Results of the simulations of the section 5.2

Simulated samples of an exponential distribution with mean $\mathrm{E}(S) = \dfrac{A}{(\phi_C - \phi)^\gamma}$ and variance $\mathrm{var}(S) = \left(\dfrac{A}{(\phi_C - \phi)^\gamma}\right)^2$ have been generated using the values estimated by Janda et al. (2008) as values of the parameters, $\theta^{(0)} = (\ 12.7,\ 1.1 \times 10^{11},\ 8.5\ )$. We have generated $N = 1000$ simulations of $n_1 = 30$ values of S for each point ϕ of the 8–point design used by the experimenters. Then 1000 simulations of $n_2 = 80$ values of S for each point ϕ of the D$-$optimal design

$$\xi_D^\star = \left\{ \begin{array}{ccc} 1.53 & 4.17 & 5.63 \\ 1/3 & 1/3 & 1/3 \end{array} \right\}. \tag{1}$$

Thus, for each simulation we have 240 observations for each of the two designs and the results will be comparable.

The LSE, $\hat{\theta}_{LSE}$, for a design supported at k points and r replications of each point minimizes the function

$$\sum_{i=1}^{k} \sum_{j=1}^{r} \left(S_{ij} - \frac{A}{(\phi_C - \phi_i)^\gamma} \right)^2,$$

where S_{ij} is the $j-$th replication generated by the exponential distribution of mean $A/(\phi_C - \phi_i)^\gamma$ and ϕ_i is the diameter of the outlet considered.

The MLE, $\hat{\theta}_{MLE}$, for a design supported at k points and r replications of each point maximizes the function

$$\prod_{j=1}^{k} \frac{(\phi_C - \phi_j)^\gamma}{A} \exp\left\{ \prod_{j=1}^{k} \left(\frac{-A}{(\phi_C - \phi_i)^\gamma} \right) \sum_{i=1}^{k} \sum_{j=1}^{r} S_{ij} \right\}.$$

To quantify the difference between LSE and MLE the Mean Squared Error (MSE), approximated with the simulations, is used,

$$MSE = \frac{1}{N} \sum_{i=1}^{N} \left(\hat{\theta}_i - \theta^{(0)} \right)^2,$$

where $\hat{\theta}_i$ is the $i-$th estimator of the vector of the unknown parameters and N the number of simulations.

In addition, the bias is also approximated by the difference between the empirical mean of the estimators and the actual value of the parameter,

$$\mathrm{Bias}(\hat{\theta}) = \theta^{(0)} - \frac{1}{N} \sum_{i=1}^{N} \hat{\theta}_i.$$

The empirical covariance matrices of the estimators of the parameters for each method and for each design are:

$$\Sigma_{LSE}^{(\xi_8)} = \begin{pmatrix} 2.133 \times 10^{19} & -4.613 \times 10^{6} & 1.003 \times 10^{8} \\ -4.613 \times 10^{6} & 0.087 & -0.081 \\ 1.003 \times 10^{8} & -0.081 & 0.084 \end{pmatrix},$$

$$\Sigma_{MLE}^{(\xi_8)} = \begin{pmatrix} 4.273 \times 10^{19} & 5.879 \times 10^{7} & 1.381 \times 10^{8} \\ 5.879 \times 10^{7} & 0.006 & -0.008 \\ 1.381 \times 10^{8} & -0.008 & 0.014 \end{pmatrix},$$

$$\Sigma_{LSE}^{(\xi_D^\star)} = \begin{pmatrix} 2.166 \times 10^{19} & -4.263 \times 10^{7} & 1.401 \times 10^{8} \\ -4.263 \times 10^{7} & 0.081 & -0.076 \\ 1.401 \times 10^{8} & -0.076 & 0.076 \end{pmatrix},$$

$$\Sigma_{MLE}^{(\xi_D^\star)} = \begin{pmatrix} 4.161 \times 10^{19} & 5.917 \times 10^{7} & 1.257 \times 10^{8} \\ 5.917 \times 10^{7} & 0.001 & -0.002 \\ 1.256 \times 10^{8} & -0.002 & 0.007 \end{pmatrix},$$

and their determinants are

$$\begin{aligned} |\Sigma_{LSE}^{(\xi_8)}| &= 1521 \times 10^{13}, \\ |\Sigma_{MLE}^{(\xi_8)}| &= 36.21 \times 10^{13}, \\ |\Sigma_{LSE}^{(\xi_D^\star)}| &= 592.8 \times 10^{13}, \\ |\Sigma_{MLE}^{(\xi_D^\star)}| &= 9.695 \times 10^{13}. \end{aligned}$$