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Non-Linear Dynamics Simulation Study of a Reactive Distillation Process for the Ultra-Low Sulfur Diesel Production

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A rigorous numerical steady state multiplicity study of a reactive distillation process for ultra-low sulfur diesel production is presented. The complete bifurcation behaviour is analysed in terms of operating conditions such as holdup and reactive stages through bifurcation diagrams and dynamic simulation for two feed case scenarios. Disturbances in the hydrocarbon feed composition were found to cause transitions between parallel steady states and these were plotted using the dynamic capabilities of the column model; therefore, the reactive distillation process can display responses towards different steady states only for the first case. With the use of sensitivity criterion, it was possible to determine a start-up procedure and visualize a complex control structure for the reactive separation process. Finally, from the location of the singularities of higher codimension some conclusions are obtained to avoid the multiplicity region and to reach the required output targets.

1. Introduction

Sulfur content of diesel fuel has been cut down to ultra-low levels due to environmental regulation in many countries with the aim of reducing diesel engine’s harmful emissions improving therefore air quality. Thus, research on the production of ultra-low sulfur diesel (ULSD) has acquired enormous interest in the scientific community worldwide. The renewed interest in ULSD research is driven by the need to have a comprehensive understanding of the various factors that influence deep desulfurization of diesel up to the ultra-low sulfur content level making cost effective ways for ULSD production as well. It is generally believed that a two-stage deep hydrodesulfurization (HDS) process will be required by most, if not by all the refiners, to achieve a diesel product with less than 10 ppm of sulfur. A design consistent with this technological approach has been proposed by Haldor Topsøe, which includes a first stage that reduces the sulfur content to around 250 ppm or lower, and a second stage that completes the reduction to less than 10 ppm. Based on the philosophy of previous work, it could be considered a two-stage deep desulfurization process where the first stage is a currently conventional HDS process that reduces the sulfur content up to 500 ppm, and a hypothetical second stage consisting of a reactive distillation process (RDP), which should remove the sulfur from diesel to the desired specification. However, Reactive Distillation (RD) is not extensively used in industry since it is perceived that its operation will always be more difficult and will pose higher requirements on the quality of the design and control system than conventional flowsheet in which a chemical reactor is typically followed by a sequence of distillation columns. This fact can be mainly attributed to the complex interactions between vapor-liquid equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics (Taylor and Krishna, 2000). These interactions between reaction and separation, lead to a highly nonlinear behaviour in reactive distillation processes indicating the possible

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existence of multiple steady states (MSS) and complex dynamics; for this reason, the increasing interest in RD has been accompanied by the development of various simulation algorithms related to the study of operation and control of the process (Taylor and Krishna, 2000; Kumar and Kaistha, 2007; Cárdenas-Guerra et al., 2010; Yamaki and Matsuda, 2012). A key point is that the analysis of a single steady state (SSS) or MSS provides in which parameter space (process operability) a RDP is operating, to understand how the column will respond to changes in operating variables (process controllability). Thus, in this work the bifurcation behaviour of RDP for the ULSD production is studied in terms of operating conditions such as holdup and reactive stages. The multiplicity analysis is performed for two feed case scenarios, showing its implication in the operation and control of the RDP. Also, we study the influence of the operating conditions over the main variables to control, i.e., the organo-sulfur compound conversion and the temperature. Finally, the RDP can display dynamics towards different steady states. With the use of sensitivity criterion, it was possible to determine a start-up procedure and visualize a complex control structure for the RDP.

2. The reactive system

The "sulfured" diesel has been modelled as a hydrocarbon (HC) feed of four organo-sulfur compounds thiophene (Th), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenthiophene (4,6-DMDBT), and a paraffinic mixture containing n-undecane (n-$C_{11}H_{24}$), n-dodecane (n-$C_{12}H_{26}$), n-tridecane (n-$C_{13}H_{28}$), n-tetradecane (n-$C_{14}H_{30}$) and n-hexadecane (n-$C_{16}H_{34}$). There are two possible reaction pathways for sulfur removal from the organo-sulfur compounds as illustrated for 4,6-DMDBT in Figure 1. The first pathway is the sulfur atom direct extraction (hydrogenolysis) from the sulfured molecule. In the second pathway (hydrogenation), one aromatic ring is pre-hydrogenated and the sulfur atom is subsequently removed by direct extraction. Both reaction pathways occur in parallel employing different active sites of the catalyst surface.

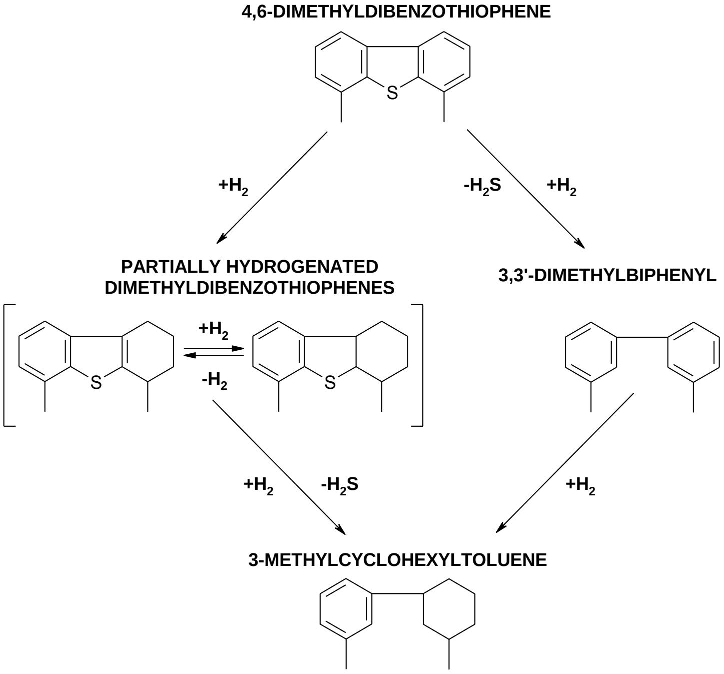
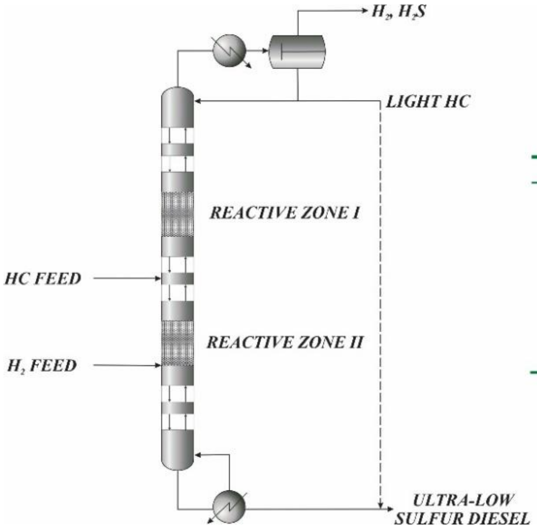


Figure 1: Reaction pathways for 4,6-DMDBT.

The HDS reactions for Th, BT and DBT progress via the hydrogenolysis pathway (Stanislaus et al., 2010). On the other hand, it is also well known that around 80% of 4,6-DMDBT goes by the hydrogenation reaction pathway while DBT is mostly converted by the hydrogenolysis reaction pathway. In general, when alkyl substituents are attached to the carbon atoms adjacent to the sulfur atom, the rate for direct sulfur extraction is diminished whereas the sulfur removal rate via the hydrogenation pathway is relatively unaffected. $CoMo/Al_2O_3$ catalysts are better for desulfurization via the hydrogenolysis pathway, while the $NiMo/Al_2O_3$ catalysts are preferable for HDS of refinery streams that require extensive hydrogenation (Stanislaus et al., 2010). Which reaction pathways predominates depends on the nature of the organo-sulfur compounds, the reaction conditions (H_2 and H_2S partial pressures), and the catalyst used.

3. Reactive Distillation Process

Viveros-García et al. (2005) developed a conceptual design of RDP for the ULSD production through a thermodynamic analysis of the reactive system in terms of the reaction-separation feasibility. The configuration obtained (Figure 2) consisted of 14 stages with two reactive zones (where two types of catalysts can be used) and three non-reactive zones. In a process simulator, such as ASPEN PLUS®, it is possible to generate the previously superstructure using an equilibrium stage model and considering homogeneous liquid chemical reactions. It was fixed an operating pressure of 30 atm in the RDP and a H_2 to HC feed ratio of 3 was used. The phase equilibrium calculations were performed using the Peng-Robinson equation of state. Figure 2 shows the process details used for the simulations.



Design and operation parameters	Value
Location of the stages of reactive zone I	5-7
Location of the stages of reactive zone II	10-12
HC feed stage	9
H_2 feed stage	12
HC feed flowrate (kmol/h)	100
Total distillate flowrate (kmol/h)	340
Reflux ratio (molar)	0.5
Holdup (kg of catalyst)	10,000

Figure 2: Design specifications of the reactive distillation process for ULSD production.

4. Bifurcation Analysis

The MSS solutions are analysed through bifurcation diagrams, which are built using a continuation method (Guckenheimer and Holmes, 1983), raking the steady state of the model when a bifurcation parameter value is increased or decreased. Two multiplicity types can be found: input and output multiplicities. Output multiplicity occurs when one set of input variables (manipulated variables) results in two or more unique and independent sets of output variables (measured variables). In chemical reactors and conventional distillation columns there are usually three steady states associated to ignition (high conversion), extinction (low conversion) and medium unstable conversion. Input multiplicity occurs when two or more unique sets of input variables produce the same output condition. This multiplicity has important implications for close loop control since it is related to the so-called zero dynamics of the system, which is associated with unusual, unexpected, or inverse responses of the outputs after a step change has been applied to the inputs.

4.1 Case studies

With the purpose of finding SSS or MSS regions, two feed composition cases considering different HDS reaction pathways are studied. The cases are as follows:
Case 1. HC feed composition with Th, BT, and DBT as the organo-sulfur compounds present in the HC feed (see Table 3 in Cárdenas-Guerra et al., 2010), and following only the hydrogenolysis reaction pathway.
Case 2. HC feed composition considering Th, BT, DBT and 4,6-DMDBT as the organo-sulfur compounds present in the HC feed (see Table 3 in Cárdenas-Guerra et al., 2010) and following both, the hydrogenolysis and hydrogenation reaction pathways.
Target conversion of 99.90 % for DBT, 99.3 % for 4,6-DMDBT, and complete elimination of Th and BT were assumed as part of the design specifications considering the feed composition and the reaction pathway described in Table 3 by Cárdenas-Guerra et al. (2010). Afterwards, bifurcation diagrams are constructed to find the SSS and MSS regions by increasing or decreasing several operating or design parameters, such as the reactive stages and catalyst load (liquid holdup). The reaction rate expressions, reaction rate coefficients and adsorption equilibrium constants of Th, BT, DBT and 4,6-DMDBT used for the determination of the steady state solutions are given in Cárdenas-Guerra et al. (2010).

4.2 Influence of the reactive stages

The influence of the reactive stages for case 1 showed that there is no evidence of multiplicity, i.e., only a SSS was observed; nevertheless, for case 2 we found a multiplicity region as shown in Figure 3(a). In this point, it is interesting to say that, while the DBT conversion is highly affected by the variation of the reactive stages, the 4,6-DMDBT conversion is practically constant (~99 %). In fact, it is found that there are two stable branches for DBT conversion (low and high) and an output multiplicity is determined for DBT conversion. This multiplicity is due to a hysteresis behaviour when the direction of change starts from the set of reactive stages 5-12, high conversions (ignition reactive zone) are obtained until the set of reactive stages 11-12, then when arriving to only one reactive stage (stage 12) there is a drastic decrease in the conversion (extinction reactive zone), and when the direction of change starts from the same set 12-12, the same values for the low conversions are obtained until the set of reactive stages 10-12, but then again a new branch with stable steady states appears.

4.3 Influence of the temperature

To show the effect of HLP, it is assumed that the catalyst in the reactive zones is completely wet; also, the HLP values are in the range of the catalyst loads used in the HDS conventional catalytic reactors (Stanislaus et al., 2010). This parameter was selected since it is a key variable (i.e., manipulated variable) to operate the process. The temperature along the column is the output variable determining the steady state multiplicity existence. The influence of the HLP for case 1, where the nonlinearities of 4,6-DMDBT kinetic expressions are not incorporated in the computation, exhibited no evidence of multiplicity (i.e., only a SSS). Figure 3(b) shows the influence of the HLP at the reactive zones on the performance of the RDP and it is clear that output multiplicity exits between HLP and the temperature along the column. For a value of 6,650 kg, the temperature will experience a downward jump to the lower branch when catalyst loaded at the reactive zones is increased slightly beyond the nominal operating condition; however, for a value of 4,300 kg the jump in temperature is upward when the HLP is, again, increased slightly beyond the nominal operating condition. Obviously, the temperature is a good candidate as a measured variable to be manipulated by HLP. On the other hand, regarding the three steady states for the temperature, two correspond to low and high conversion and they are stable, while the medium conversion one is unstable. Along the branch containing unstable steady state solutions, open loop operation is not possible and the control of unstable states becomes more difficult than controlling stable states. This means that the stable steady states of the upper branch (i.e., high conversion) outside the MSS region are a better selection as operating points (set points).

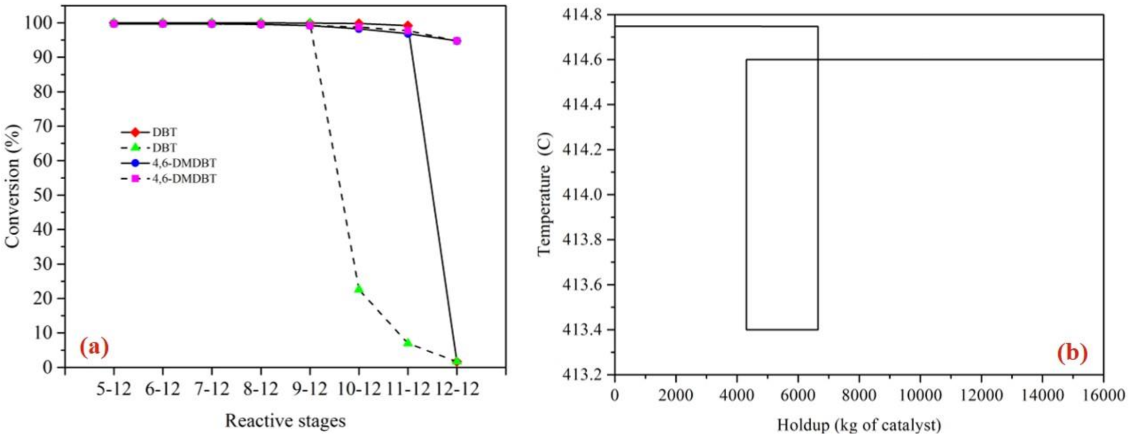


Figure 3: Bifurcation diagrams for DBT and 4,6-DMDBT conversion with the variation of (a) the reactive stages and (b) the holdup.

4.4 Steady state transitions

An open loop dynamic simulations was carried out in ASPEN DYNAMICS$^{®}$. The temperature and the operating pressure were increased by 0.5 % in a step change over 360 min. Only for the case 1, the column returned to the initial operating point quickly (i.e., for the pressure) without significant disturbance from the original condition. However, over the same period on the temperature, the column jumped to a low steady state. The responses for both output variables are shown in Figure 4.

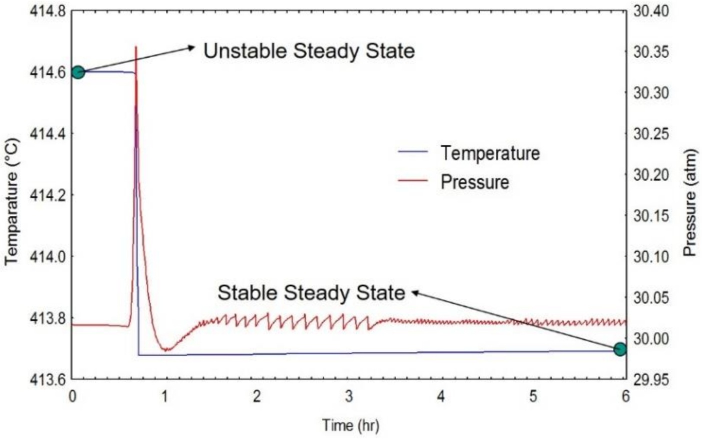


Figure 4: Transient behaviours for a positive step change in the HC feed composition.

5. Control System Design

As mentioned in previous section, the type of multiplicity can occur depending on the selection of the input or manipulated variable and of the output or measured variable, which are related to the control variables. The selection of these variables depends on the control objectives, for instance in a low-level control the objectives are to maintain the column pressure and the liquid levels of the reflux drum and reboiler sump. While in a high-level control, the interest is on the product compositions at the RDP bottoms or top. Therefore, the manipulated variables can be selected as: the reflux flowrate (RF), the reboiler heat duty (QR), the bottoms flowrate (BF) or the distillate flowrate (DF), and the control outputs are the product composition at the bottoms or top, or temperatures inside the RDP. Control system design consists of the selection of a control structure and a control algorithm. Regarding the control configurations, as in conventional distillation columns, there are six basic control configurations: RF-QR, RF-BF, RF-DF, DF-QR, DF-BF, QR-BF. The RF-QR configuration (see Figure 6a) considers the product composition at one or two points (top or/and bottoms) as measured variables and manipulates the RF and the QR (Kumar and Kaistha, 2007). This configuration agrees with the study of Cárdenas-Guerra et al. (2010) in the sense that it was shown that the most important manipulated variable at the top was the reflux ratio (equivalent to RF), while at the bottoms it was the QR; and the control output would be the bottoms composition that corresponds to the ULSD. Thus, an inferential control structure should be preferred, inferring the product composition from temperature measurements along the RDP according to the previous MSS analysis. To determine the temperature sensor location in our RDP, a sensitivity criterion has been done by applying step changes in the input variables (RF and QR) and in the main disturbance, hydrocarbon feed flowrate (HCFF). The idea is to find the stage where there is the largest change in temperature for a change in the manipulated variable. The corresponding results, reported as temperature changes along the RDP, are shown in Figure 5.

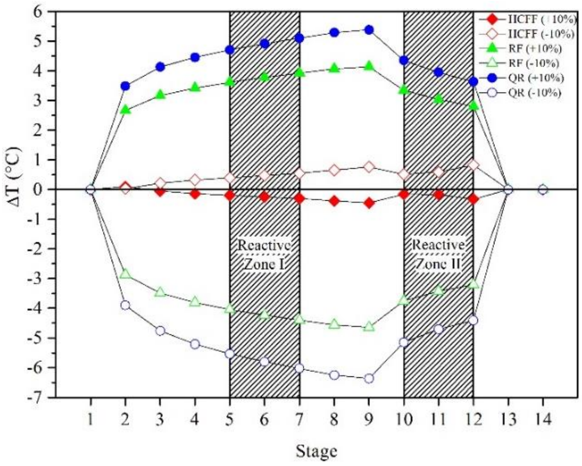


Figure 5: Stage temperature sensitivities for ±10 % changes in manipulated variables: HCFF, QR and RF.

It can be observed that the stage temperatures are quite sensitive to changes in RF and QR, while they do not change significantly when the HCFF is modified. These results suggest a preliminary control structure as follows: as the RDP temperatures are not sensitive to changes in HCFF and the main interest is on maintaining the H_2 to HC feed ratio equal to 3, then a feed ratio control scheme is required as shown in Figure 6(b). Regarding the top and bottoms RDP control, the most sensitive stages are 9 and 12 (the feed stages). However, following the methodology of two-point control structures, a third measure point is selected for our RDP in stage 4 (rectifying zone). So, that temperature sensors in stages 4 and 9 would be used to manipulate the RF and the one in stage 12 to manipulate the QR. In conclusion, the proposed inferential control structure for our RDP is presented in Figure 6(b).

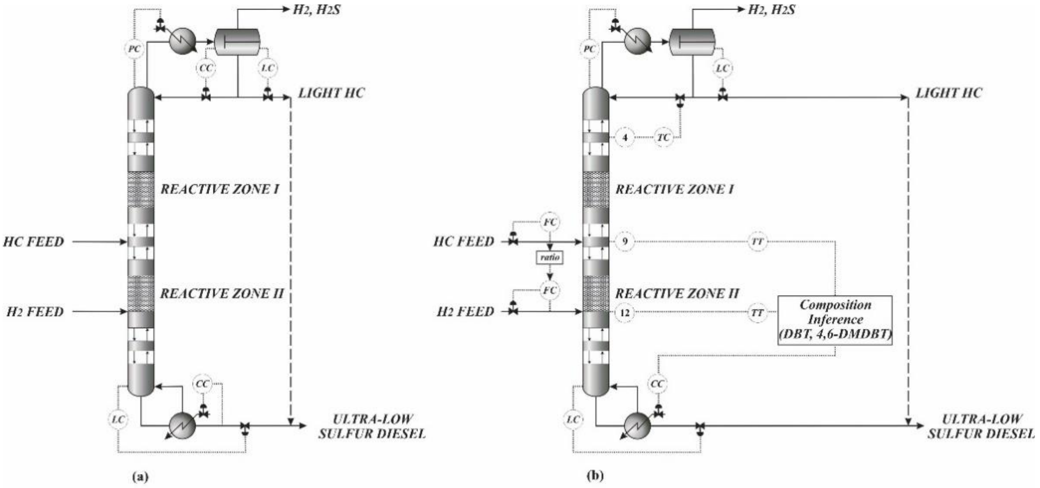


Figure 6: Reactive distillation control configurations: (a) conventional; (b) inferential temperature control.

6. Conclusions

A numerical bifurcation analysis of a RDP for the ULSD production has been presented. A multiplicity region still existed although the number of reactive stages was varied from 5 to 12. Nevertheless, by placing the HLP in one reactive stage (stage 12), there was a reduction in DBT conversion. A higher DBT conversion was achieved when the same amount of catalyst was distributed over 8 reactive stages (stages 5 to 12). The amount of catalyst loaded (up to 8,000 kg) into the reactive zones is in agreement with the extremely low reaction rate expression for 4,6-DMDBT elimination. For the output variable, as is the operating pressure, there was no evidence of a transition to another steady state for the disturbance considered. For the case 2, numerical errors associated with rapid changes in state variables produced incomplete solutions, possibly indicating an instability caused by a depletion of liquid in one part of the column. The inferential control of the diesel composition could be improved considered the delay time due to feed disturbances by means of an observer or detector (i.e., a control algorithm).

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