0.6	104.58	2.8	2543.70	0.0
0.20	0.0	4.89	0.7	118.82	3.0	2890.06	0.0
0.23	0.0	5.55	0.8	135.00	3.2	3283.58	0.0

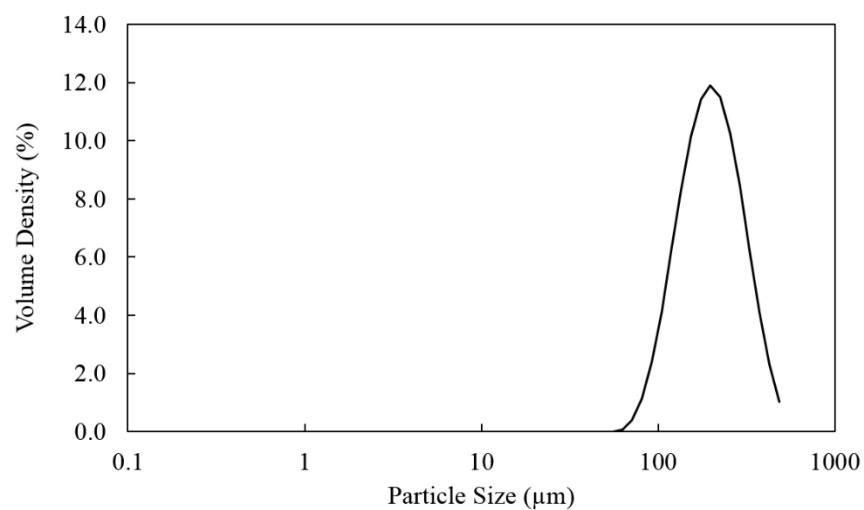


Figure C.8: Size distribution of coal 8

Table C.8: Size distribution data of coal 8

Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)	Size (μm)	Volume Density (%)
0.11	0.0	1.06	0.0	10.51	0.0	104.58	4.1
0.12	0.0	1.20	0.0	11.94	0.0	118.82	6.2
0.14	0.0	1.36	0.0	13.56	0.0	135.00	8.3
0.16	0.0	1.55	0.0	15.41	0.0	153.38	10.1
0.18	0.0	1.76	0.0	17.51	0.0	174.27	11.4
0.20	0.0	2.00	0.0	19.89	0.0	197.99	11.9
0.23	0.0	2.27	0.0	22.60	0.0	224.95	11.5
0.26	0.0	2.58	0.0	25.68	0.0	255.58	10.3
0.29	0.0	2.93	0.0	29.18	0.0	290.39	8.4
0.33	0.0	3.33	0.0	33.15	0.0	329.93	6.3
0.38	0.0	3.78	0.0	37.66	0.0	374.85	4.1
0.43	0.0	4.30	0.0	42.79	0.0	425.89	2.3
0.49	0.0	4.89	0.0	48.62	0.0	483.88	1.0
0.56	0.0	5.55	0.0	55.24	0.0		
0.63	0.0	6.31	0.0	62.76	0.1		
0.72	0.0	7.16	0.0	71.31	0.4		
0.82	0.0	8.14	0.0	81.02	1.1		
0.93	0.0	9.25	0.0	92.05	2.4		

Calculation of the Sauter Mean Diameter

Equation C.1 defines the Sauter mean diameter, d_{32} (m), as a function of the scalar variable, f_i and the discrete particle size, d_i (m).

$$d_{32} = \frac{1}{\sum \frac{f_i}{d_i}} \quad (C.1)$$

Therefore, when the volume distribution of the feed particles is known Equation C.1 becomes

$$d_{32} = \frac{1}{\sum \frac{V_i}{d_i}} \quad (C.2)$$

Where V_i is the volume fraction of the particles of size d_i .

Following on, a sample calculation for the d_{32} of is presented using the data for coal 8.

$$\begin{aligned} \sum \frac{V_i}{d_i} &= \frac{0.001}{62.7} + \frac{0.004}{71.3} + \frac{0.011}{81.0} + \frac{0.024}{92.0} + \frac{0.041}{104.6} + \frac{0.062}{118.8} + \frac{0.083}{135.0} + \frac{0.101}{153.4} + \frac{0.114}{174.3} \\ &\quad + \frac{0.119}{198.0} + \frac{0.115}{225.0} + \frac{0.103}{255.6} + \frac{0.084}{290.4} + \frac{0.063}{329.9} + \frac{0.041}{374.9} + \frac{0.023}{425.9} + \frac{0.010}{483.9} \\ \sum \frac{V_i}{d_i} &= 0.00549 \end{aligned}$$

Therefore,

$$\begin{aligned} d_{32} &= \frac{1}{0.00549} \\ d_{32} &= 182 \mu m \end{aligned}$$

Calculation of the Specific Surface Area

The specific surface area of the particles can then be calculated using the volume, V (m³), and surface area, A_s (m²), of a single particle with diameter, d_{32} ,

$$SA = \frac{A_s}{V} \quad (C.3)$$

Then by assuming spherical particles, the specific surface area of the particles can be directly related to the Sauter mean diameter of the particles using,

$$SA = \frac{6}{d_{32}} \quad (C.4)$$

Of course, in the context of coal and mineral mixtures, the particles are unlikely to be spherical. However, only a relative measure between the different feeds was required and thus Equation C.4 was considered sufficient.

A sample calculation of the specific surface area is presented below using the d_{32} calculated for coal 8 above,

$$SA = \frac{6}{182 \times 10^{-6}}$$

$$SA = 32\,967 \frac{m^2}{m^3}$$

Sauter Mean and Specific Surface Area of Coal Feeds

Using the data above and Equations C.2 and C.4 the Sauter mean and specific surface areas of each coal feed was calculated as per the sample calculation provided. The final values are presented below in Table C.9.

Table C.9: Sauter mean diameter and specific surface area of coal feeds 1 – 8.

Feed	d_{32} (μm)	Specific Surface Area $\text{m}^2 / \text{m}^3_{\text{coal}}$
1	9.1	660928
2	10.9	551188
3	13.9	430725
4	26.4	227212
5	17.6	340909
6	63.5	94429
7	25.4	236220
8	182.0	32967

APPENDIX D: Binder Functionality Data

Eight different coals were examined to investigate the influence of the specific surface area of the feed on the dosage required to achieve agglomeration. The Sauter mean diameter of the feed samples was presented in Appendix C. This chapter presents the results of the investigation into the dosage required for each feed to achieve agglomeration.

As discussed in Section 7.4 of Chapter 7 the dosage required to achieve agglomeration was the point at the commencement of the plateau in the yield-dosage curve. Therefore, a standardised analysis was developed to determine this point for the kerosene binder and the emulsion binder for each coal. Interestingly, a different method was required for each binder. In the case of the emulsion, it was found that the best fit for the data was a positive gradient straight line commencing from the origin to the point at which the maximum yield was achieved, followed by a horizontal line at maximum yield. Figure D.1 presents an example plot for the emulsion binder with the analysis method applied.

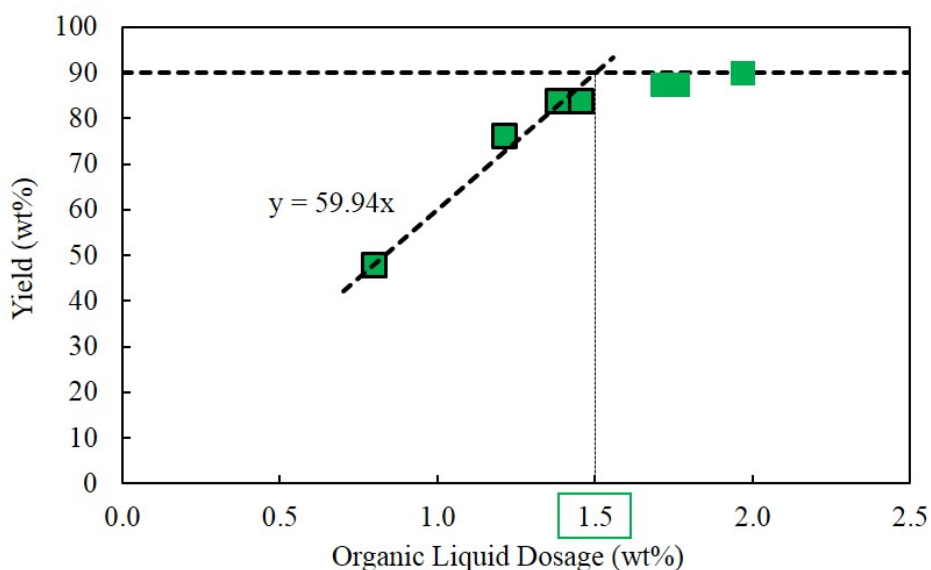


Figure D.1: Yield as a function of organic liquid dosage example plot for the emulsion binder with the curve fit analysis applied

As can be seen a straight line has been fitted to the data prior to the commencement of the plateau in yield. The data points included in the curve fit have been outlined in bold. A straight, horizontal line has also been fitted to the data to indicate the maximum yield recoverable from this feed. In this case the maximum yield is 90 wt% as the feed had an

ash content of 10%. The dosage required to achieve agglomeration was then considered to be the point at which the positive gradient straight line from the origin intersected the horizontal maximum yield line. In this example, the dosage was $90/59.94 = 1.5$ wt%. As can be seen in this figure, this dosage is effectively at the commencement of the plateau and thus after the significant increases in yield which occur at lower binder levels.

As mentioned above, in the case of the kerosene binder it was found that the best fit for the data was different from the emulsion. It was found that the best fit was first order reaction type curve which related the yield, Y (wt%), with the dosage, D (wt%), in the following manner,

$$Y = Y_{max}(1 - e^{-kD})$$

where Y_{max} is the maximum yield for a given feed and k is a first order coefficient which is also feed dependent. Figure D.2 presents an example plot for the kerosene binder with the analysis method applied. In this example the maximum yield was 44 wt% and $k = 0.23$.

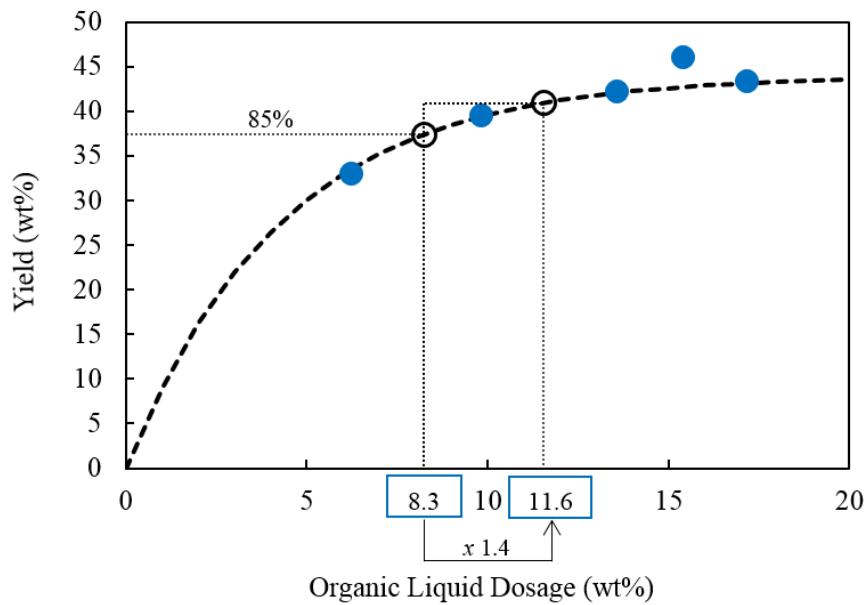


Figure D.2: Yield as a function of organic liquid dosage example plot for the kerosene binder with the curve fit analysis applied. The two open circles indicate the points along the curve which the analysis was based around.

As can be seen in the figure, the first order curve provides a good fit. Construction lines can also be seen on the figure which indicate the method by which the dosage required to

achieve agglomeration, *i.e.* the dosage at the start of the plateau was calculated. As indicated by the construction lines, the dosage at 85% of the maximum yield was determined which was, in this case, 8.3 wt%. This value was then multiplied by 1.4 to provide the dosage at the start of the plateau which was 11.6 wt%. The two points on the curve which were used in the analysis method are indicated by the open circles in Figure D.2. The open circle on the right hand side, which indicates the dosage required to achieve agglomeration can be seen to sit after the main changes in curvature of the data but prior to the levelling out of the data.

Emulsion Binder Data and Analysis

Coal 1

Yield as a function of dosage is presented in Figure D.3 with the curve fit analysis applied. Table D.1 presents the raw data.

Table D.1: Summary of results for the emulsion binder for coal 1

Organic Liquid Dosage (wt%)	Yield (wt%)
1.3	15.7
1.9	23.8
2.1	26.3
2.3	29.0
2.4	26.5

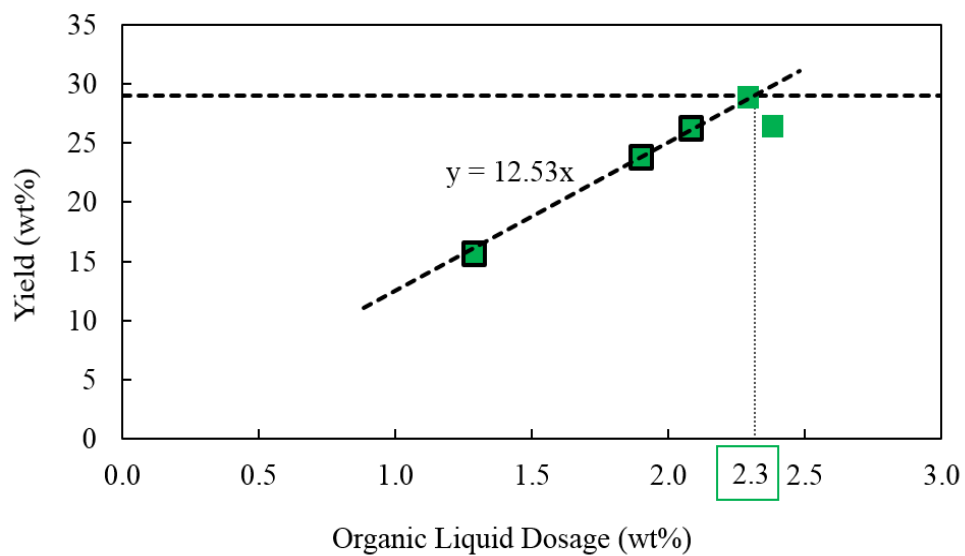


Figure D.3: Yield as a function of organic liquid dosage for coal 1 with the curve fit analysis applied

As shown in Figure D.3, the point of intersection corresponds to a dosage of 2.3 wt%. Now, it should be noted that this value accounts for the total mass of the feed but the binder only acts on the hydrophobic coal. Therefore, a more representative and universal value to present for this coal is the dosage relative to the mass of dry coal only. As 29% of this feed was recoverable via agglomeration and screening, this was considered to be the proportion of coal in the feed which responds to the hydrophobic binder. Therefore, the minimum dosage to reach complete agglomeration for coal 1 using the emulsion binder is $0.023/0.29 = 0.080 \text{ kg}_{\text{organic liquid}}/\text{kg}_{\text{coal}}$.

Coal 2

Yield as a function of dosage is presented in Figure D.4 with the curve fit analysis applied. Table D.2 presents the raw data.

Table D.2: Summary of results for the emulsion binder for coal 2

Organic Liquid Dosage (wt%)	Yield (wt%)
2.0	29.0
2.2	31.6
2.1	32.0
1.9	28.2

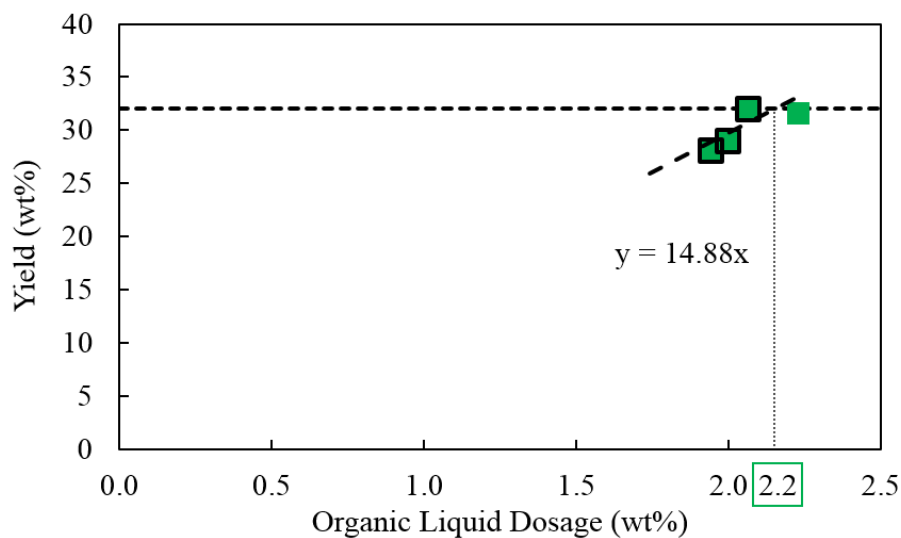


Figure D.4: Yield as a function of organic liquid dosage for coal 2 with the curve fit analysis applied

As shown in Figure D.4, the point of intersection corresponds to a dosage of 2.15 wt%. As 32% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.0215/0.32 = 0.067$ kg_{organic liquid}/kg_{coal}

Coal 3

Yield as a function of dosage is presented in Figure D.5 with the curve fit analysis applied. Table D.3 presents the raw data.

Table D.3: Summary of results for the emulsion binder for coal 3

Organic Liquid Dosage (wt%)	Yield (wt%)
3.4	61.0
4.7	77.7
1.9	34.4
3.0	50.0
4.0	73.8

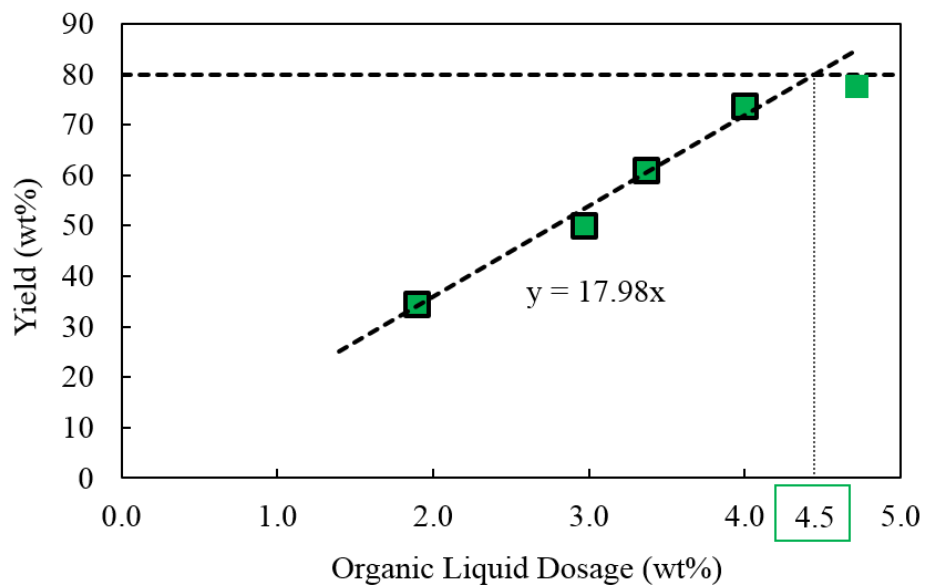


Figure D.5: Yield as a function of organic liquid dosage for coal 3 with the curve fit analysis applied

As shown in Figure D.5, the point of intersection corresponds to a dosage of 4.45 wt%. As 80% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.0445/0.8 = 0.056$ kg_{organic liquid}/kg_{coal}

Coal 4

Yield as a function of dosage is presented in Figure D.6 with the curve fit analysis applied. Table D.4 presents the raw data. The data for coal 4 was also presented above in the example analysis.

Table D.4: Summary of results for the emulsion binder for coal 4

Organic Liquid Dosage (wt%)	Yield (wt%)
0.8	47.8
1.2	76.2
1.5	83.8
1.4	83.8
1.8	87.5
1.7	87.6
2.0	90.1

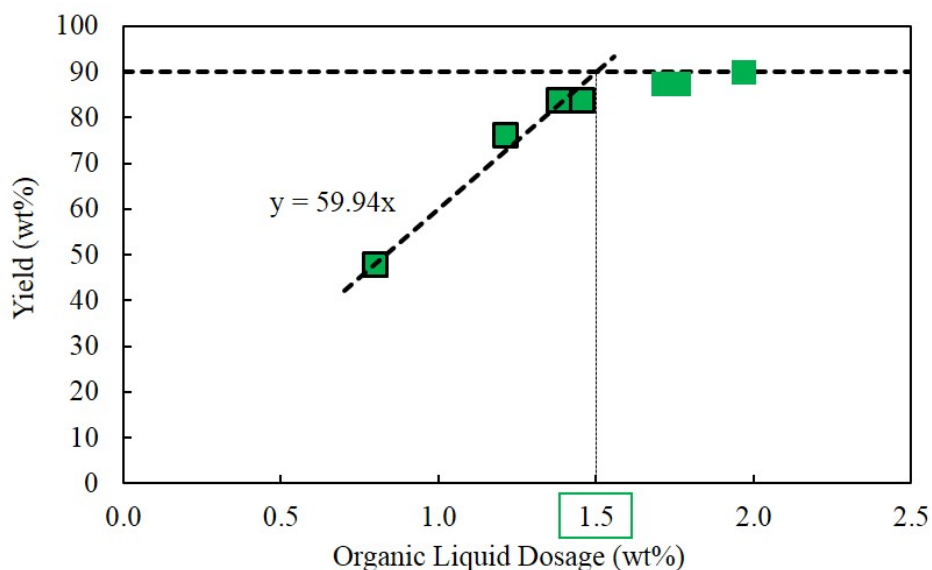


Figure D.6: Yield as a function of organic liquid dosage for coal 4 with the curve fit analysis applied

As shown in Figure D.6, the point of intersection corresponds to a dosage of 1.50 wt%. As 90% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.015/0.9 = 0.017$ kg_{organic liquid}/kg_{coal}

Coal 5

Yield as a function of dosage is presented in Figure D.7 with the curve fit analysis applied. Table D.5 presents the raw data.

Table D.5: Summary of results for the emulsion binder for coal 5

Organic Liquid Dosage (wt%)	Yield (wt%)
2.24	46.2
1.71	32.4
1.30	22.4
1.13	19.3
2.40	45.5
1.41	24.8

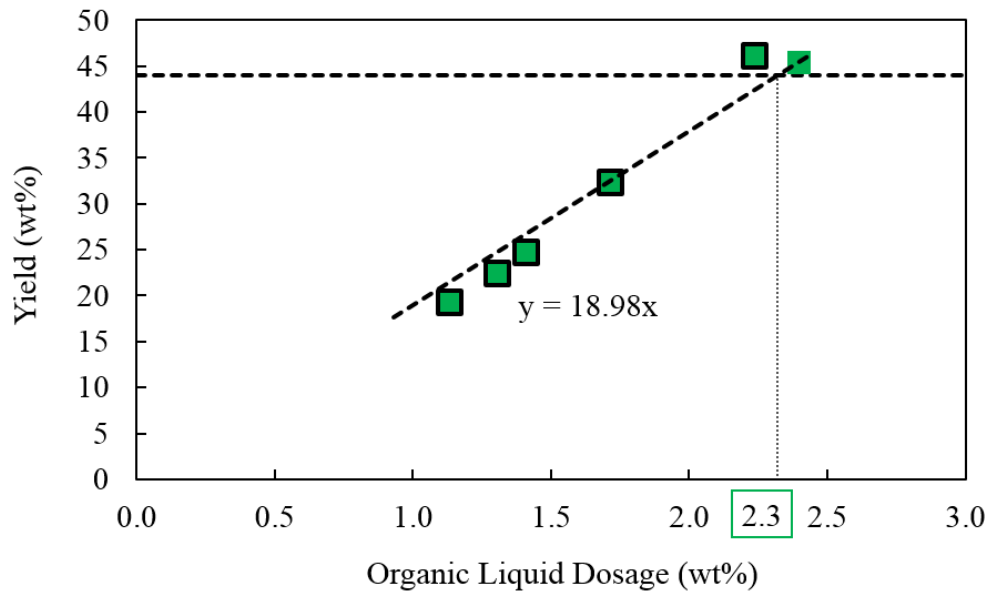


Figure D.7: Yield as a function of organic liquid dosage for coal 5 with the curve fit analysis applied

As shown in Figure D.7, the point of intersection corresponds to a dosage of 2.32 wt%. As 44% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.0232/0.44 = 0.053$ kg_{organic liquid}/kg_{coal}

Coal 6

Yield as a function of dosage is presented in Figure D.8 with the curve fit analysis applied. Table D.6 presents the raw data.

Table D.6: Summary of results for the emulsion binder for coal 6

Organic Liquid Dosage (wt%)	Yield (wt%)
0.10	9.0
0.48	23.0
0.42	20.4
0.30	12.6
0.18	10.0
0.53	20.5
0.54	23.1

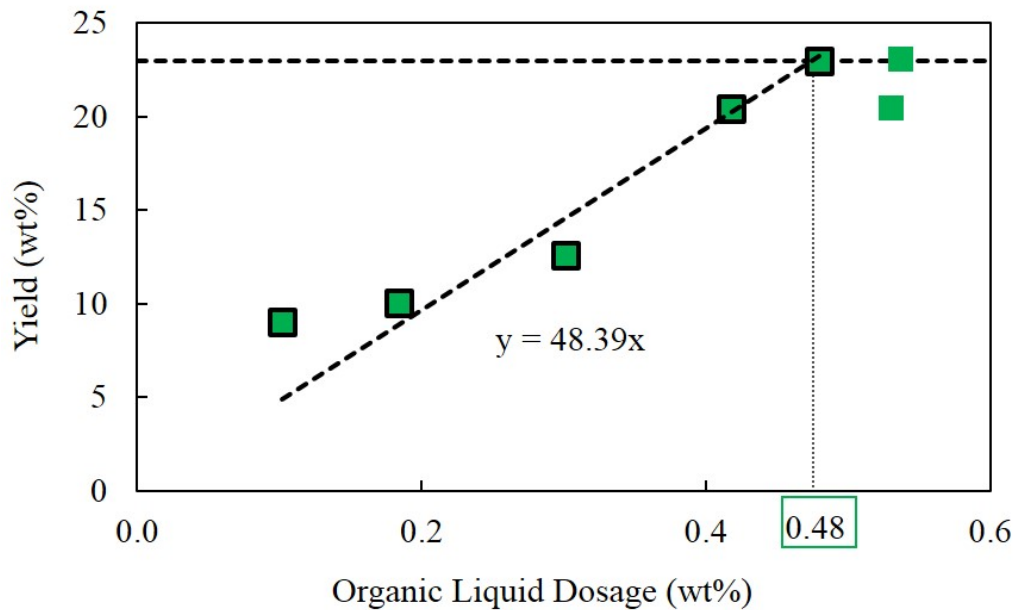


Figure D.8: Yield as a function of organic liquid dosage for coal 6 with the curve fit analysis applied

As shown in Figure D.8, the point of intersection corresponds to a dosage of 0.48 wt%. As 23% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.0048/0.23 = 0.021$ kg_{organic liquid}/kg_{coal}

Coal 7

Yield as a function of dosage is presented in Figure D.9 with the curve fit analysis applied. Table D.7 presents the raw data.

Table D.7: Summary of results for the emulsion binder for coal 7

Organic Liquid Dosage (wt%)	Yield (wt%)
0.77	45.9
0.58	31.3
0.40	18.7
1.15	53.1
1.49	54.6

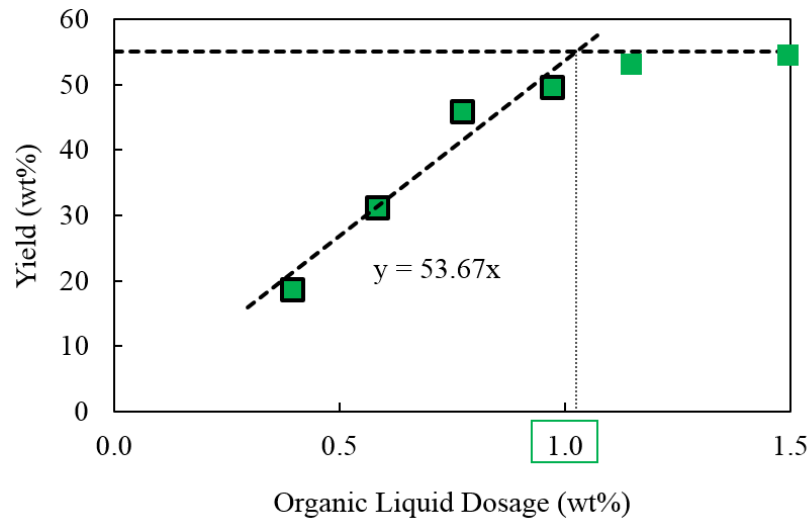


Figure D.9: Yield as a function of organic liquid dosage for coal 7 with the curve fit analysis applied

As shown in Figure D.9, the point of intersection corresponds to a dosage of 1.02 wt%. As 55% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.0102/0.55 = 0.019$ kg_{organic liquid}/kg_{coal}

Coal 8

Yield as a function of dosage is presented in Figure D.10 with the curve fit analysis applied. Table D.8 presents the raw data.

Table D.8: Summary of results for the emulsion binder for coal 8

Organic Liquid Dosage (wt%)	Yield (wt%)
0.96	96.3
0.91	94.3
0.78	84.3

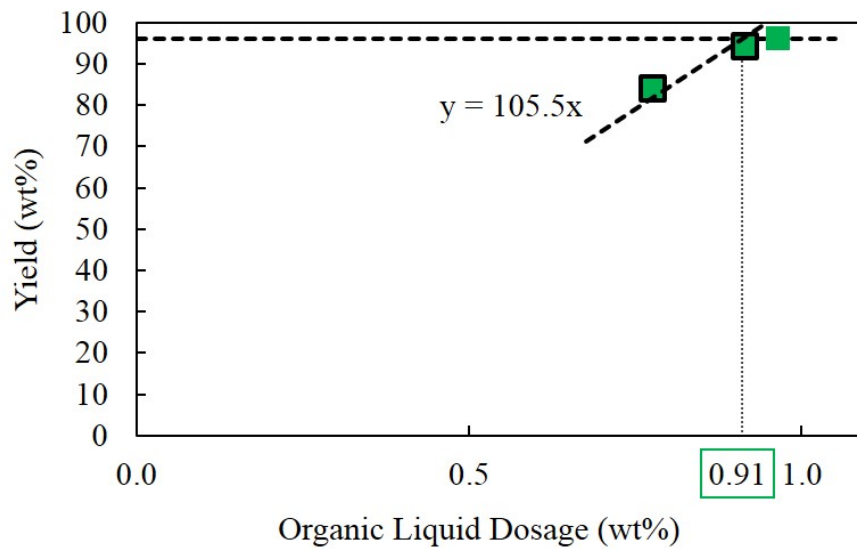


Figure D.10: Yield as a function of organic liquid dosage for coal 8 with the curve fit analysis applied

As shown in Figure D.10, the point of intersection corresponds to a dosage of 0.91 wt%. As 96% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.0091/0.96 = 0.009$ kg_{organic liquid}/kg_{coal}

Pure Kerosene Binder Data and Analysis

Coal 1

Yield as a function of dosage is presented in Figure D.11 with the curve fit analysis applied. The maximum yield is 29 wt% and $k = 0.27$. Table D.9 presents the raw data.

Table D.9: Summary of results for the kerosene binder for coal 1

Organic Liquid Dosage (wt%)	Yield (wt%)
9.9	29.3
6.9	20.5
11.4	28.8
14.8	27.6

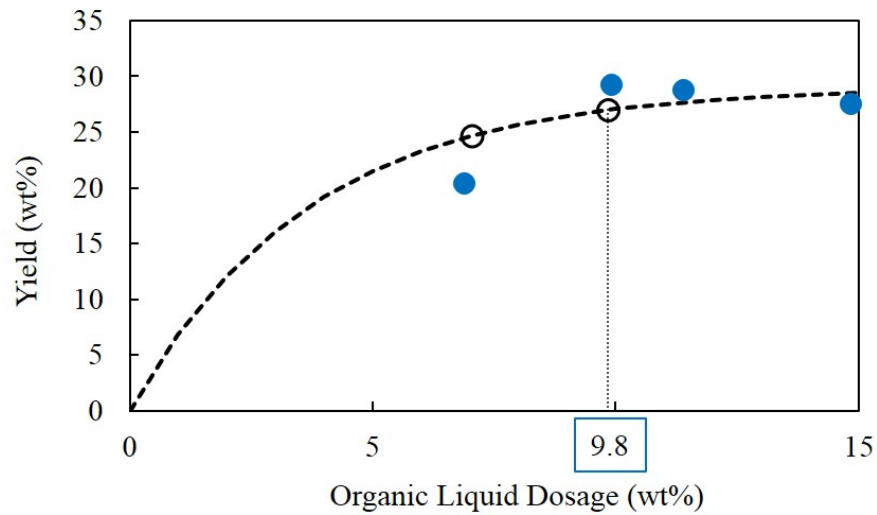


Figure D.11: Yield as a function of organic liquid dosage for coal 1 with the curve fit analysis applied. The maximum yield is 29 wt% and $k = 0.27$.

As shown in Figure D.11, the second construction point corresponds to a dosage of 9.8 wt%. As 29% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.098/0.29 = 0.34$ kg_{organic liquid}/kg_{coal}

Coal 2

Yield as a function of dosage is presented in Figure D.12 with the curve fit analysis applied. The maximum yield is 32 wt% and $k = 0.27$. Table D.10 presents the raw data.

Table D.10: Summary of results for the kerosene binder for coal 2

Organic Liquid Dosage (wt%)	Yield (wt%)
15.9	32.6
10.7	32.4
6.4	22.5

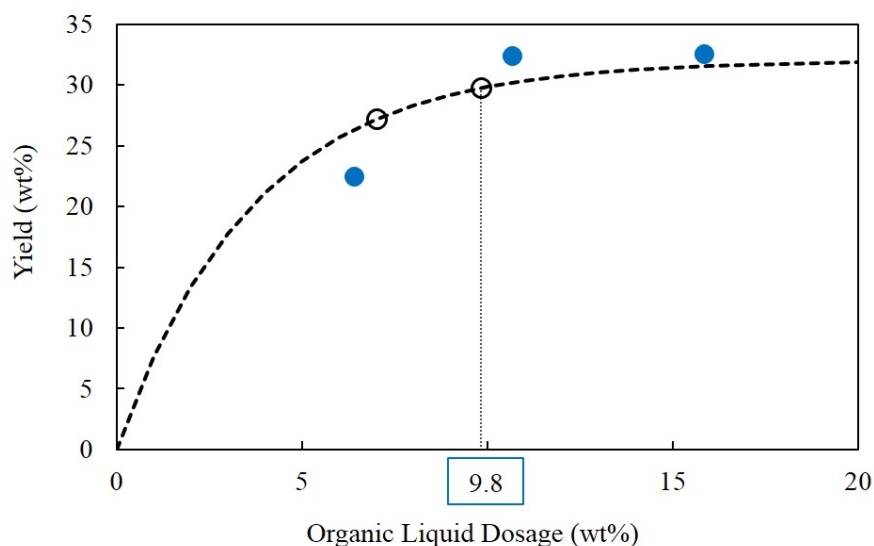


Figure D.12: Yield as a function of organic liquid dosage for coal 2 with the curve fit analysis applied. The maximum yield is 32 wt% and $k = 0.27$.

As shown in Figure D.12, the second construction point corresponds to a dosage of 9.8 wt%. As 32% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.098/0.32 = 0.31$ kg_{organic liquid}/kg_{coal}

Coal 3

Yield as a function of dosage is presented in Figure D.13 with the curve fit analysis applied. The maximum yield is 80 wt% and $k = 0.18$. Table D.11 presents the raw data.

Table D.11: Summary of results for the kerosene binder for coal 3

Organic Liquid Dosage (wt%)	Yield (wt%)
28.3	79.1
24.4	82.0
19.5	79.5
14.3	74.2

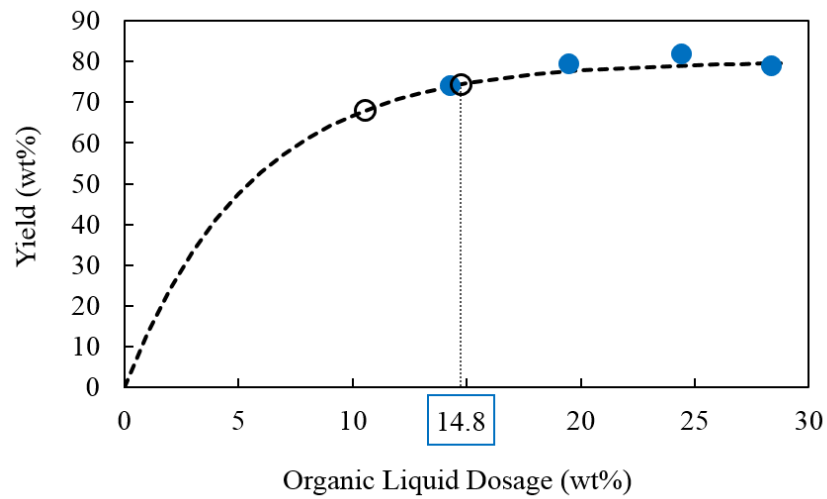


Figure D.13: Yield as a function of organic liquid dosage for coal 3 with the curve fit analysis applied. The maximum yield is 80 wt% and $k = 0.18$

As shown in Figure D.13, the second construction point corresponds to a dosage of 14.8 wt%. As 80% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.148/0.80 = 0.18$ kg_{organic liquid}/kg_{coal}

Coal 4

Yield as a function of dosage is presented in Figure D.14 with the curve fit analysis applied. The maximum yield is 90 wt% and $k = 0.16$. Table D.12 presents the raw data.

Table D.12: Summary of results for the kerosene binder for coal 4

Organic Liquid Dosage (wt%)	Yield (wt%)
13.1	81.5
17.2	85.6
10.7	69.8
8.5	70.1
20.1	89.9

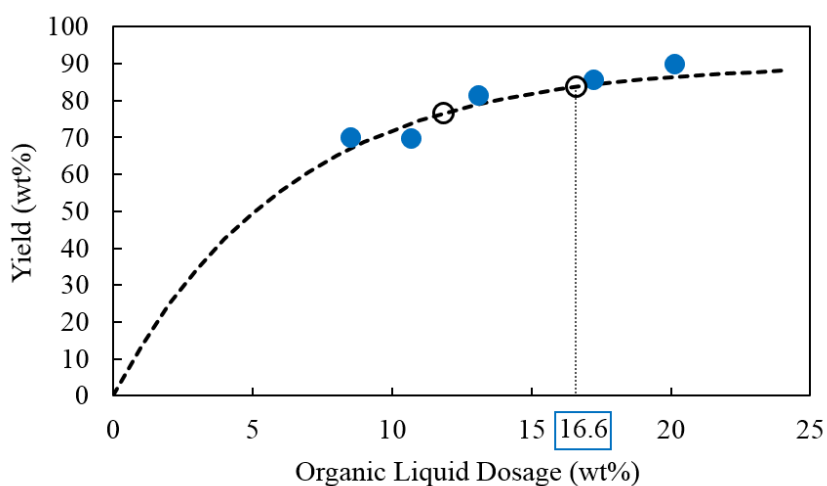


Figure D.14: Yield as a function of organic liquid dosage for coal 4 with the curve fit analysis applied. The maximum yield is 90 wt% and $k = 0.16$

As shown in Figure D.14, the second construction point corresponds to a dosage of 16.6 wt%. As 80% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.166/0.90 = 0.18$ kg_{organic liquid}/kg_{coal}

Coal 5

Yield as a function of dosage is presented in Figure D.15 with the curve fit analysis applied. The maximum yield is 80 wt% and $k = 0.18$. Table D.13 presents the raw data. The data for coal 5 was also presented above in the example analysis.

Table D.13: Summary of results for the kerosene binder for coal 5

Organic Liquid Dosage (wt%)	Yield (wt%)
13.55	42.3
9.80	39.6
6.23	33.1
15.40	46.2
17.16	43.4

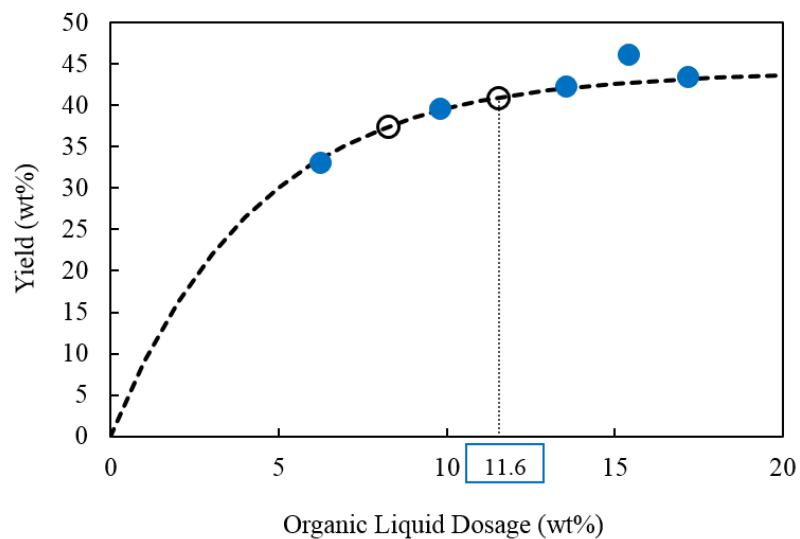


Figure D.15: Yield as a function of organic liquid dosage for coal 5 with the curve fit analysis applied. The maximum yield is 44 wt% and $k = 0.23$

As shown in Figure D.15, the second construction point corresponds to a dosage of 11.6 wt%. As 44% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.116/0.44 = 0.26$ kg_{organic liquid}/kg_{coal}

Coal 6

Yield as a function of dosage is presented in Figure D.16 with the curve fit analysis applied. The maximum yield is 17 wt% and $k = 0.9$. Table D.14 presents the raw data.

Table D.14: Summary of results for the kerosene binder for coal 6

Organic Liquid Dosage (wt%)	Yield (wt%)
4.4	16.6
2.9	17.1
1.5	13.9
0.9	4.1

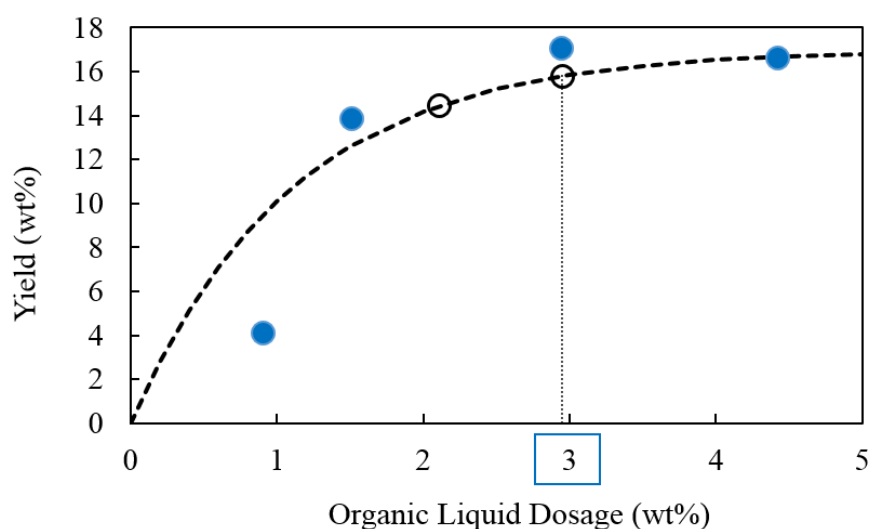


Figure D.16: Yield as a function of organic liquid dosage for coal 6 with the curve fit analysis applied. The maximum yield is 17 wt%¹ and $k = 0.9$

As shown in Figure D.16, the second construction point corresponds to a dosage of 3.0 wt%. As 23% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.03/0.23 = 0.13$ kg_{organic liquid}/kg_{coal}

¹It may be noted that the maximum yield for the kerosene binder is lower than that for the emulsion binder. This occurred because in this feed the agglomerates were recovered via scooping from the top of the suspension and then placing them on a screen for washing and desliming. This technique was used due to the presence of coarse mineral matter which could also be retained if the entire agglomerated suspension was poured over the screen. Therefore, the lower yield does not indicate that the particles were not agglomerated, rather they did not have sufficient buoyancy to float to the surface.

Coal 7

Note: This coal was not tested using the kerosene binder

Coal 8

Yield as a function of dosage is presented in Figure D.17 with the curve fit analysis applied. The maximum yield is 96 wt% and $k = 0.45$. Table D.15 presents the raw data.

Table D.15: Summary of results for the kerosene binder for coal 8

Organic Liquid Dosage (wt%)	Yield (wt%)
3.2	75.5
8.5	95.7
5.2	86.0
7.0	88.5

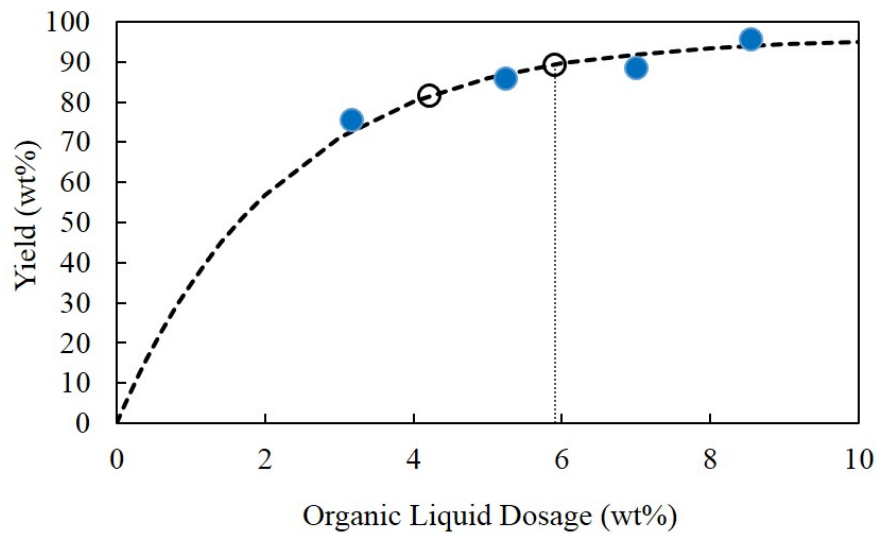


Figure D.17: Yield as a function of organic liquid dosage for coal 8 with the curve fit analysis applied. The maximum yield is 96 wt% and $k = 0.45$

As shown in Figure D.17, the second construction point corresponds to a dosage of 5.9 wt%. As 96% of this feed was recoverable via agglomeration the minimum dosage to reach complete agglomeration for the binder on a dry coal only basis is $0.059/0.44 = 0.061$ kg_{organic liquid}/kg_{coal}

Table D.16 presents a summary of the results presented in this appendix. The dosage values have also been calculated on a volumetric basis to be consistent with Equation 7.1. The density of coal was assumed to be 1350 kg/m³.

Table D.16: Summary of results for the investigation into the influence of specific surface area on the dosage required to achieve agglomeration.

Coal	SA m ² / m ³ _{coal}	Kerosene		Emulsion	
		Dosage (kg _{organic} liquid/kg _{coal})	Dosage (m ³ _{organic} liquid/m ³ _{coal})	Dosage (kg _{organic} liquid/kg _{coal})	Dosage (m ³ _{organic} liquid/m ³ _{coal})
1	660928	0.34	0.57	0.080	0.121
2	551188	0.31	0.51	0.067	0.102
3	430725	0.18	0.31	0.056	0.084
4	227212	0.18	0.31	0.017	0.025
5	340909	0.13	0.44	0.053	0.080
6	94429	0.13	0.21	0.021	0.031
7	236220	-	-	0.019	0.028
8	32967	0.061	0.10	0.009	0.014

APPENDIX E: Emulsion Rheology Characterisation

To consider the effect of continuous phase viscosity on the rheology of the emulsion and, in turn, the functionality of the emulsion, the relationship between the overall emulsion viscosity and the shear rate was measured and compared for the SMO/kerosene based binder and the PIB/diesel based binder. The former emulsion includes the less viscous continuous phase components studied in this work and the latter continues the more viscous continuous phase components which have been studied. The composition of the two emulsions investigated is presented in Table E.1. The methodology used for the preparation of the two emulsions is the same as that presented in the main body of this thesis in Section 6.2.2.

Table E.1: The composition of the two emulsions examined in the investigation into the rheology of the emulsion.

<i>Emulsion</i>	<i>Aqueous Phase</i>	<i>Organic Phase</i>	
	<i>3 wt% aqueous NaCl</i>	<i>Emulsifier</i>	<i>Oil</i>
<i>SMO/kerosene</i>	0.90	0.05	0.05
<i>PIB/diesel</i>	0.90	0.05	0.05

As shown in Table E.1 the volume fractions of each phase were kept constant and the only variation between the two emulsions was the constituents of the organic phase.

The viscosity measurements were carried out with AR-G2 rheometer (TA instruments) using a plate and cone geometry. In each case the temperature was held constant at 25 °C. Figure E.1 presents the viscosity of the emulsion as a function of the shear rate.

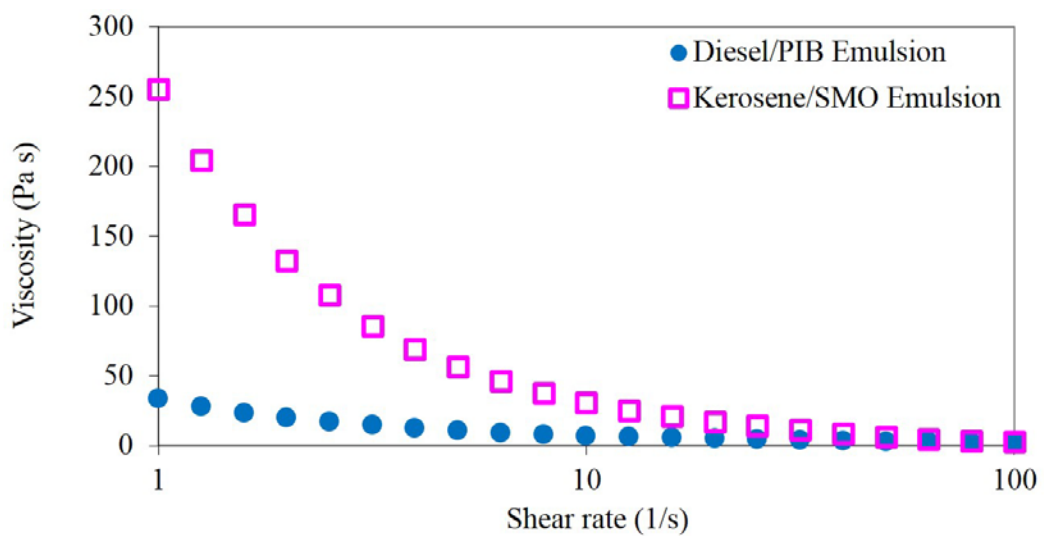


Figure E.1: Viscosity as a function of shear rate for the diesel/PIB based emulsion and the kerosene/SMO based emulsion.

In general, Figure E.1 shows that high internal phase emulsions are non-Newtonian fluids as the viscosity changes as a function of the shear applied. Furthermore, by comparing the two data-sets in Figure E.1 it can be seen that the viscosity of the SMO/kerosene based emulsion is higher than that of the PIB/diesel based emulsion. This difference is especially significant at low shear rates. Therefore, these results indicate that an emulsion with a reduced continuous phase viscosity has an increased overall viscosity. Moreover, as the SMO/kerosene emulsion had the best performance in the selective agglomeration experiments, it may be concluded that emulsions with higher overall viscosities have greater functionality as a binder in the agglomeration process.

Of course, it must be acknowledged at this point that the results above are very limited. That is, the rheological behaviour of only two emulsions was studied and these were only at low shear. However, as this investigation was supplementary to the main work of this thesis and as the rheology of high internal phase emulsions is a complex area of study, these investigations were not pursued further. In the future it would be highly beneficial to carry out a more detailed investigation into the rheology of the emulsion binder and compare it to its functionality as a binder in agglomeration. Moreover, as part of this work it would be valuable to consider the behaviour of a complex non-Newtonian fluid such as the HIP emulsion in a high shear, three phase system.