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1 **Stabilization time modeling for hydroprocessing:**
2 **identification of the dominant factors**

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18 **Abstract**

19 Hydroprocessing stabilization has been assessed using experimental data acquired at transient
20 conditions. These data were obtained from a hydrotreating pilot plant in a wide range of
21 operating conditions. It has been found that the stabilization evolution follows a first-order
22 response and could be characterized by a stabilization time τ . A linear model was developed to
23 relate τ to its most influential parameters. The model can then be combined with online transient
24 data to predict the steady-state performance. By testing against new data with other feedstocks,
25 the model has been found to provide a good prediction of the stabilization evolution and the
26 ultimate steady-state hydrotreating performance. It is, hence, possible to “online” calculate the
27 steady-state performance without the need to reach this steady state.

28 **Keywords:** hydrocarbon, hydrotreating, stabilization, transient data.

29 **1 Introduction**

30 Hydrotreating is a catalytic conversion process in petroleum refining, among others for
31 removing impurities such as nitrogen and sulfur from hydrocarbon streams. It eliminates such
32 heteroatoms in oil fractions from compounds by mixing them with hydrogen and treating this
33 mixture in a fixed bed catalytic reactor at high temperature and pressure. The catalyst used in
34 hydrotreating usually is molybdenum (group VI metal) based and promoted with cobalt or nickel
35 (group VIII metal) and supported on alumina or silica-alumina. The most common catalysts used
36 in hydrotreating are CoMo/Al₂O₃ and NiMo/Al₂O₃. CoMo favors the sulfur removal and olefin
37 saturation while NiMo is used for removing nitrogen and saturating aromatic compounds (Treese
38 et al., 2015). Hydrotreating/hydrocracking catalysts require several days before achieving stable
39 operation while the residence time in the reactor is of the order of maximum a few hours. The
40 observed transient phenomena can, hence, at most partly be attributed to hydrodynamics

41 phenomena in the equipment used and mainly to chemical phenomena occurring at the catalyst
42 level. These are distinct from and, hence, are not to be confused with the long-term catalyst
43 deactivation. There is very few literature on this subject. Sau et al. (2005) investigated the effects
44 of organic nitrogen on hydroprocessing reactions. The authors did some hydrocracking
45 experiments using a zeolite-based catalyst and determined the evolution of the conversion with
46 time. When the reactor temperature was increased from 390 to 405 °C while processing a
47 hydrotreated vacuum gas oil feed containing 320 ppmw organic nitrogen, a slow stabilization of
48 the conversion was observed. The phenomenon was explained by the slow rate of nitrogen
49 desorption from the catalyst with increasing temperature. Thanks to this nitrogen desorption, the
50 concentration of active acid sites increases and, hence does the conversion. As the nitrogen
51 desorption is slow, the observed conversion takes long time to reach the steady state as well.
52 Similarly, these authors also investigated the effect of increasing nitrogen content in the feed
53 from 5 to 125 ppmw. The observed time to reach the stabilization of conversion is also around
54 eight days and is attributed to the adsorption of nitrogen on the active sites of the catalyst.
55 According to Elizalde et al. (2016), the Liquid Hourly Space Velocities (LHSV) has an impact
56 on the dynamic behavior of hydrocracking process. LHSV is the ratio of liquid volumetric
57 flowrate and the catalyst volume. It is the inverse of the reactor space time. A lower LHSV is
58 equivalent with a higher space time, so the time to reach the steady state is longer because the
59 product concentration needs more time to reach the steady state. However, the authors reported
60 that the temperature in the range of 380-400 °C does not seem to significantly affect the dynamic
61 behavior. It means that no matter what the exact reactor temperature is, the time to reach the
62 steady state remains similar.

63 A kinetic model is a significant asset, not to say essential, for the adequate design and
64 simulation of processes, especially of large-scale operations with narrow profit margins. Since
65 crude oil contains a lot of compounds with difficult structures, kinetic modeling of
66 hydroprocessing is a challenging and time-consuming task (Jarullah et al., 2011). There are
67 various approaches for hydroprocessing modeling, such as the detailed kinetic (Schweitzer et al.,
68 1999; Oyekunle and Edafe, 2009; Charon-Revellin et al., 2011; Nguyen et al., 2015; Raghuv
69 et al., 2016; Nguyen et al., 2017; Doukeh et al., 2018), lumping modeling (Bonnardot, 1998;
70 López García et al., 2010; Lababidi and AlHumaidan, 2011; Tang et al., 2013; Becker et al.,
71 2015; Esmael et al., 2016) and black-box approach (Elkamel et al., 1999; Bahmani et al., 2010;
72 Sadighi and Reza Zahedi, 2013; Sadighi and Mohaddecy, 2018). The most common and widely
73 used is the lumping approach which consists of regrouping chemical compounds with similar
74 properties (Oliveira et al., 2016). In these approaches, the model parameters are generally
75 estimated by fitting the model to steady-state experimental data. Stabilization phenomena lead to
76 long experimentation times in order to obtain sufficient steady-state data for kinetic modeling.
77 However, in the transient regime towards this steady state, the analyses of liquid effluent are
78 already carried out at regular time intervals to verify whether the steady state has effectively
79 been reached and to ensure that the reaction is under control. These transient data are currently
80 not used for kinetic modeling because the stabilization behavior is not well understood. It leads
81 to a true challenge, meaning that experimental data acquisition to ‘calibrate’ the model is a time
82 and money consuming task.

83 The aim of this work is, first, to acquire a better understanding of the stabilization behavior
84 during these transient conditions and secondly, to use these data in order to predict, from the first
85 transient points, the steady-state performance. If this value is far from a target, the operators can

86 change the operating condition without waiting for stabilization and without the use of a complex
87 model.

88 **2 Materials and methods**

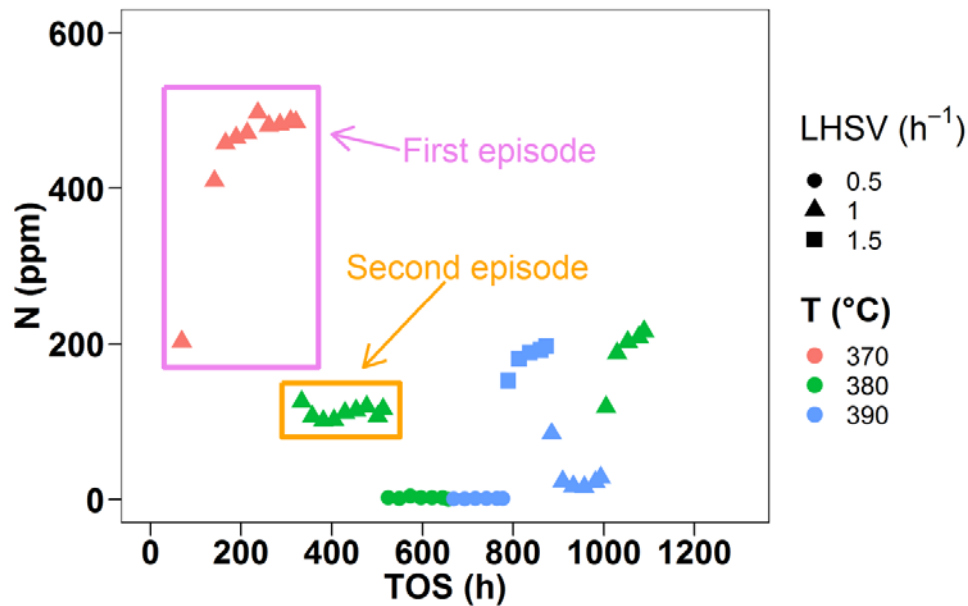
89 **2.1 Pilot plant**

90 The experimental data are acquired using a pilot plant located at IFP Energies Nouvelles,
91 Solaize, France. It consists of four parallel fixed beds, operated in down-flow mode, which are
92 used for hydrotreatment of feeds varying from gas oil to vacuum gas oil. The total catalyst
93 volume in each reactor amounts to 50 cm³. The pilot plant operates at isothermal conditions with
94 the temperature being controlled along the reactor. Once the unit is in continuous operation, the
95 density, nitrogen content and refractive index of the liquid effluent are analyzed every 24 hours.
96 The steady state is ensured by having observed the stabilization of these characteristics.
97 Operating conditions are adjusted after having reached the steady state corresponding with the
98 previous operating conditions.

99 **2.2 Data representation**

100 The acquired data cover 11 Vacuum Gas Oil (VGO) feeds over two similar catalysts. Liquid
101 Hourly Space Velocities (LHSV) vary between 0.5 and 4 h⁻¹, the temperature from 350 to 410 °C
102 and the total pressure between 50 and 140 bar. Performance data are measured in terms of
103 different properties of the liquid effluent such as density, refractive index and nitrogen contents
104 over time on stream, totaling 920 measurements. A series of consecutive points corresponding to
105 one experimental run is denoted as an '*episode*'. The latter characterizes the intended steady state
106 kinetic analyses rather than the systematic, c.q., repeated, analysis of transient behavior. Figure 1
107 shows 7 episodes corresponding with 42 data points acquired in about 45 days. The first from
108 these 7 episodes corresponds to the start of the test at specific operating conditions, while later

109 episodes are initiated by a change of operating conditions such as LHSV or temperature. Other
110 variables that may also change between consecutive episodes are pressure and feedstock
111 composition. It is noted that the deactivation phenomena in the pilot plant are negligible for the
112 test with duration less than 45 days.



113

114 Figure 1. Data illustration - Liquid effluent nitrogen as a function of time on stream (TOS).

115 2.3 Stabilization modeling

116 A computational study on the pilot plant has been carried out using a tracer technique to
117 estimate the stabilization time purely due to hydrodynamic phenomena. The objective is to
118 identify whether the experimentally observed stabilization time is determined by hydrodynamic
119 or chemical phenomena. The corresponding dynamic simulation of the pilot plant (without
120 chemical reaction) was carried out using Matlab & Simulink R2014b in order to follow the flow
121 of an unreactive tracer component through the pilot plant.

122 Exploratory data analysis (Tukey, 1977) (see also Figure 1) shows that the stabilization
123 phenomena follow a first-order transfer function as shown in Equation (1).

$$y_{(TOS)} = y_{init} + (y_{final} - y_{init}) \left(1 - \exp \left(\frac{-(TOS - TOS_{init})}{\tau} \right) \right) \quad (1)$$

124 Where y is the liquid effluent property at a specific time on stream (such as nitrogen content,
 125 density, refractive index); y_{init} is the liquid effluent property corresponding to the first
 126 experimental point of episode (ppm); y_{final} is the last experimental point of episode (ppm); TOS
 127 is the time on stream (h); TOS_{init} is the time on stream corresponding to y_{init} (h) and τ is the
 128 characteristic time of the episode (h). The characteristic time τ of each episode presented in the
 129 equation is estimated via nonlinear least-squares technique using Gauss-Newton algorithm
 130 (Bates and Watts, 1988).

131 The estimated characteristic time τ can logically be supposed to depend on some variables
 132 such as feed properties and operating conditions. A linear function accounting for possible
 133 interaction among the variables is defined to describe the characteristic time τ (Equation (2)).

$$\tau = a_1x_1 + a_2x_2 + a_{12}x_1x_2 + \dots + b \quad (2)$$

134 Where x_1 , x_2 are the input variables, which can be LHSV, temperature, pressure or feed
 135 properties such as organic nitrogen content, organic sulfur content, resin content in feed, etc.;
 136 x_1x_2 is the interaction term between x_1 and x_2 ; a_1 , a_2 , a_{12} ,... and b are the coefficients.

137 The most influential input variables of the model are determined via variable selection
 138 technique called 'leaps' (Furnival and Wilson, 1974). The main idea of this technique is based on
 139 an efficient branch-and-bound algorithm which was first proposed by Land and Doig (1960). It
 140 searches for all possible subset solutions and stores them in the branches of a tree with the full
 141 set at the root. The algorithm runs an exhaustive search and shows the best variable subsets. It
 142 reveals the linear dependence of stabilization on the input variables. The quality of each subset is
 143 evaluated by a metric called adjusted R^2 . In terms of statistics, higher adjusted R^2 means a better

144 quality. However, the number of variables in the model should not to be excessive. The selected
145 model is a compromise between adjusted R^2 and the number of variables in the subset.

146 The adjusted R^2 , see Equation (3), is a measure of model fitting quality taking into account the
147 number of variables. It is usually employed to compare multiple linear models.

$$\bar{R}^2 = 1 - (1 - R^2) \frac{n - 1}{n - p - 1} \quad (3)$$

148 Where R^2 is the ‘coefficient of determination’ or multiple R^2 ; n is the number of observations
149 in data sample; p is the number of predictors, c.q., variables and/or parameters, in the model.
150 Multiple R^2 is calculated via Equation (4).

$$R^2 = 1 - \frac{\sum(y_i - \hat{y}_i)^2}{\sum(y_i - \bar{y})^2} \quad (4)$$

151 Where y_i are observed values; \hat{y}_i are predicted values; \bar{y} are mean of sample.

152 **2.4 Stabilization prediction**

153 One of the properties of Equation (1) is that 95% of the value at steady state is reached after 3τ
154 and 99% of the steady-state value after 5τ . It is a characteristic of first-order function which can
155 be found in the literature (Smith and Campbell, 2016). The time required to reach steady state
156 can be estimated thanks to the τ predicted by the model.

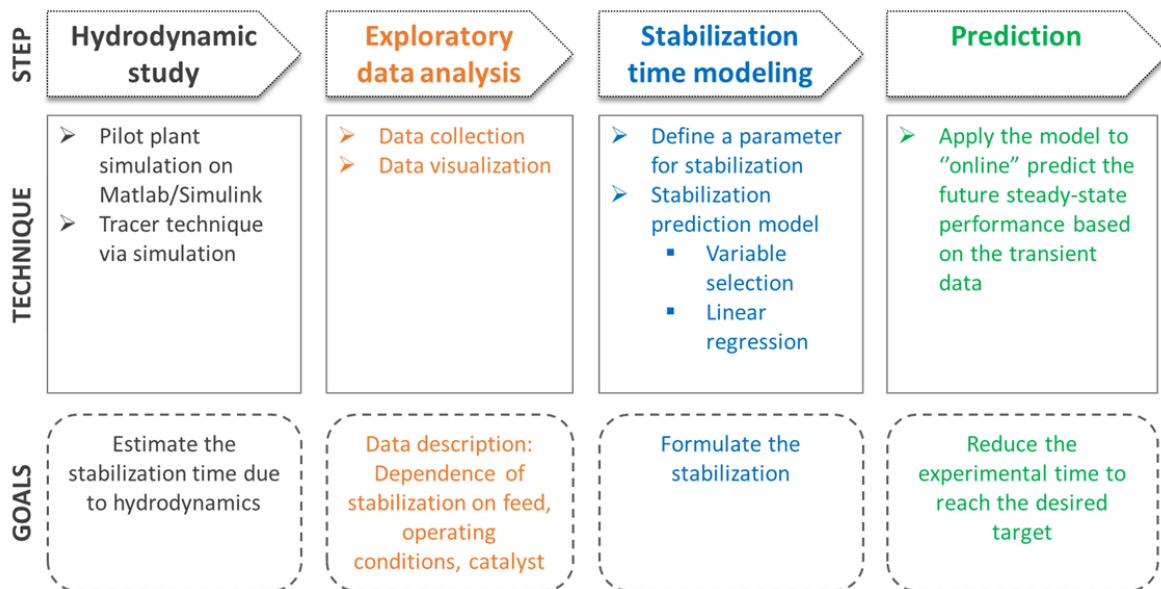
157 The model for τ can then be used for stabilization performance prediction. For each episode, τ
158 is calculated by the model. Knowing τ and the first two experimental points of the episode
159 suffices to predict the episode evolution and, ultimately, the behavior at steady state using
160 Equation (5), exemplified for the nitrogen content. If the predicted steady-state value is far from
161 the target, the operating condition can be adjusted without waiting for stabilization. The
162 prediction can be updated daily based on the new measurements.

$$N_{final} = \frac{N_2 - N_1}{1 - \exp\left(-\frac{TOS_2 - TOS_1}{\tau}\right)} + N_1 \quad (5)$$

163 Where N_{final} is the liquid product nitrogen at steady state (ppm); N_2 is the liquid product
 164 nitrogen corresponding to the second point of episode (ppm); N_1 is the liquid product nitrogen
 165 corresponding to the first point of episode (ppm); TOS_2 is the time on stream corresponding to
 166 the second point of episode (h); TOS_1 is the time on stream corresponding to the first point of
 167 episode (h) and τ is the characteristic time predicted by model (h).

168 3 Results and discussion

169 This section exhibits the results of each step in the methodology shown in Figure 2. First part
 170 represents the hydrodynamic study of the pilot plant where the experimental data were acquired.
 171 The analysis of stabilization behavior and its dependence on operating conditions, feedstock are
 172 displayed. Stabilization model is then constructed and the prediction against new data is
 173 performed.

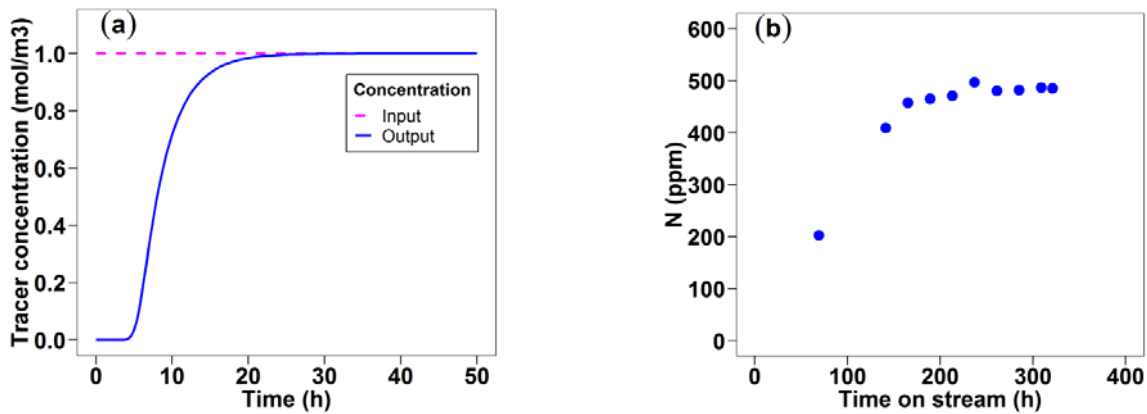


174
 175 Figure 2. Methodology adopted throughout this work.

176 **3.1 Pilot plant hydrodynamics**

177 A computational analysis of the pilot plant hydrodynamics has been carried out using Matlab
178 & Simulink via the simulation of the behavior of an unreactive tracer component running
179 through the pilot plant. The outlet concentration as a function of time provides insight into the
180 stabilization behavior purely due to hydrodynamics. The pilot plant was simulated as several
181 blocks representing each part of the pilot plant such as a heater, a reactor, a separator to remove
182 hydrogen-rich gas from liquid stream and a stripping column to remove gas dissolved in the
183 liquid stream such as H₂S, NH₃. Each element was modeled by considering it as a plug flow
184 reactor (PFR) or as a continuous stirred-tank reactor (CSTR). Pipeline, heater and reactor were
185 modeled as PFR while separator and stripping column were simulated as CSTR. Mass balance
186 was then written for each block. In the simulation, the input stream is a tracer solution with a
187 concentration set randomly at 1 mol/m³. The volumetric flowrate of the input stream was
188 simulated at 50 cm³/h, which is similar to the one in the experimental data that would be used to
189 compare. Temperature and pressure in the reactor were set at 370 °C and 140 bar respectively.
190 There was no simulation of the chemical reaction expected.

191 Figure 3 compares the transient behavior of tracer concentration in pure hydrodynamics mode
192 with the effluent properties in reactive mode. The figure on the left represents the tracer outlet
193 concentration. The figure on the right shows the transient behavior of liquid product nitrogen in
194 reactive mode. As can be seen, the hydrodynamic stabilization of the pilot plants occurs within
195 25 hours while the observed stabilization of the pilot plant in reactive mode requires around 200
196 hours. The hydrodynamic response to a tracer step reached steady state significantly faster than
197 the stabilization of the hydrodenitrogenation behavior. Hence, stabilization is mainly driven by
198 chemical phenomena.

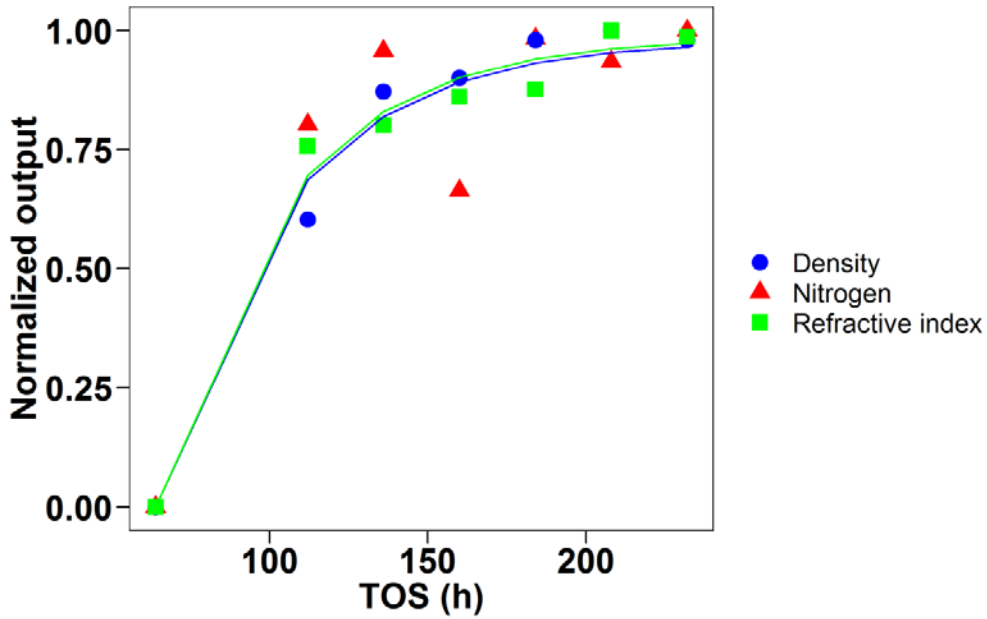


199

200 Figure 3. Calculated effluent concentration profiles of tracer (a) and experimentally observed
 201 liquid effluent nitrogen content as a function of time on stream in the pilot plant (b) (LHSV = 1
 202 h^{-1} , $T = 370\text{ }^{\circ}\text{C}$, $P = 140\text{ bar}$).

203 3.2 Exploratory data analysis

204 Stabilization was found to exhibit a first-order behavior, which is similar to the observations
 205 by Sau et al. (2005). The first-order characteristic time τ can be calculated from the evolution of
 206 effluent characteristics such as the nitrogen content, density and/or refractive index. Figure 4
 207 compares the transient behavior of these properties, normalized between $[0, 1]$, for the same
 208 experimental run. The stabilization behavior of these properties is similar and the values of τ are
 209 essentially the same. Following the evolution of stabilization by density and refractive index are
 210 more suitable than by the nitrogen content for the following reasons: (1) for episodes with low
 211 nitrogen level ($< 10\text{ ppm}$), it becomes difficult to observe the behavior in the nitrogen curve,
 212 while it remains feasible for density and refractive index; (2) density and refractive index
 213 measurements are typically more precise than for nitrogen and (3) density and refractive index
 214 measurements are easier (and less expensive) to carry out than nitrogen measurements.

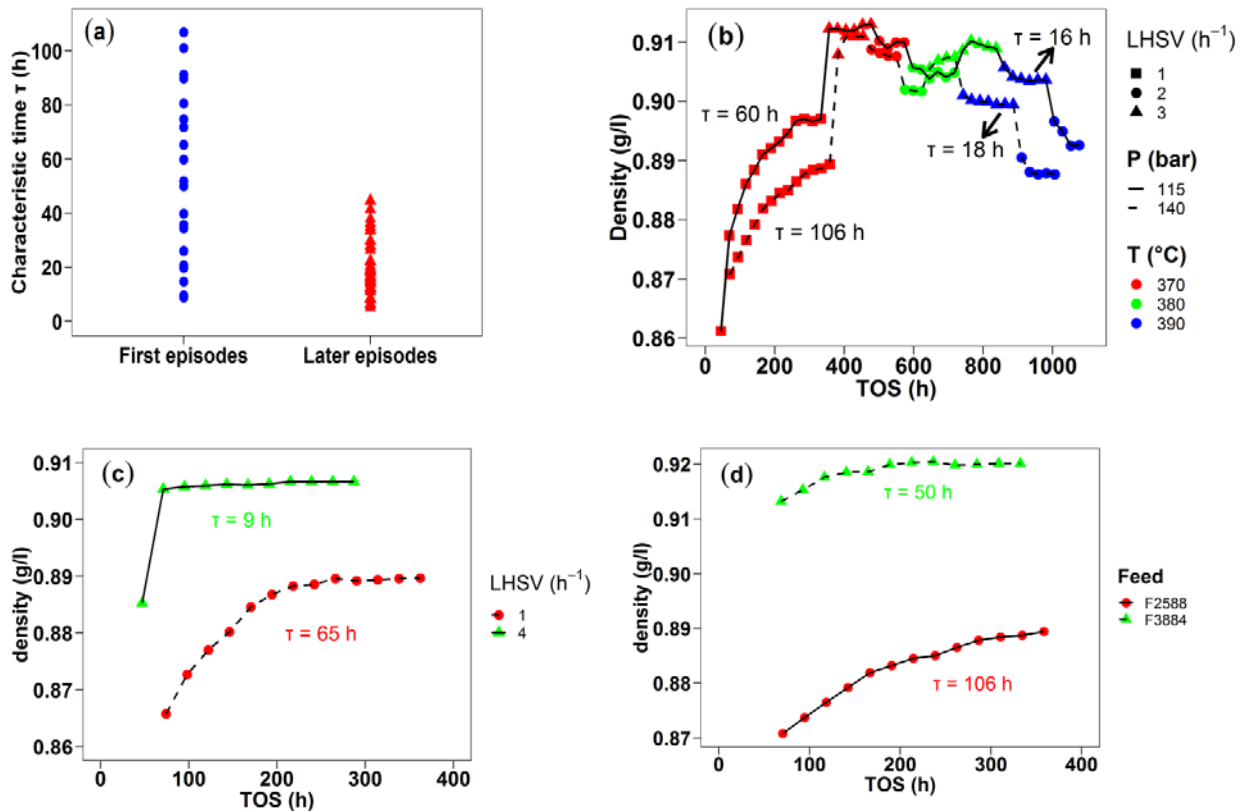


215

216 Figure 4. Comparison of transient behavior of nitrogen/density/refractive index (outputs are
 217 normalized between [0, 1]). Values of τ are 39.8, 36.3, 39.2 h calculated respectively from
 218 density, nitrogen content and refractive index evolution.

219 There were 54 values of τ which have been classified into 21 first episodes and 33 later
 220 episodes, which are shown in Figure 5(a). It can be seen, indeed, that first episodes, on average,
 221 require more time to reach steady state as compared to later episodes. It was, hence, decided not
 222 to describe the τ of first and later episodes with a single model, but to develop dedicated models,
 223 i.e., one for the τ from first episodes and one for the τ of later episodes.

224



225 Figure 5. (a) Classification of τ regarding the type of episode; (b, c, d) Impact of pressure (solid
 226 line: 115 bar, dashed: 140 bar, feed F2588); LHSV (feed F4384, $P = 140$ bar, $T = 370$ °C) and
 227 feedstock (LHSV = 1 h^{-1} , $P = 140$ bar, $T = 370$ °C) respectively on transient behavior of liquid
 228 effluent density.

229 Figure 5(b), (c) and (d) show the transient behavior of liquid effluent density as a function of
 230 time on stream. Figure 5(b) displays the evolution of stabilization at two different pressures, i.e.,
 231 115 and 140 bar. It can be observed that for the first episodes, the evolution of the curve of 115
 232 bar ($\tau = 60$ h) is more rapid than the curve of 140 bar ($\tau = 106$ h). For the later episodes, the
 233 difference in stabilization behavior between 115 and 140 bar seems to be less pronounced.

234 The impact of LHSV was analyzed using data from two tests with the same feed and identical
 235 pressure and temperature ($P = 140$ bar, $T = 370$ °C) with LHSVs amounting to 1 and 4 h^{-1} . As

236 can be seen in Figure 5(c), a higher LHSV leads to a much quicker stabilization. The value of τ
237 in the case of LHSV of 4 h^{-1} was 9 h which is lower than 65 h in the case of 1 h^{-1} .

238 The feedstock is also found to have an impact on the stabilization. Figure 5(d) compares the
239 evolution of liquid effluent density as a function of time on stream between two feedstocks. The
240 evolution with F3884 having a higher resin and nitrogen content stabilizes quicker than the one
241 with F2588.

242 Other factors, such as temperature, catalyst were found to exert a less pronounced impact on
243 the stabilization behavior.

244 **3.3 Model for τ prediction**

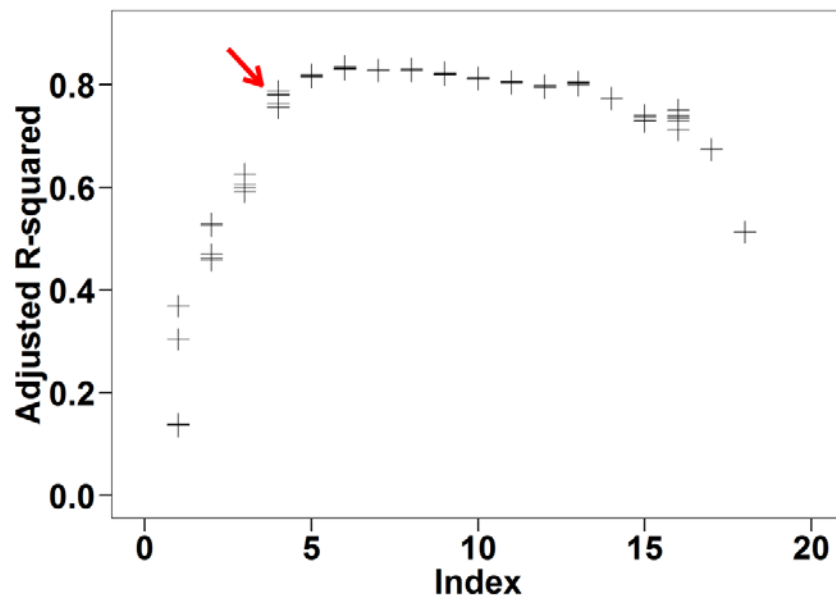
245 τ is modeled using linear regression accounting for interactions. As indicated before, two linear
246 models for τ were built; one for first episodes and another for other episodes.

247 **3.3.1 First episodes model**

248 There are in total 21 values of characteristic time τ corresponding to first episodes. The
249 possible input variables are operating conditions (LHSV, temperature, total pressure) and feed
250 properties (organic nitrogen content N_{feed} , organic sulfur content S_{feed} , resin of feed res_{feed} ,
251 density d_{feed} and the weighted average temperature of simulated distillation TMP_{feed}). All input
252 variables and the interaction terms which are products of operating conditions and feed
253 properties are used in variable selection procedure. Figure 6 shows the evolution of the adjusted
254 R^2 of the 5 best subsets of each size as a function of the size of subsets. It seems that 4 variables
255 represents a good compromise between model accuracy and overfitting (bias/variance
256 compromise), i.e., although the adjusted R^2 still slightly increases when including more than 4
257 variables, the increase seems so marginal that it is preferred to limit the number of variables in
258 the model to 4.

259 Table 1 presents an overview of the selected variables in the best subsets with the number of
260 variables in subset from 1 to 7. The 5 best subsets with 4 variables are detailed as well. Among
261 these 5 best subsets, the subset (LHSV, P, res_{feed}, LHSV*res_{feed}) giving the highest adjusted R² is
262 selected. This model contains only 1 interaction term LHSV*res_{feed}, which also appears in the 4
263 left. It is a robust and less complicated model.

264 The model presents an adjusted R² of 0.79 and a multiple R² of 0.83. The corresponding parity
265 diagram is given in Figure 7. The results are quite good for all the feedstocks.

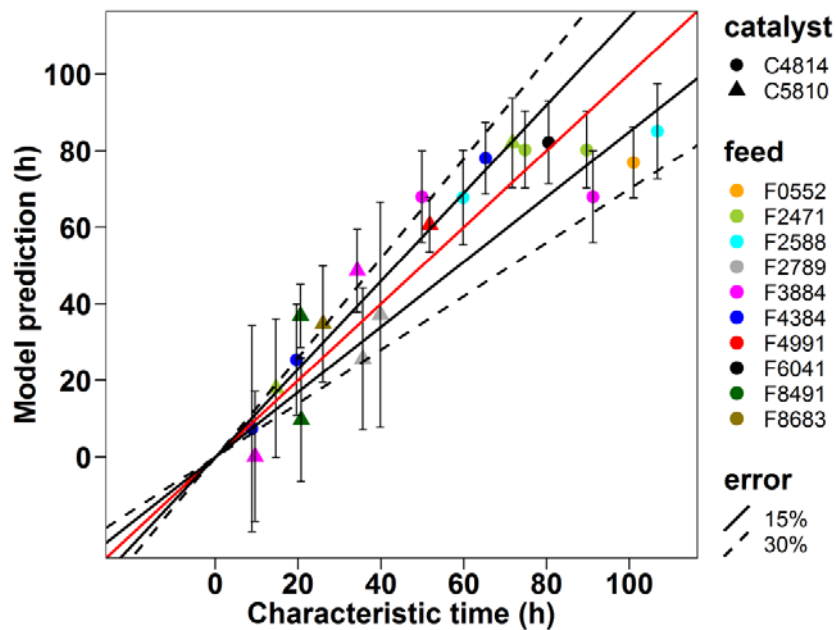


266
267 Figure 6. Variable selection using leaps for linear model with interaction (first episodes).

268

269 Table 1. Selected variables corresponding to each subset obtained from variable selection in
 270 Figure 6 (only show the best selected subsets of ‘from 1 to 7’ variables and 5 best subsets of 4
 271 variables)

| Index | Selected variables | Adjusted R ² |
|-----------|--|-------------------------|
| 1 | P | 0.369 |
| 2 | P, LHSV*S _{feed} | 0.528 |
| 3 | T, P, LHSV*S _{feed} | 0.625 |
| 4a | LHSV, P, res_{feed}, LHSV*res_{feed} | 0.788 |
| 4b | LHSV, res _{feed} , LHSV*res _{feed} , P*TMP _{feed} | 0.782 |
| 4c | res _{feed} , LHSV*res _{feed} , LHSV*TMP _{feed} , P*TMP _{feed} | 0.780 |
| 4d | LHSV, P, LHSV*res _{feed} , T*res _{feed} | 0.763 |
| 4e | LHSV, LHSV*res _{feed} , T*res _{feed} , P*TMP _{feed} | 0.756 |
| 5 | LHSV, T, P, res _{feed} , LHSV*res _{feed} | 0.819 |
| 6 | P, res _{feed} , LHSV*res _{feed} , LHSV*TMP _{feed} , T*res _{feed} , P*N _{feed} | 0.835 |
| 7 | LHSV, P, N _{feed} , LHSV*Res _{feed} , T*TMP _{feed} , T*N _{feed} , P*N _{feed} | 0.828 |



272

273 Figure 7. Parity plot with 95% confidence interval ($R^2 = 0.83$) (first episodes model).

274 The coefficients of the model as well as the statistical values are presented in Table 2. The
 275 global p value amounts to 5.3×10^{-6} and the F value for the global significance of the regression
 276 exceeds the 95% quantile by far, which both indicate that the model is statistically significant.
 277 All variables are individually significant as well as their p value is sufficiently low. As can be
 278 seen, a negative correlation was determined between LHSV and τ . The modeling confirmed that
 279 temperature is not a dominant factor. These two results are coherent with those acquired by
 280 Elizalde et al. (2016). A positive proportionality between pressure and τ was observed. However,
 281 the impact of pressure is less pronounced than that of other variables. The interaction term shows
 282 that the impact of LHSV on τ depends on the value of feed resin, i.e., the polar components with
 283 high molecular weight.

284 Table 2. Coefficient and statistical values for first episodes model

| | Intercept | LHSV | P | res _{feed} | LHSV*res _{feed} |
|-------------|-----------------------|-----------------------|----------------------|-----------------------|--------------------------|
| Coefficient | 63.339 | -69.055 | 0.693 | -7.081 | 5.481 |
| p-value | 3.33×10^{-3} | 3.15×10^{-6} | 7.1×10^{-6} | 5.31×10^{-5} | 1.9×10^{-4} |

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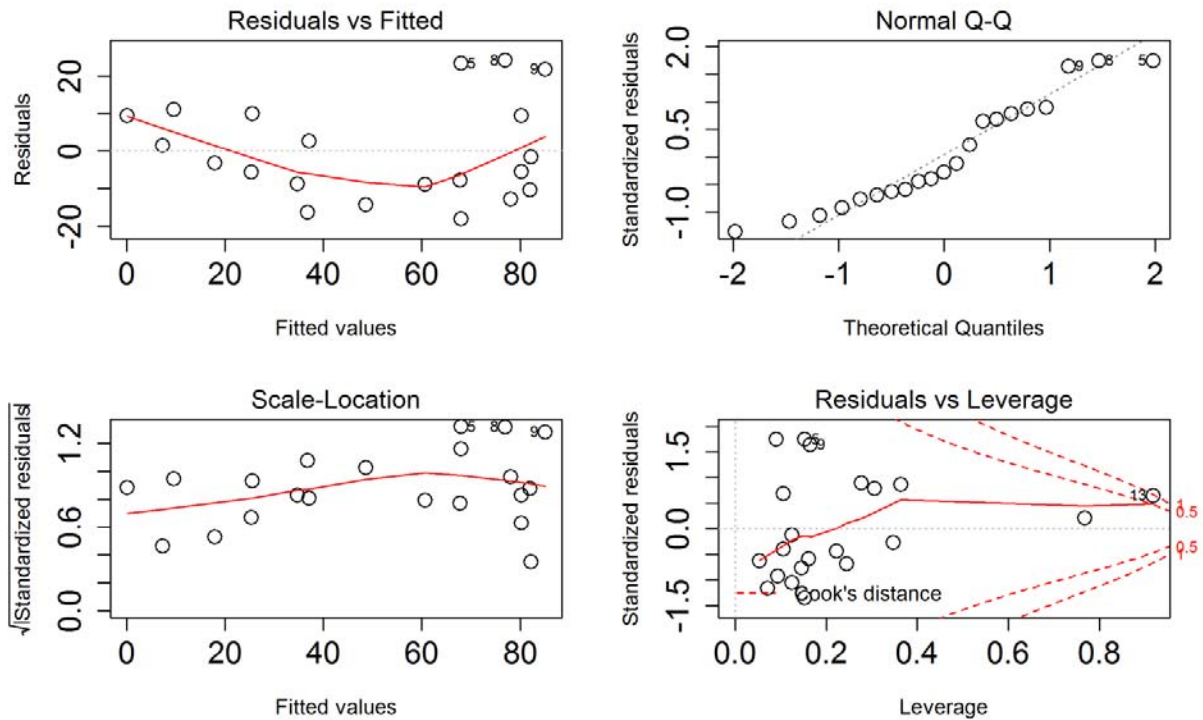
| Global p-value | F | F _{95%} |
|----------------------|-------|------------------|
| 5.3×10^{-6} | 19.55 | 3.01 |

286

287 An overview of the diagnostics for the multiple linear regression with interaction yielding the
 288 combination (LHSV, P, res_{feed}, LHSV* res_{feed}) as best performing one, is displayed in Figure 8.

289 The analysis is as below:

- 290 • Residuals vs. fitted shows that there is linear trend.
- 291 • The normal Q-Q indicates that the residuals are almost normally distributed.
- 292 • The assumption of equal variance is also valid by checking the scale-location.
- 293 • Residuals vs. Leverage show that there is no influential observation. Even the
 294 observation #13 is on the Cook's distance line (red dashed line on the Residual vs
 295 Leverage plot), it is not an influential observation. Because when this point is
 296 excluded from the regression, multiple R² changes from 0.8301 to 0.8335, which
 297 means a small impact.



298

299 Figure 8. Diagnostic plots for linear model with interaction (first episodes model).

300 3.3.2 Later episodes model

301 There are 33 observations of τ in the whole data set for later episodes. The same procedure for
 302 variable selection was applied. The input variables are the feed properties, operating conditions
 303 of the current episode as well as of the previous episode. Variables relating to the previous
 304 episode are, e.g., temperature and LHSV of this previous episode: T_{pre} , $LHSV_{pre}$; and ratio of
 305 temperature and LHSV of the episode and the previous one. Only a selection of interaction terms
 306 was allowed based on the inspiration acquired by modeling the first episodes, to keep the number
 307 of considered variables and, hence, adjustable parameters, within reasonable constraints. Table 3
 308 shows the 17 input variables taken into account in variable selection procedure.

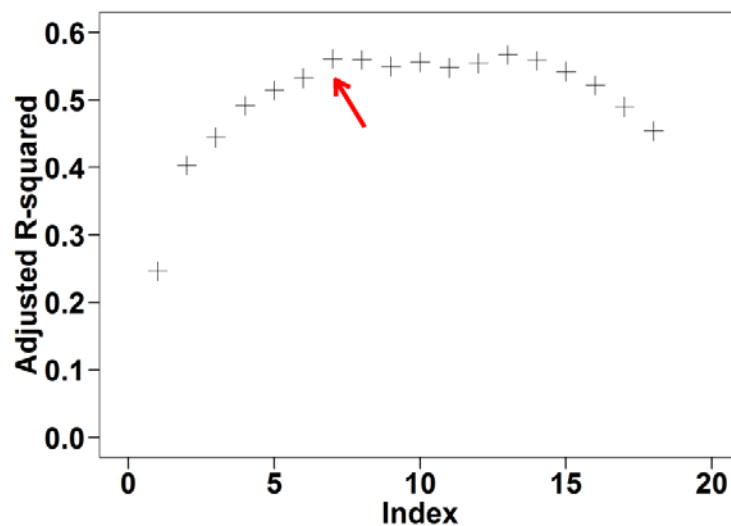
309

310 Table 3. Variables used in variable selection technique for later episodes regression

| Feed | Operating conditions | Condition switching | Interaction terms |
|----------------------------|----------------------------|--|--|
| N_{feed} | LHSV | $\frac{T}{T_{\text{pre}}}$ | $\text{LHSV} * \text{res}_{\text{feed}}$ |
| S_{feed} | T | $\frac{\text{LHSV}}{\text{LHSV}_{\text{pre}}}$ | $\text{LHSV} * N_{\text{feed}}$ |
| res_{feed} | P | $\frac{T_{\text{pre}}}{T}$ | $\text{LHSV} * S_{\text{feed}}$ |
| d_{feed} | LHSV_{pre} | $\frac{\text{LHSV}_{\text{pre}}}{\text{LHSV}}$ | |
| TMP_{feed} | T_{pre} | | |

311

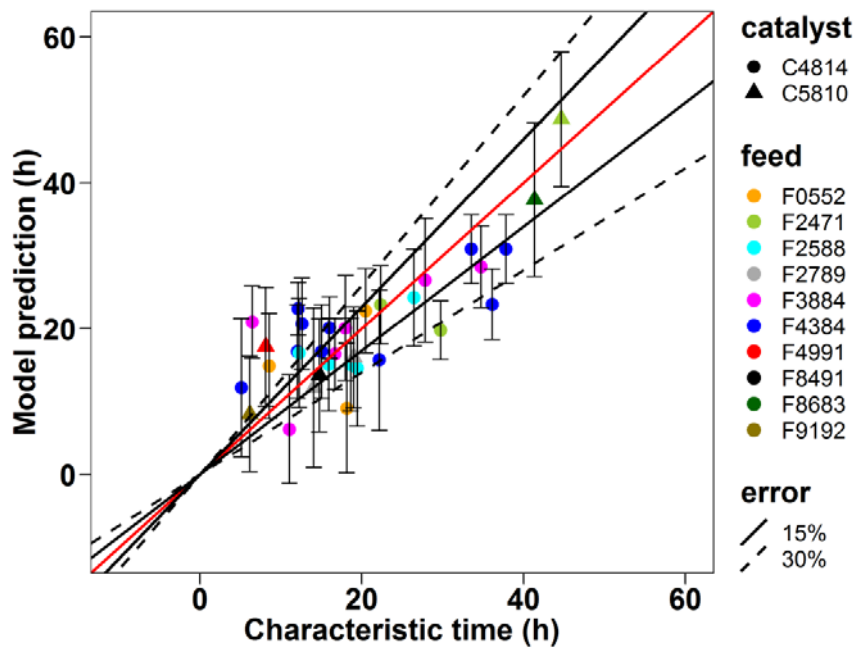
312 Figure 9 show the evolution of the adjusted R^2 of the best subsets as a function of the number
 313 of variables. On similar grounds as for the first episodes modeling (Section 3.3.1), for the later
 314 episodes regression 7 variables is determined to be a good compromise between accuracy and
 315 over fitting for these later episodes.



316

317 Figure 9. Variable selection using leaps for later episodes model.

318 These 7 variables selected are: $LHSV$, S_{feed} , $LHSV_{pre}$, T_{pre} , $LHSV * res_{feed}$, $\frac{LHSV}{LHSV_{pre}}$, $\frac{LHSV_{pre}}{LHSV}$. The
 319 model gives an adjusted R^2 amounting to 0.55 and a multiple R^2 to 0.66. Figure 10 shows the
 320 parity diagram of the model. The quality of the model is lower than that of first episode model,
 321 which is, at least partly, explained by the fact that the results are closer to each other, i.e., there is
 322 less spread for a higher number of variables.



323
 324 Figure 10. Parity plot with 95% confidence interval ($R^2 = 0.66$) (later episodes model).

325 The regression is globally statistically significant since the global p-value is sufficiently small
 326 and the F value exceeds the critical value.

327 Table 4 displays the parameter values obtained for the model and their individual statistical
 328 significance. The p values for the individual variables indicate that S_{feed} and $LHSV_{pre}$ are at the
 329 margin of statistical significance ($P = 0.11$ and $P = 0.07$, respectively) and that the other
 330 variables are significant. $LHSV$, sulfur and resin content in the feed represent the operating
 331 conditions and feed properties. Other variables represent the impact of previous conditions on the

332 τ . The τ of later episodes is more complicated to model than the first episodes and depends on the
 333 conditions of the previous episode.
 334 τ fitted by data has an uncertainty due to the measurement error of the output such as liquid
 335 effluent nitrogen or density. In another database, one episode was repeated several times. The
 336 values of τ fitted by the obtained data are 45, 45, 50, 64, 54 and 59 (hours). The obtained mean is
 337 53 hours and the standard deviation is about 8 hours. Besides that, the residual standard deviation
 338 of the model is 7. It is shown that τ fitted by data varies from one experiment to another
 339 experiment under the same conditions. The latter can lead to the inaccuracy of model since the
 340 values of fitted τ were used to train the model. The proposed model can be sufficient since it
 341 simulates well the order of magnitude of fitted τ and the model is easy to establish and
 342 understand.

343 Table 4. Coefficient and statistical values for later episodes model

| | Intercept | LHSV | S_{feed} | LHSV_{pre} |
|-------------|-----------------------|---------|-------------------|----------------------------|
| Coefficient | 177.349 | -10.943 | 2.589 | 8.851 |
| p-value | 8.32×10^{-5} | 0.036 | 0.114 | 0.071 |

344

| | T_{pre} | $\text{LHSV} * \text{res}_{\text{feed}}$ | $\frac{\text{LHSV}}{\text{LHSV}_{\text{pre}}}$ | $\frac{\text{LHSV}_{\text{pre}}}{\text{LHSV}}$ |
|-------------|-----------------------|--|--|--|
| Coefficient | -0.379 | -0.828 | 8.832 | -11.713 |
| p-value | 8.34×10^{-4} | 3.85×10^{-3} | 5.78×10^{-3} | 0.020 |

345

| Global p-value | F | $F_{95\%}$ |
|----------------------|------|------------|
| 1.4×10^{-4} | 6.83 | 2.40 |

346

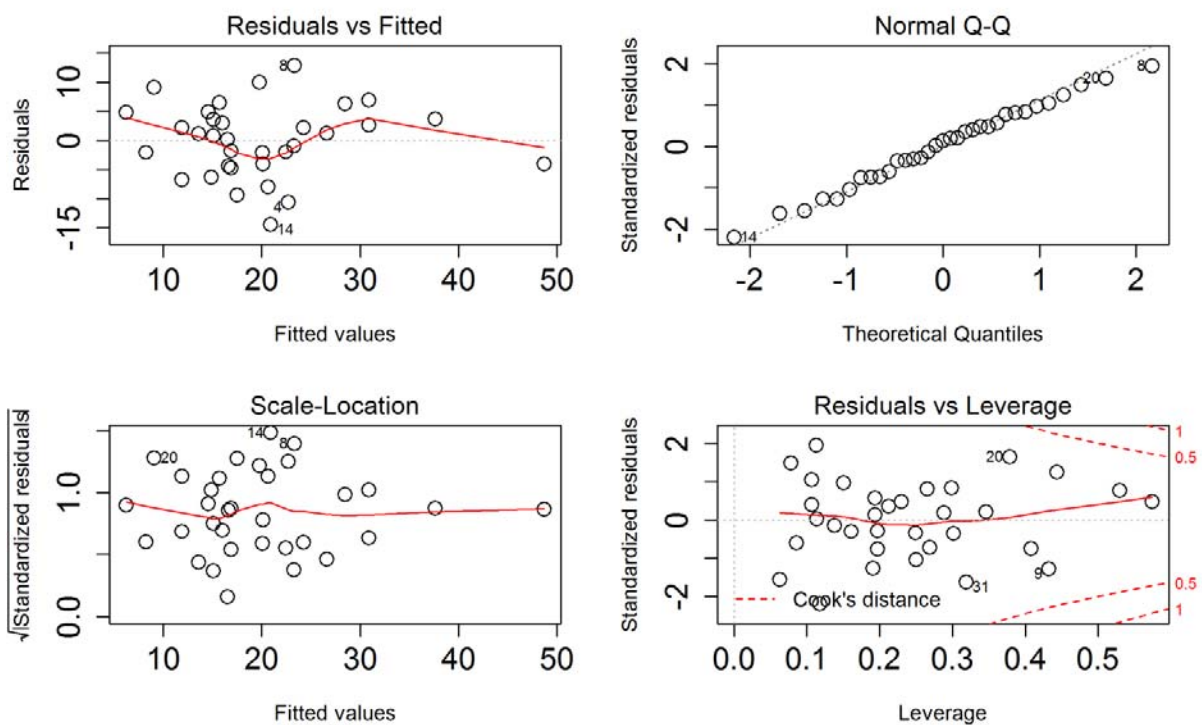
347 Diagnostics of model for later episodes is discussed as below (see also Figure 11).

348 • Residuals vs. fitted shows that there is a linear trend.

349 • The normal Q-Q indicates a normal distribution.

350 • Scale-location shows that the assumption of equal variance is valid.

351 • Residuals vs. Leverage show no influential observation.



352

353 Figure 11. Diagnostic plots for linear model with interaction (later episodes model).

354 3.4 Prediction

355 The model was used to predict τ and the steady-state performance was calculated via Equation

356 (5) assuming that the first two points of the episode have already been measured. The prediction

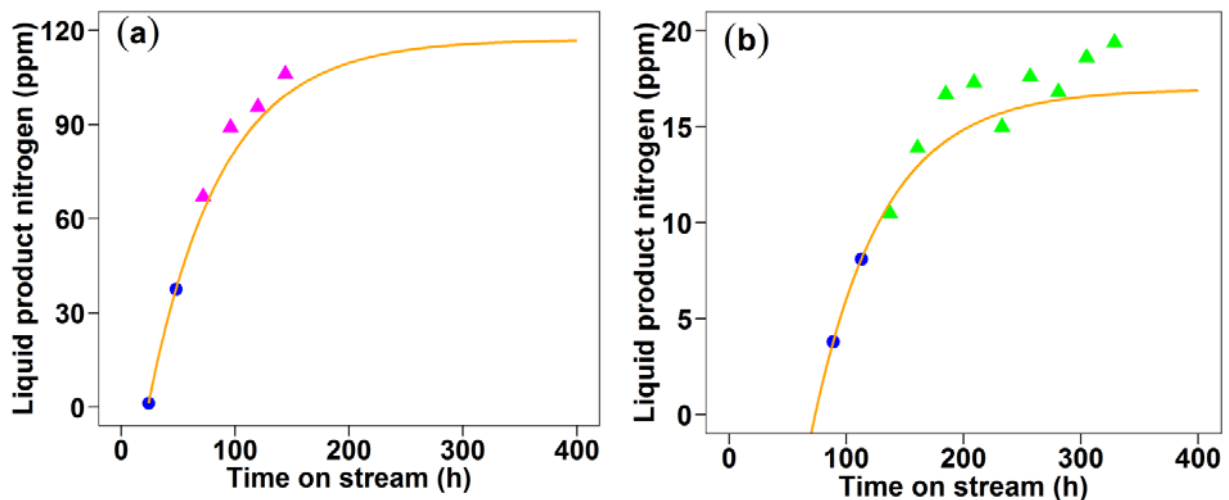
357 was carried out on a new experimentation with another feedstock operating on another pilot plant

358 but the same catalyst.

359 3.4.1 First episodes

360 First episodes model is tested using new data from other feedstocks. Figure 12 shows two
361 examples of such predictions by the model. The first two points of the episode which are used to
362 predict the steady-state value are shown as circles. The remaining data in the episode are
363 represented by triangles. The predicted nitrogen values are very close to the measured ones. The
364 model has been found to provide a good prediction of the stabilization evolution and the steady-
365 state value.

366 Using the model for τ prediction enables the calculation of the steady-state performance
367 without the need to wait for reaching steady state. The advantage is that if the steady-state value
368 could be far from target, operators can change the operating condition without waiting for
369 stabilization.



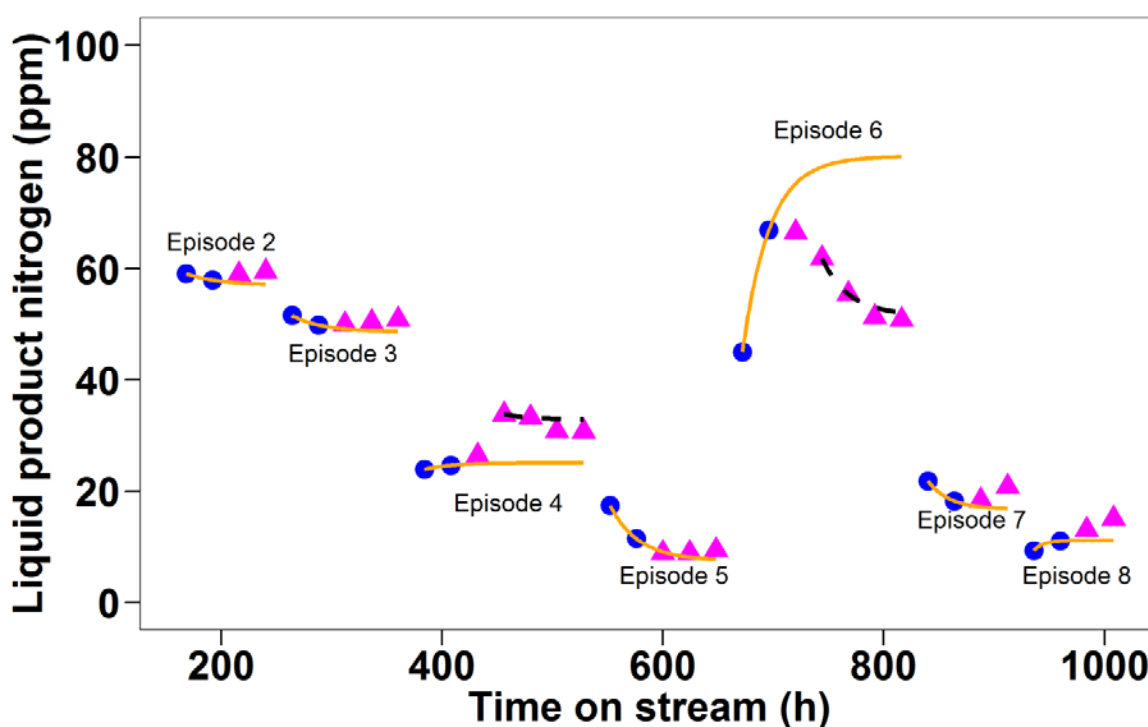
370 Figure 12. Two test predictions using the first two points of episode (points: experimental data,
371 solid line: model prediction; Test (a): LHSV = 1.34 h^{-1} , P = 132 bar, T = 370 °C; Test (b): LHSV
372 = 1.71 h^{-1} , P = 140 bar, T = 386 °C).

373 3.4.2 Later episodes

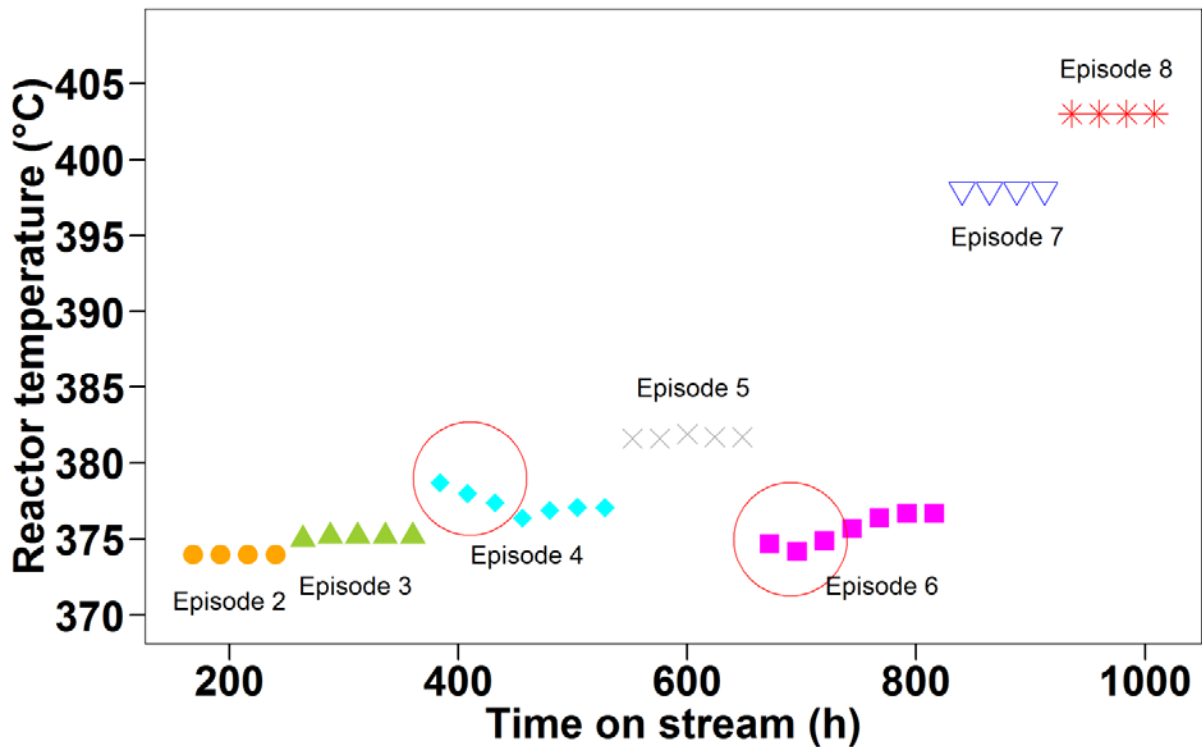
374 Later episodes model is tested using new data from other feedstocks as well. Figure 13
375 compares the prediction (solid line) and the experimental data. Again, the first two points of
376 episode which are used to estimate the steady-state value are shown as circles. The remaining
377 data in the episode are represented by triangles. The model predicts well the evolution of
378 episodes 2, 3, 5, 7 and 8. Since nitrogen values are low in episode 7 and 8, the prediction is
379 considered not far from the experimental value, even if the evolution is not perfectly in line with
380 the experimentally observed one. Moreover, during the first point of an episode, hydrodynamic
381 effects still may have a certain impact, indicating that we should be careful with the reliability of
382 this first point.

383 Regarding episode 4 and 6, the stabilization behavior did not follow the first-order response
384 since the reactor temperature was slightly adjusted to reach an intended nitrogen level. The
385 reactor temperature profile is shown in Figure 14. A target of 30 ppm was fixed for the value of
386 liquid effluent nitrogen in episode 4. The reactor temperature was firstly set at 378.7 °C. The
387 prediction using the first two points was 25 ppm (see solid line in episode 4, Figure 13). The
388 reactor temperature was, hence, gradually decreased to 377.1 °C. The temperature profile was
389 considered constant from the fourth point. The steady-state value prediction using the fourth and
390 fifth point was 32.8 ppm, which is not far from the target (see dashed line in Figure 13). The
391 third point was not used for prediction since the temperature was adjusted during that time.
392 Similar to episode 4, the liquid effluent nitrogen target of episode 6 was 50 ppm. The
393 temperature was firstly set at 374.7 °C for episode 6 and the steady-state forecast using the first
394 two points was 80 ppm. The temperature was gradually modified to 376.7 °C. The steady-state
395 value prediction using the fourth and fifth point was 52 ppm, which was close to the target (see
396 also dashed line in episode 6, Figure 13). As the liquid product nitrogen values seem to be

397 sensitive to the reactor temperature value, it is needed to carefully control the temperature
398 profile. As can be seen, the steady-state performance prediction depends not only on the
399 predicted value of τ but also on the first two “online” measurements. This ‘online’ prediction is,
400 hence, flexible and the operators should consider the certainty of experimental data and adapt to
401 what really happen (modification of operating conditions, measurement error and equipment
402 problem).



403
404 Figure 13. Prediction with the first two points of other episodes (points: experimental data, solid
405 line: model prediction using the first two points, dashed line: prediction while discarding the first
406 three points).

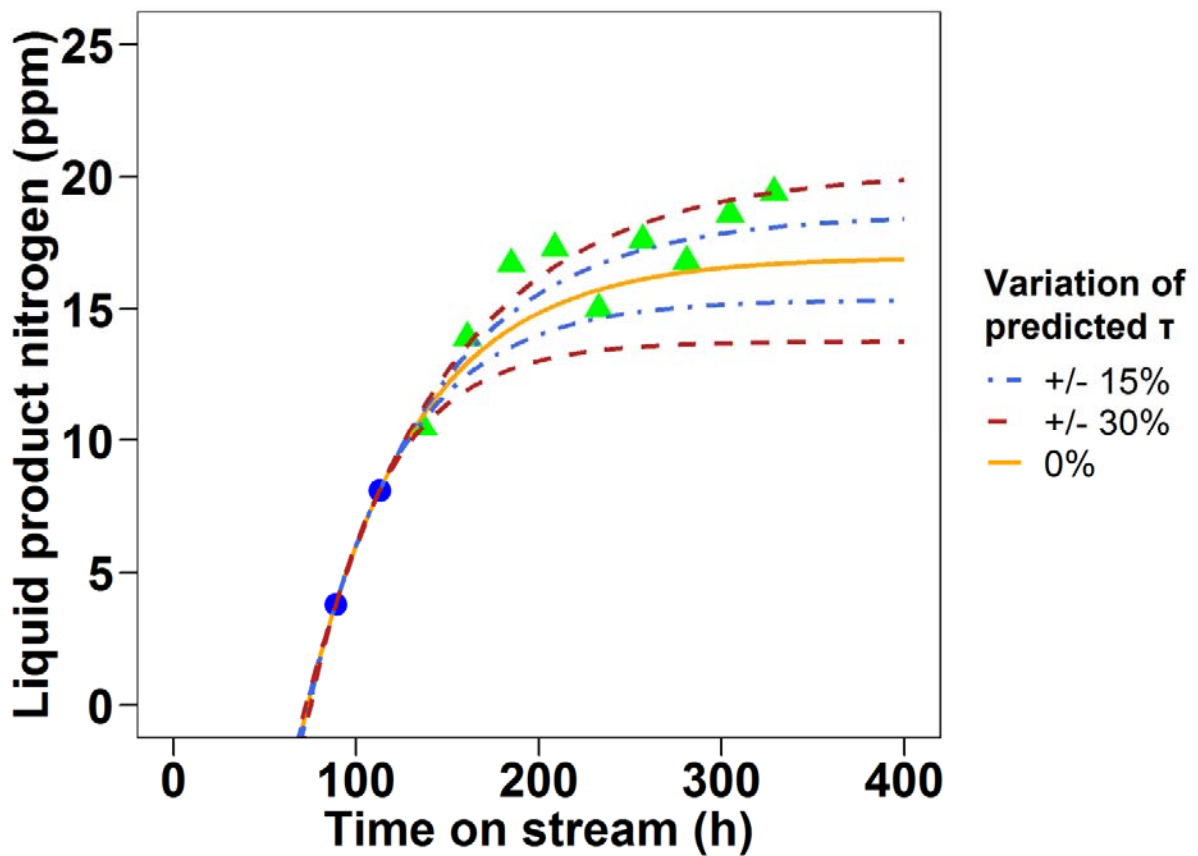


407

408 Figure 14. Reactor temperature profile corresponding to each episode

409 Even if the quality of the model seems limited, the model reproduces well the order of
 410 magnitude of τ . The impact of τ predicted by model on the stabilization evolution prediction was
 411 carried out for one episode. Figure 15 shows the steady-state prediction based on the first two
 412 points and different values of predicted τ . In fact, a variation of $\pm 15\%$ and $\pm 30\%$ was added on τ
 413 predicted by model in order to study the impact of predicted τ on the steady-state prediction. As
 414 can be seen, the nitrogen value comes to its steady state at about 14 – 20 ppm for $\pm 30\%$ variation
 415 of predicted τ . The steady-state value of nitrogen is 15.5 – 18.5 ppm for $\pm 15\%$ variation. It is
 416 shown that a small variation of τ does not impact significantly on the prediction. Moreover, the
 417 model can be employed at the experimentation scheduling step. The predicted τ (in hours) can be
 418 used to estimate the order of magnitude of the time required to reach steady-state (in days). As
 419 explained in Section 2.4, the steady state can be considered to reach after about $3\tau - 5\tau$.

420 The proposed methodology can be applied to any reaction where the chemical stabilization
421 requires significantly more time than the hydrodynamic stabilization and analysis time to
422 forecast the evolution towards the steady state. The latter can help the operator to follow the
423 trend of the stabilization behavior. It enhances the decision making in process operation to reach
424 an intended target.



425
426 Figure 15. Sensitivity of predicted τ by model on the steady-state prediction (points:
427 experimental data; line: prediction based on the first two points and different values of τ)

428

429 **4 Conclusions**

430 Stabilization is crucial for hydroprocessing. In this work, transient hydrotreating data were
431 used to probe the details of this stabilization, which was found to follow a first-order response.
432 Two models, i.e., one for the first episodes, another for the later episodes, for stabilization time
433 ‘ τ ’ prediction were constructed. It was found that a higher LHSV leads to a quicker stabilization.
434 The extent of the impact of LHSV on τ depends on the feed resin content. A proportional
435 relationship between pressure and stabilization was found. Temperature is not a dominant factor.
436 Stabilization of later episodes depends not only on the feedstock and operating conditions but
437 also on the operating conditions of the previous episode.

438 The availability of two initial measurements during stabilization typically suffices to predict
439 the steady-state hydrotreating performance. Good prediction results were obtained, particularly
440 for the first episodes. The stabilization of later episodes is more complicated to predict. The
441 prediction results indicate that transient data can be used to optimize the steering of pilot plants
442 to reach quickly some targets.

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445 Notes: The authors declare no competing financial interest.

446 **Nomenclature**

447 CSTR: continuous stirred-tank reactor

448 LHSV: liquid hourly space velocity (h^{-1})

449 P: pressure (bar)

450 PFR: plug flow reactor

451 T: temperature ($^{\circ}\text{C}$)

452 TOS: time on stream (h)

453 ppm: parts-per-million

454 VGO: vacuum gas oil

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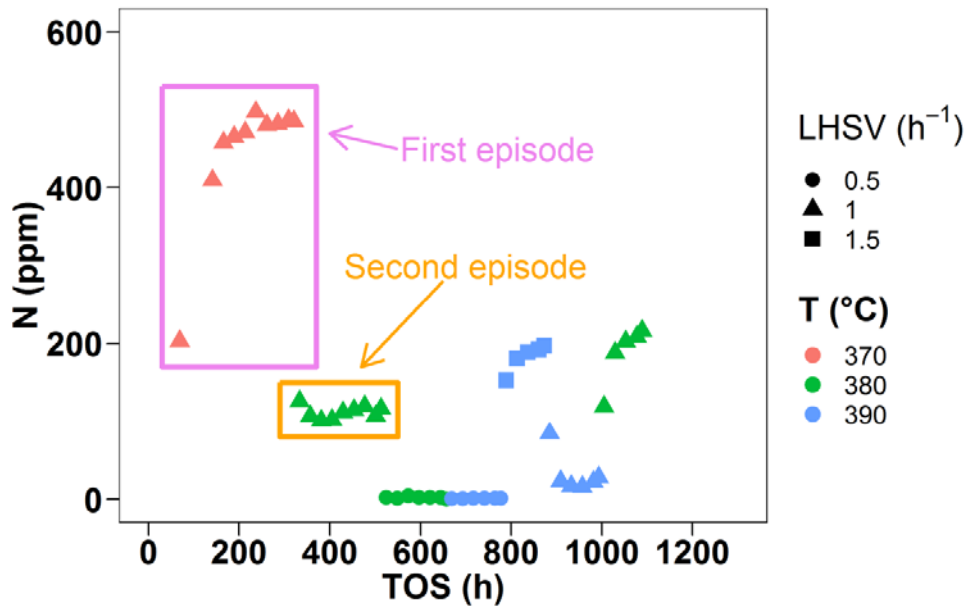
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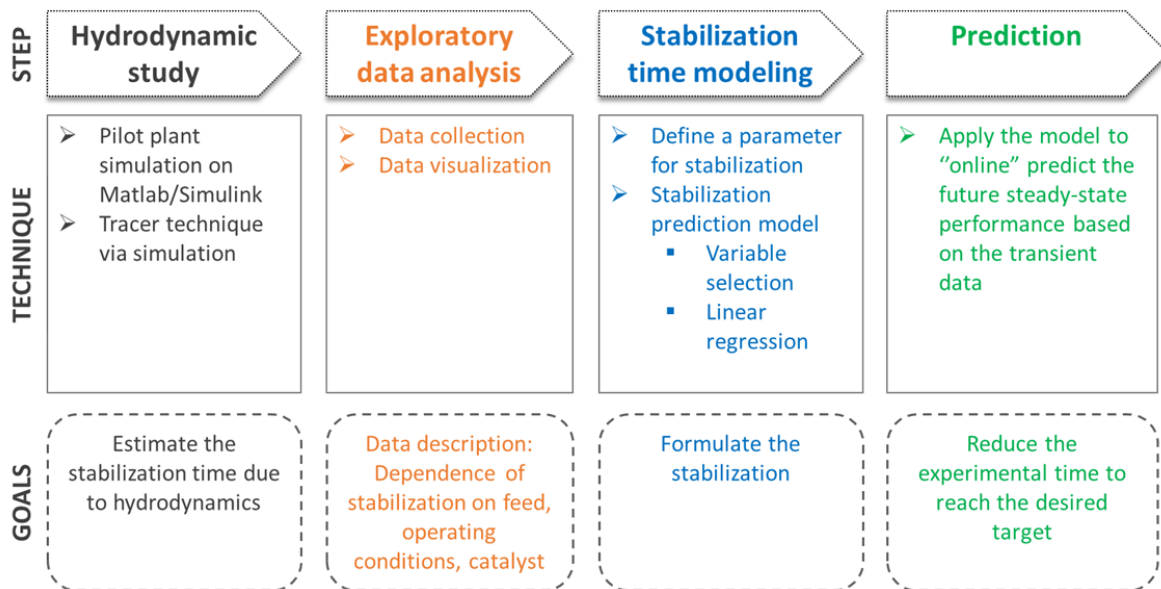
529 **Figures & Tables**

530 **Figures**



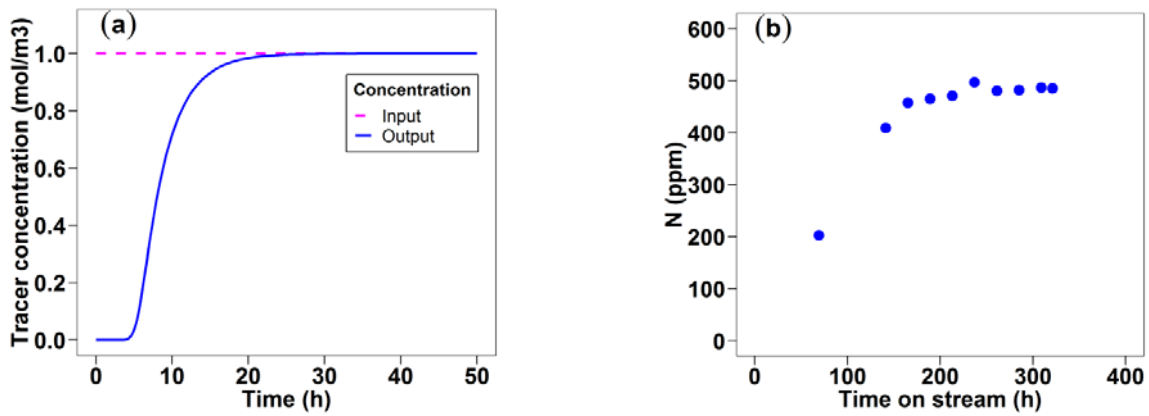
531

532 Figure 1. Data illustration - Liquid effluent nitrogen as a function of time on stream (TOS).

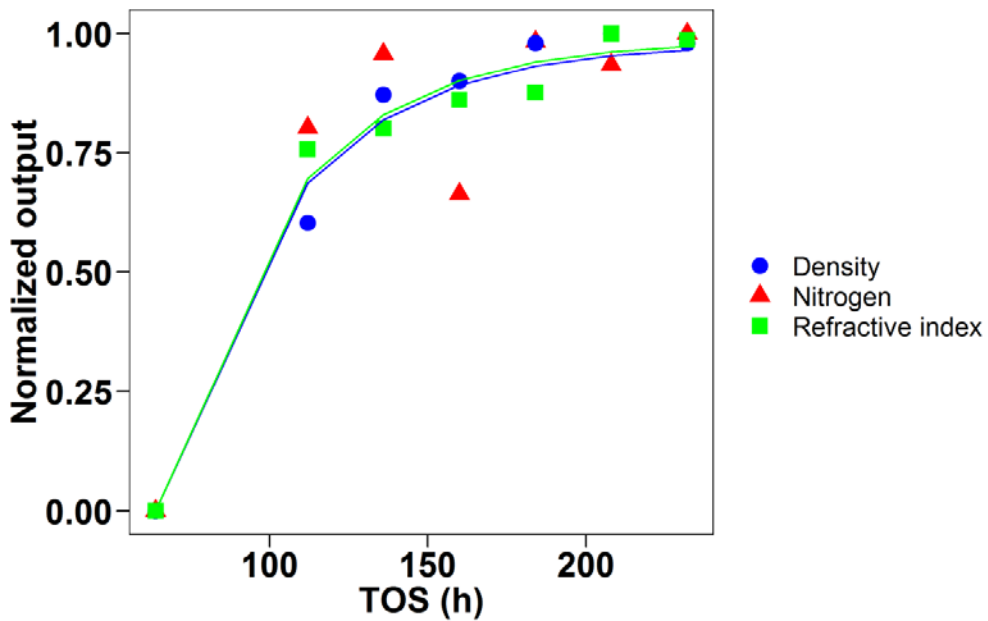


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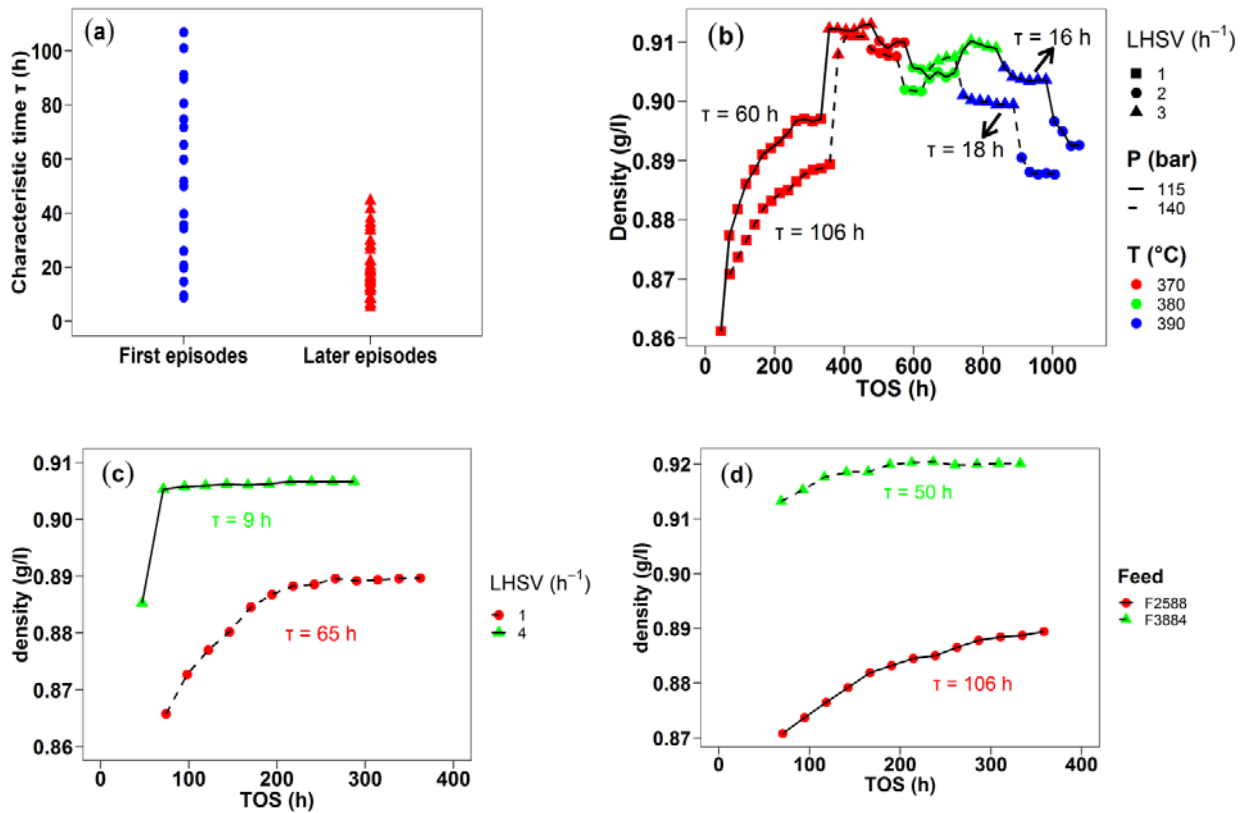
534 Figure 2. Methodology adopted throughout this work.



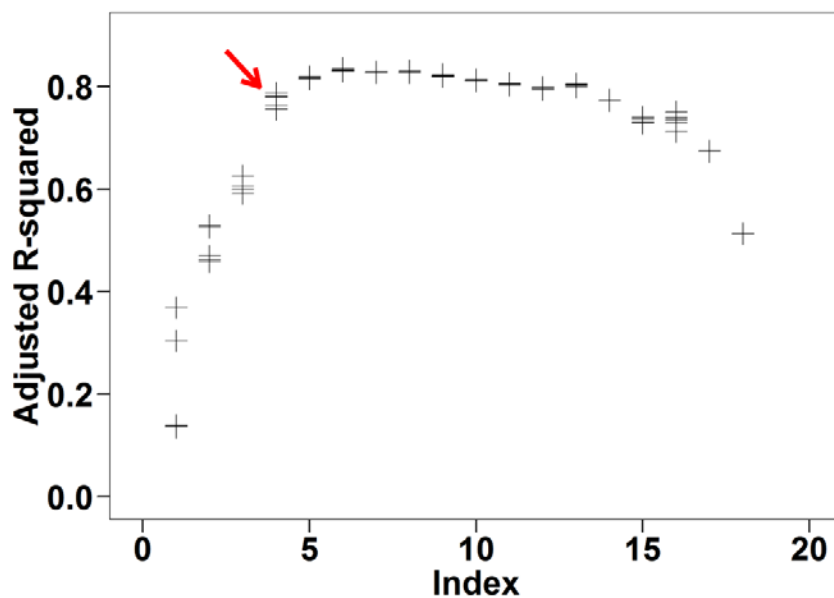
535
 536 Figure 3. Calculated effluent concentration profiles of tracer (a) and experimentally observed
 537 liquid effluent nitrogen content as a function of time on stream in the pilot plant (b) (LHSV = 1
 538 h^{-1} , $T = 370\text{ }^{\circ}\text{C}$, $P = 140\text{ bar}$).



539
 540 Figure 4. Comparison of transient behavior of nitrogen/density/refractive index (outputs are
 541 normalized between [0, 1]). Values of τ are 39.8, 36.3, 39.2 h calculated respectively from
 542 density, nitrogen content and refractive index evolution.

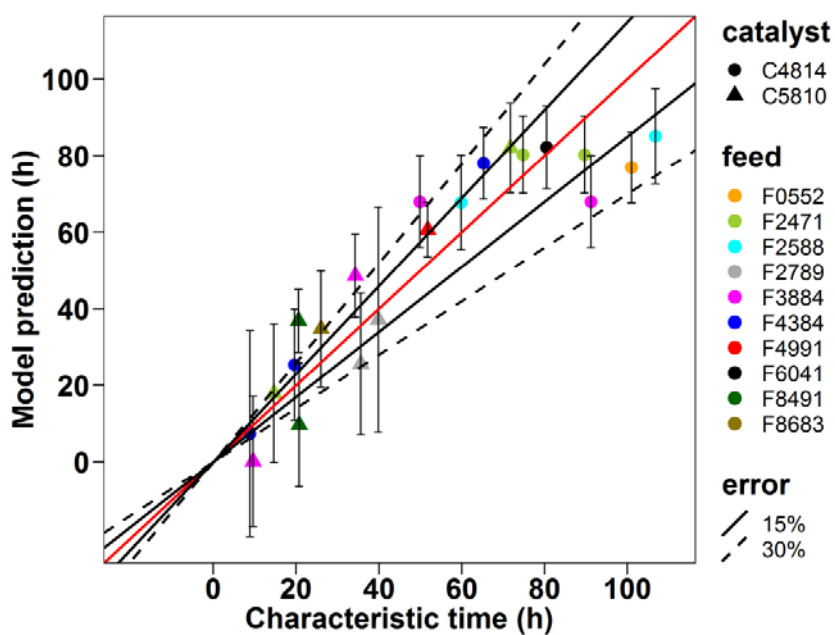


543 Figure 5. (a) Classification of τ regarding the type of episode; (b, c, d) Impact of pressure (solid
 544 line: 115 bar, dashed: 140 bar, feed F2588); LHSV (feed F4384, $P = 140$ bar, $T = 370$ °C) and
 545 feedstock ($LHSV = 1$ h⁻¹, $P = 140$ bar, $T = 370$ °C) respectively on transient behavior of liquid
 546 effluent density.



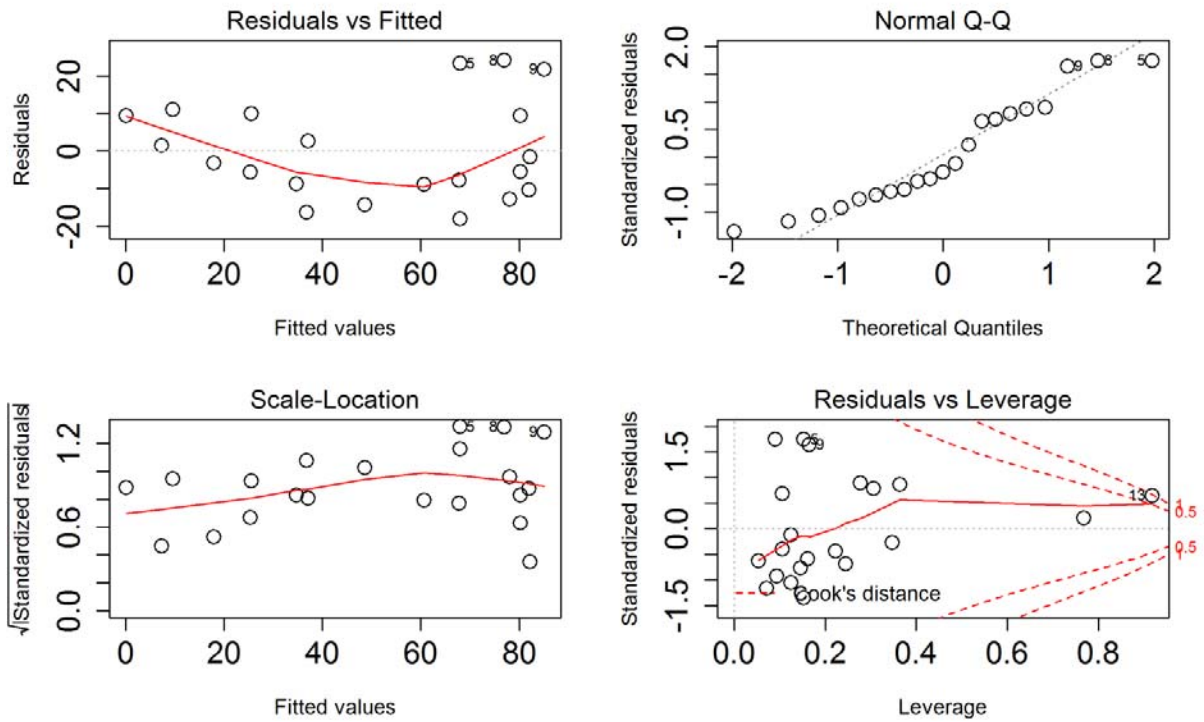
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548 Figure 6. Variable selection using leaps for linear model with interaction (first episodes).



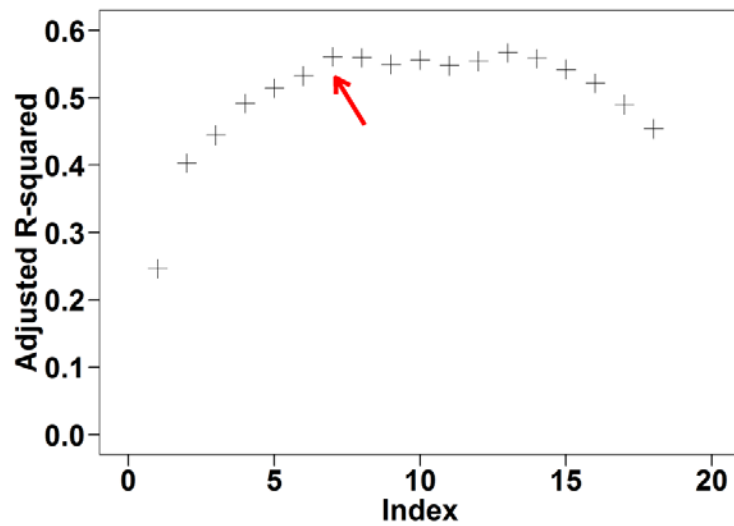
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550 Figure 7. Parity plot with 95% confidence interval ($R^2 = 0.83$) (first episode model).



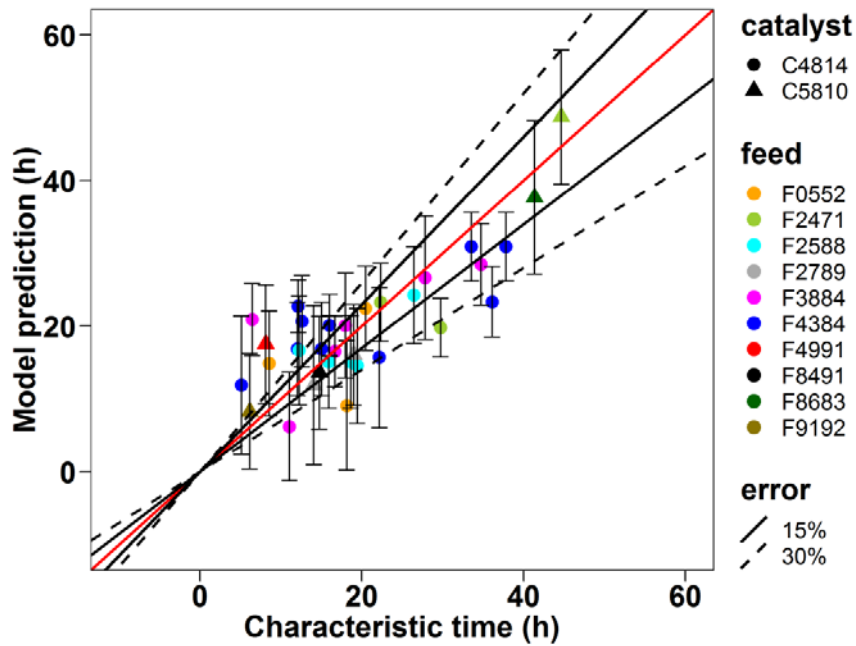
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552 Figure 8. Diagnostic plots for linear model with interaction (first episodes model).



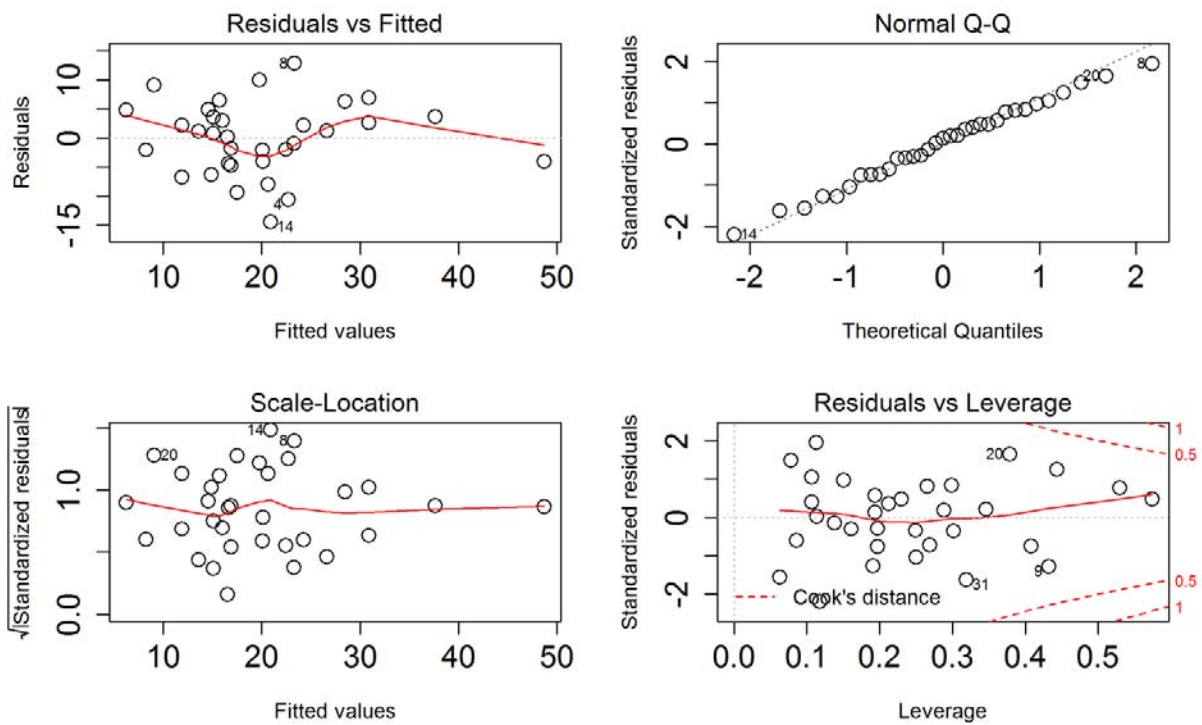
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554 Figure 9. Variable selection using leaps for later episode model.



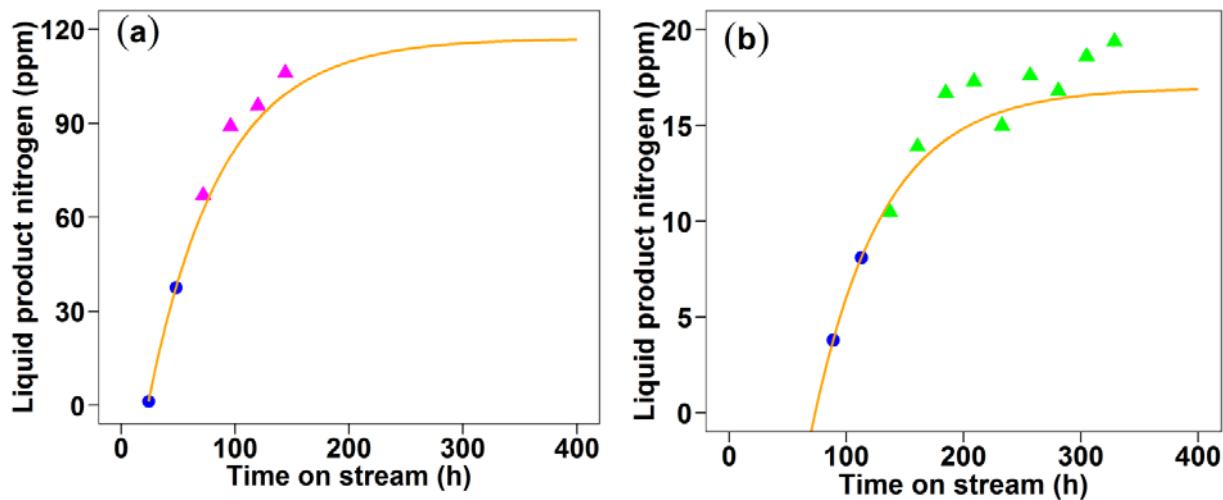
555

556 Figure 10. Parity plot with 95% confidence interval ($R^2 = 0.66$) (later episodes model).



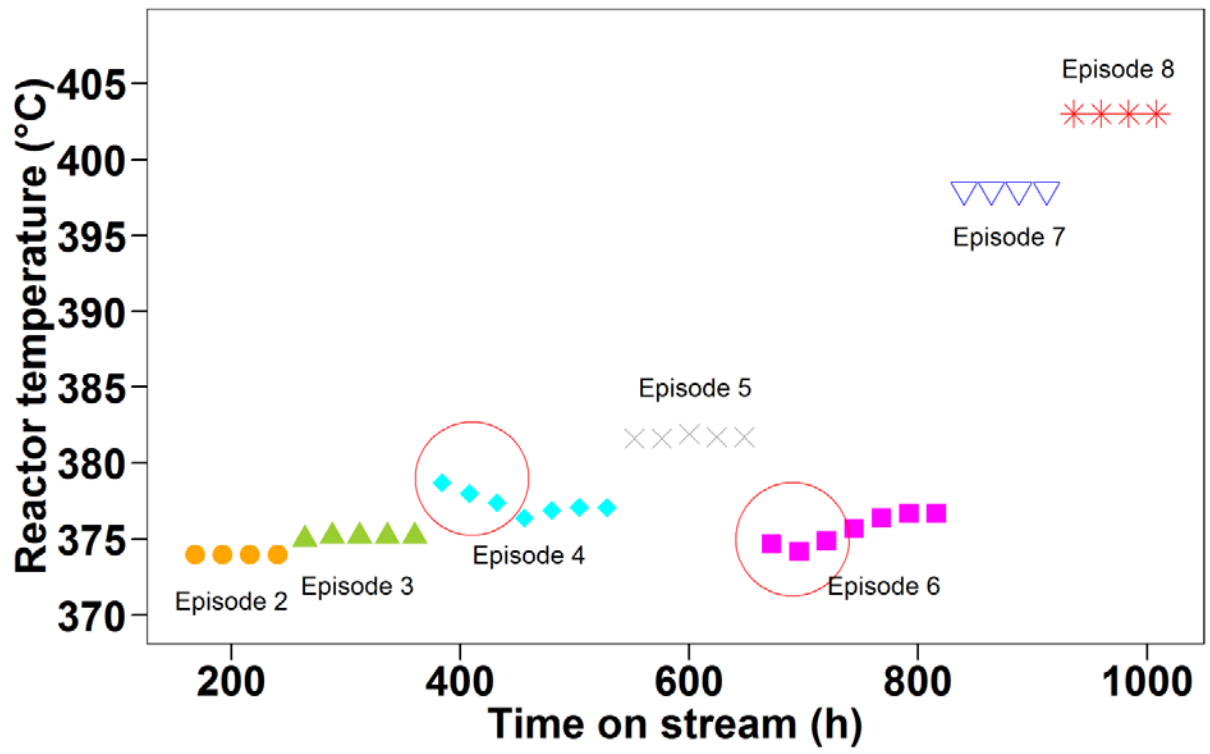
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558 Figure 11. Diagnostic plots for linear model with interaction (later episodes model).



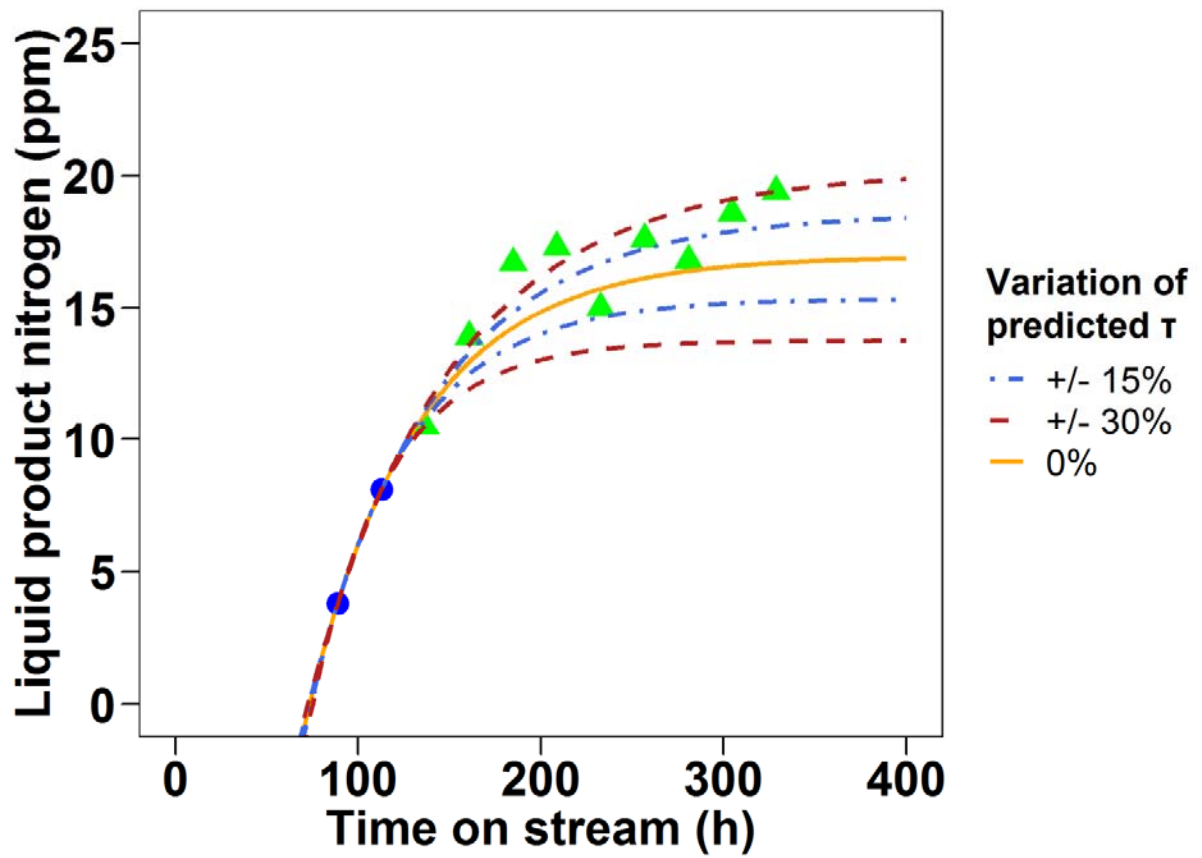
559 Figure 12. Two test predictions using the first two points of episode (points: experimental data,
 560 solid line: model prediction; Test (a): LHSV = 1.34 h⁻¹, P =132 bar, T = 370 °C; Test (b): LHSV
 561 = 1.71 h⁻¹, P =140 bar, T = 386 °C).

562



567

568 Figure 14. Reactor temperature profile corresponding to each episode



569

570 Figure 15. Sensitivity of predicted τ by model on the steady-state prediction (points :
 571 experimental data; line: prediction based on the first two points and different values of τ)

572

573 **Tables**

574 Table 1. Selected variables corresponding to each subset obtained from variable selection in
 575 Figure 6 (only show the best selected subsets of ‘from 1 to 7’ variables and 5 best subsets of 4
 576 variables)

| Index | Selected variables | Adjusted R² |
|--------------|--|-------------------------------|
| 1 | P | 0.369 |
| 2 | P, LHSV*S _{feed} | 0.528 |
| 3 | T, P, LHSV*S _{feed} | 0.625 |
| 4a | LHSV, P, res_{feed}, LHSV*res_{feed} | 0.788 |
| 4b | LHSV, res _{feed} , LHSV*res _{feed} , P*TMP _{feed} | 0.782 |
| 4c | res _{feed} , LHSV*res _{feed} , LHSV*TMP _{feed} , P*TMP _{feed} | 0.780 |
| 4d | LHSV, P, LHSV*res _{feed} , T*res _{feed} | 0.763 |
| 4e | LHSV, LHSV*res _{feed} , T*res _{feed} , P*TMP _{feed} | 0.756 |
| 5 | LHSV, T, P, res _{feed} , LHSV*res _{feed} | 0.819 |
| 6 | P, res _{feed} , LHSV*res _{feed} , LHSV*TMP _{feed} , T*res _{feed} , P*N _{feed} | 0.835 |
| 7 | LHSV, P, N _{feed} , LHSV*Res _{feed} , T*TMP _{feed} , T*N _{feed} , P*N _{feed} | 0.828 |

577

578

579 Table 2. Coefficient and statistical values for first episodes model

| | Intercept | LHSV | P | res _{feed} | LHSV*res _{feed} |
|-------------|-----------------------|-----------------------|----------------------|-----------------------|--------------------------|
| Coefficient | 63.339 | -69.055 | 0.693 | -7.081 | 5.481 |
| p-value | 3.33×10^{-3} | 3.15×10^{-6} | 7.1×10^{-6} | 5.31×10^{-5} | 1.9×10^{-4} |

580

| Global p-value | F | F _{95%} |
|----------------------|-------|------------------|
| 5.3×10^{-6} | 19.55 | 3.01 |

581

582 Table 3. Variables used in variable selection technique for later episodes regression

| Feed | Operating conditions | Condition switching | Interaction terms |
|---------------------|----------------------|---------------------------|--------------------------|
| N _{feed} | LHSV | $\frac{T}{T_{pre}}$ | LHSV*res _{feed} |
| S _{feed} | T | $\frac{LHSV}{LHSV_{pre}}$ | LHSV*N _{feed} |
| res _{feed} | P | $\frac{T_{pre}}{T}$ | LHSV*S _{feed} |
| d _{feed} | LHSV _{pre} | $\frac{LHSV_{pre}}{LHSV}$ | |
| TMP _{feed} | T _{pre} | | |

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585 Table 4. Coefficient and statistical values for later episodes model

| | Intercept | LHSV | S _{feed} | LHSV _{pre} |
|-------------|-----------------------|---------|-------------------|---------------------|
| Coefficient | 177.349 | -10.943 | 2.589 | 8.851 |
| p-value | 8.32×10 ⁻⁵ | 0.036 | 0.114 | 0.071 |

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| | T _{pre} | LHSV*res _{feed} | $\frac{\text{LHSV}}{\text{LHSV}_{\text{pre}}}$ | $\frac{\text{LHSV}_{\text{pre}}}{\text{LHSV}}$ |
|-------------|-----------------------|--------------------------|--|--|
| Coefficient | -0.379 | -0.828 | 8.832 | -11.713 |
| p-value | 8.34×10 ⁻⁴ | 3.85×10 ⁻³ | 5.78×10 ⁻³ | 0.020 |

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| Global p-value | F | F _{95%} |
|----------------------|------|------------------|
| 1.4×10 ⁻⁴ | 6.83 | 2.40 |

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