Steady State Multiplicity Analysis of Reaction-Separation Sequences for Deep Hydrodesulfurization of Diesel

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1. Introduction

Stringent environmental regulations are exerting pressure on the oil industry to improve the quality of diesel fuel. Therefore the European Union and United States agreed to reduce the sulfur content of diesel to 350 wppm from the year 2000, and 50 wppm starting from the year 2005. The fulfillment of this legislation presents serious changes in the oil refineries in terms of modifying the catalyst used and/or in the technology involved in the hydrodesulfurization (HDS) process; that is, a higher activity of the commercial catalyst and structural changes in the trickle bed reactor configuration to increase the sulfur-compounds conversion, are needed. In México, the maximum sulfur content allowed in the diesel is 500 wppm and it is thought that the reduction to 50 wppm will require a very important economical investment. Furthermore this mandatory reduction of sulfur in diesel is promoting the research of new catalytic systems and technological alternatives (Babich and Moulijn, 2003; Song and Ma, 2003).

An alternative strategy to the conventional process is to use a countercurrent contacting configuration of gas and liquid phases (Krishna, 2002). In this sense, several papers have pointed out the benefits of a countercurrent operation for the HDS of diesel, concluding that a countercurrent operation of a trickle bed hydrodesulfurization leads to a higher reduction of sulfur content than the conventional cocurrent operation (van Hasselt et al., 1999; Ojeda Nava and Krishna, 2004). An analysis of the operating conditions to obtain ultra-low sulfur diesel in a conventional HDS process (van Hasselt et al., 1999; Knudsen et al., 1999) suggests that reactive distillation (RD) could be an interesting technological alternative for deep HDS of diesel. In a RD process, the countercurrent operation is the natural operation mode and the internal flows requirement can be obtained through the catalyst packing arrangement, regulating the reflux and/or the boiling ratio, and properly placing the sulfured hydrocarbon feed.

Up to now, RD has emerged as a highly promising process because it combines *in-situ* two unit operations: distillation and reaction. This integration brings numerous advantages, for example: capital and operation savings, heat integration benefits, increased conversion of reactant conversion, improved product selectivity and avoidance of azeotropes. Specifically in the area of reactive distillation columns (RDCs) design, most of the existing work is based on the transformed composition variables proposed by Doherty's group (Doherty and Malone, 2001). An alternative to this approach is the element composition concept proposed by Pérez-Cisneros et al. (1997). The main advantage of this element composition representation is that it reduces the composition space domain and simplifies the phase equilibrium with chemical reaction (equilibrium or kinetically controlled) calculations (Sánchez-Daza et al., 2003). Also, the graphical visualization of the reactive phase behavior through reactive phase diagrams and/or reactive residue curve maps, constructed in terms of these element composition variables, is simplified. Specially, the reactive residue curve maps are highly useful tools to visualize and elucidate conceptual designs of reactive distillation processes.

There are a few woks in the open literature that applies the RD to the light gas oil HDS. Taylor and Krishna (2000) discussed the possibility to apply RD concepts to HDS of heavy oils. Nevertheless, there are few HDS units via RD in operation, and most of them are in the evaluation stages. Viveros-García et al. (2005) showed a comparison between deep HDS in a conventional reactor and the operational and design alternatives offered by a reactive distillation process. They noted that all the operation requirements for a deep HDS in a conventional reactor could be fulfilled by a reactive distillation operation if an appropriate design of the process is carried out.

However, 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 reactor is typically followed by a train of distillation columns. This behavior 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. These interactions between chemical reaction and distillation, lead to a highly nonlinear behavior in reactive distillation indicating the possible existence of multiple steady states (MSS); it has also been reported that the multiplicity may depend on thermodynamic models. Therefore, 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 (Abufares and Douglas, 1995; Georgiadis et al., 2002; Monroy-Loperena et al., 2000).

The existence of MSS in conventional distillation operation has been know to humankind for almost three decades and since then considerable effort has been devoted to understand and predict this unusual feature. In spite of the development of several simulation methods (singularity based methods and dynamics equilibrium models), the causes that originate have not been completely elucidated (Higler et al., 1999). Both input and output multiplicities have been described for the cases methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) reactive distillation by Sneesby et al. (1998). The RADFRAC module (from Aspen Plus simulator) has been used by Jacobs and Krishna (1993), Hauan et al. (1997) and for investigation of MSS in RDCs. For MTBE synthesis using the Jacobs-Krishna column configuration varying the location of the stage to which methanol is fed results in either a high or low conversion. When the methanol is fed to stages 10 or 11, MSS is observed (Higler et al., 1999). Explanation for the occurrence of MSS in the MTBE process was provided by Hauan et al. (1997). The ethylene glycol RD process also appears to be particularly interesting for the investigation of MSS (Monroy-Loperena et al., 2000). Güttinger and Morari (1999a, 1999b) develop the so-called ∞/∞ analysis for RDCs. The two infinities refer to infinite internal flowrates and an infinite number of stages, and the method is for the prediction of MSS in distillation. They conclude that the MSS are easily avoided by selecting appropriate control strategies. The first of these two papers deals with what the authors call non-hybrid columns, in which the reaction is assumed to take place on every stage of the column. The second paper relaxes this restriction and considers MSS in columns with a reactive section, and non-reactive stripping and rectification sections.

The occurrence of steady state multiplicity raises other problems related with start-up strategy that would drive the column to the desired steady state. In the absence of complete information on MSS, wrong conclusions might be draw on various aspects of design, operation and control. Thus, the analysis of existence of a single steady state (SSS) or MSS should give insight into the RD process, help to avoid unsafe operation conditions, and further facilitate various subsequent studies such as control, monitoring, data reconciliation, parameter estimation and optimization of existing plants.

Therefore, the objective of the present work is to systematically define the operation conditions and parameter sensibility under which SSS or MSS may occur and to determine the effect of their presence of a reactive distillation column (RDC) for the case study of deep HDS of diesel. The conceptual design of the RDC considered here was taken from recent work by Viveros-García et al. (2005). The MSS analysis is done through bifurcation diagrams for several case scenarios, showing its implication on the design and operation of the RDC since the popular commercial simulators do not have provision to find MSS directly.

2. The HDS reactive system

The sulfured-diesel has been modeled as a hydrocarbon mixture (HC) of four organo-sulfur compounds: thiophene (Th), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenthiophene (4,6-DMDBT); and of C_{11}-C_{16} paraffin blend as solvent medium: n-undecane (n-C_{11}), n-dodecane (n-C_{12}), n-tridecane (n-C_{13}), n-tetradecane (n-C_{14}) and n-hexadecane (n-C_{16}).

In general, there are two possible reaction paths for sulfur removal from the organo-sulfur compounds as illustrated in Figures 1 and 2 for DBT and 4,6-DMDBT, respectively.

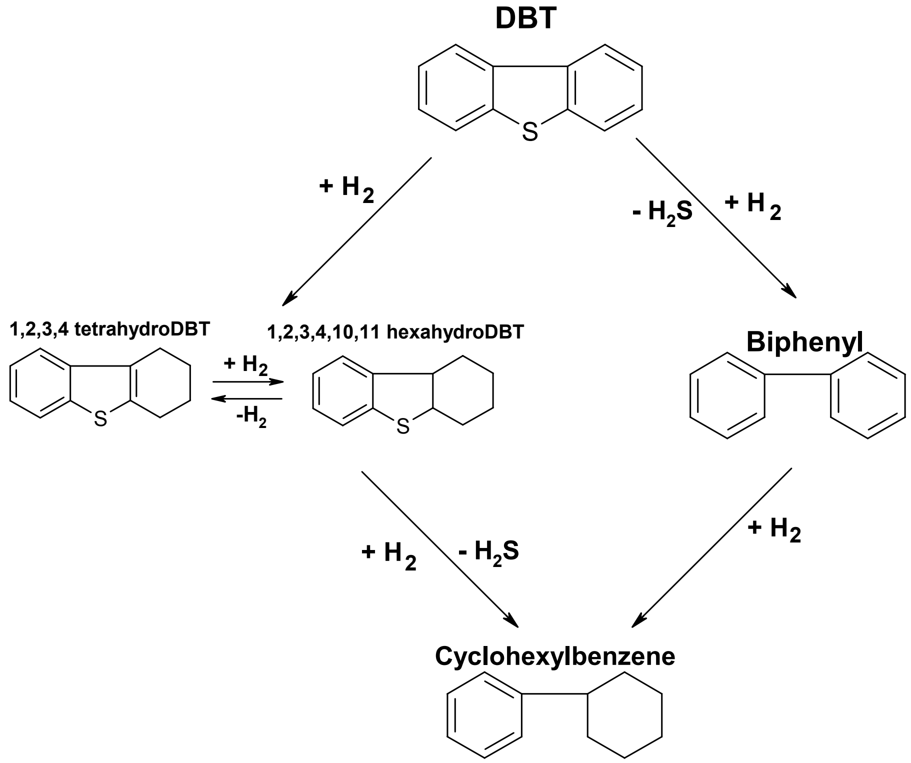

Fig. 1 Reaction pathways for dibenzothiophene hydrodesulfurization.

The first route is the sulfur atom direct extraction (hydrogenolysis) from the sulfured molecule. The second route is the hydrogenation of one aromatic ring followed by extraction of the sulfur atom extraction. The HDS reaction of Th, BT and DBT progress preferentially via the direct extraction route (Knudsen et al., 1999).

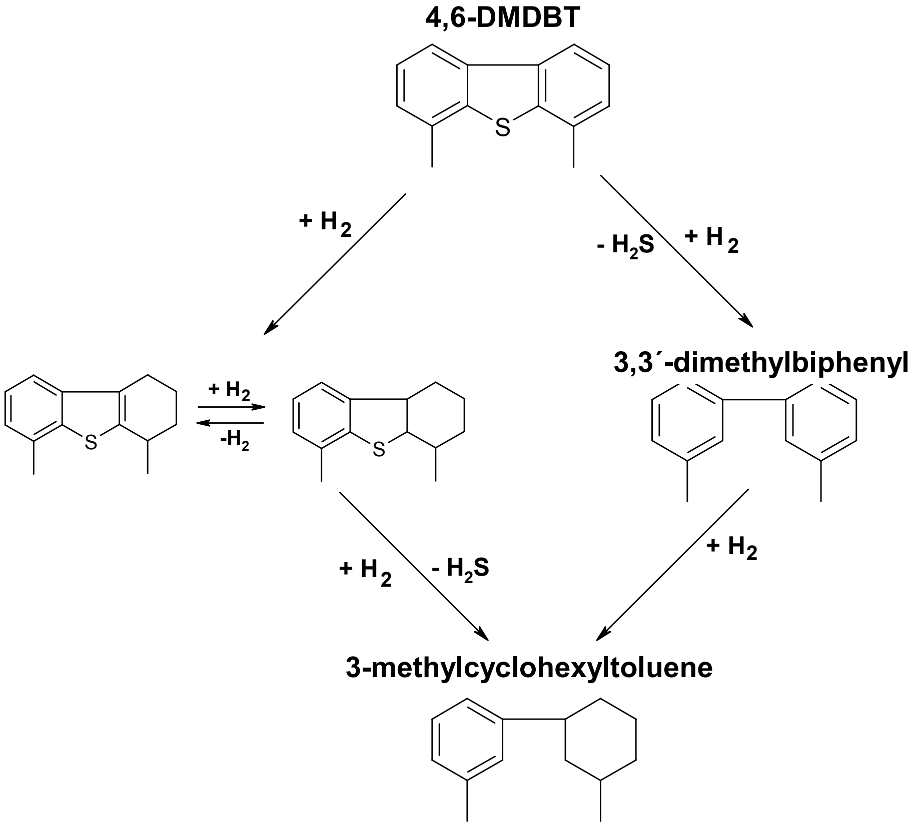

Fig. 2 Reaction pathways for 4,6-dimethyldibenzothiophene hydrodesulfurization.

When alkyl substitutes 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 route is relatively unaffected. Co-Mo catalyst desulfurize primarily via the direct (hydrogenolysis) route, while the Ni-Mo catalyst do it via the hydrogenation route. The extent to which a given catalyst acts via one route or the other is determined by the H_2 and H_2S partial pressures and feed properties. On the other hand, it is also well known that 80% of the HDS of 4,6-DMDBT goes by the hydrogenation route with conventional sulfide Ni-Mo catalysts (Bej et al., 2004). Therefore, modeling desulfurization kinetics of actual hydrocarbon streams is quite complex due to the presence of a wide variety of sulfur compounds, all of which have different reactivity.

For practical design purposes, desulfurization for various species may be lumped into the following reactions for hydrogenolysis and hydrogenation, respectively:

$$\upsilon_1 \left\{ \begin{matrix} \text{Th} \\ \text{BT} \\ \text{DBT} \\ \text{4,6-DMDBT} \end{matrix} \right\} + \upsilon_2 \text{H}_2 \rightarrow \upsilon_3 \left\{ \begin{matrix} \text{BD} \\ \text{Et} \\ \text{BPH} \\ \text{3,3'-DMBPH} \end{matrix} \right\} + \upsilon_4 \text{H}_2\text{S} \qquad (1)$$

$$\text{4,6-DMDBT} + 2\text{H}_2 \rightarrow \text{3-MCHT} + \text{H}_2\text{S} \qquad (2)$$

Where BD represents butadiene; Et, ethylbenzene; BPH, biphenyl; 3-3'-DMBPH, dimethylbiphenyl; 3-MCHT, 3-methylcyclohexyltoluene; and υ_i are the appropriate stoichiometric coefficients.

It is worth mentioning that the computation and visualization of the phase behavior of the reactive mixture is difficult. This is because of the complexity of the reactive mixture containing H_2 and H_2S, and the lack of experimental values for thermodynamic properties of some organo-sulfur compounds, i.e., 4,6-DMDBT and 3-3'-DMBPH. Compound volatilities or their normal boiling temperatures are the key thermodynamic properties, since they indicate the rate of vaporization/condensation of such compounds. Therefore, this lack of thermodynamic information leads to consider the prediction of the thermodynamic properties through group contribution methods or molecular simulation. According to the recent report of Viveros-García et al. (2005), contribution group methods of Marrero and Gani (2001) and Joback and Reid (1987) can be applied to infer the missing properties. For this work the Joback and Reid's method has been used.

The liquid phase HDS reactions (Eqs. 1-2) have been thoroughly studied and reported by several authors. In particular, kinetic expressions are taken from: Van Parijs and Froment (1986) for Th, Van Parijs et al. (1986) for BT, Broderick and Gates (1981) and

Froment et al. (1994) for DBT, Vanrysselberghe and Froment (1996) and Vanrysselberghe et al. (1998) for 4,6-DMDBT.

3. Conceptual design of the reactive distillation column

In the previous works of Pérez-Cisneros et al. (2002) and Viveros-García et al. (2005), the application of reactive distillation concepts to the deep HDS of diesel were carried out through a thermodynamic analysis considering the following aspects: *i)* the volatility of the organo-sulfur compounds, *ii)* their different reactivities, and *iii)* the analysis of reactive residue curves. Obtaining a RDC configuration (Figure 3) that consists of 14 stages with two reactive zones (where two types of catalysts are used) and three non-reactive zones.

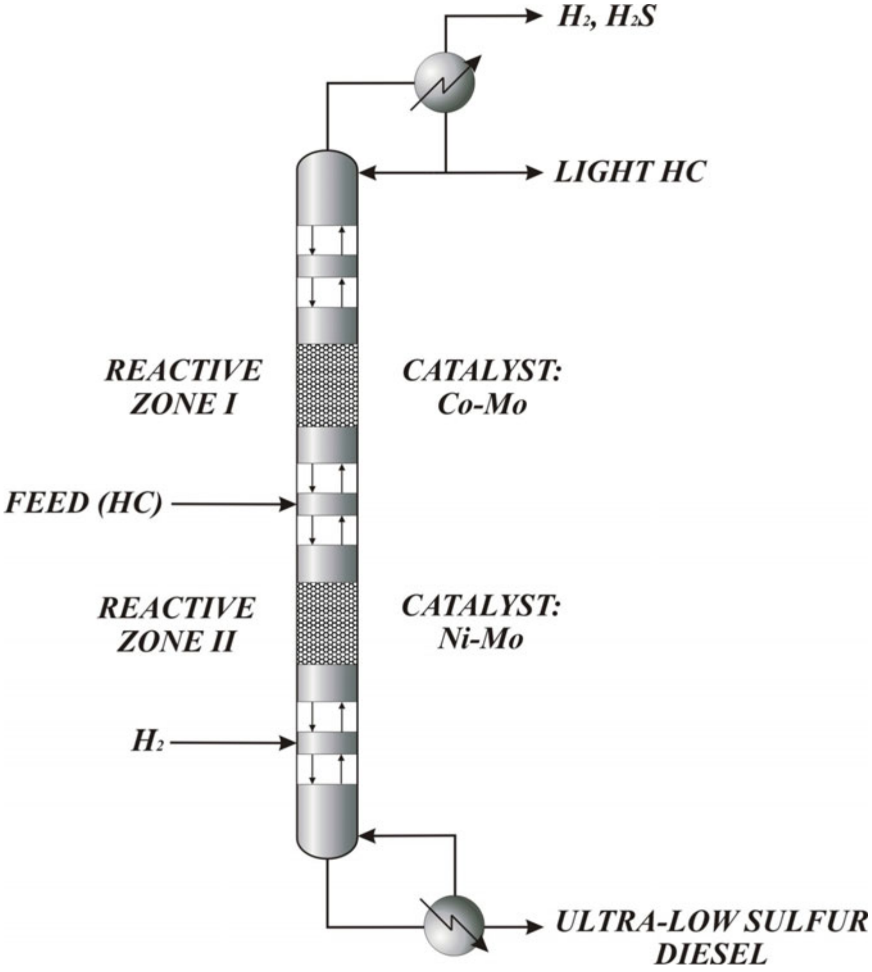

Fig. 3 Conceptual design of a reactive distillation column for ultra-low sulfur diesel production.

It was fixed an operation pressure of 30 atm in the reactive column and a H_2/HC feed relation of 3 was used. The phase equilibrium calculations were performed using the Peng-Robinson equation of state (Peng and Robinson, 1976). Table 1 shows the column configuration details for the simulations. Target conversion of 99% for the DBT and 4,6-DMDBT were assumed as part of the design specifications.

Table 1 RDC Design specifications.

Specification	Value
Number of total stages	14
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
H_2/HC feed relation	3
Molar reflux ratio	0.5
HC feed flowrate (kmol/h)	100
Distillate flowrate (kmol/h)	340
Holdup (kg catalyst)	10,000
Partial condenser temperature (K)	498.15
Column pressure (atm)	30

4. Case studies

With the purpose of analyzing the effect of the feed composition, the HDS reaction route, and the operation conditions in the existence of MSS, three case studies are considered as follows:

Case 1. HC feed composition A (given in Table 2), without including the 4,6-DMDBT, and following only the hydrogenolysis reaction route (Eq. 1).

Case 2. HC feed composition B (given in Table 2), which includes 4,6-DMDBT, and considering only the hydrogenolysis reaction route (Eq. 1).

Case 3. HC feed composition B (given in Table 2) and following both hydrogenolysis and hydrogenation reaction routes (Eqs. 1-2).

Table 2 HC feed composition.

Component	Feed A (Mole fraction)	Feed B (Mole fraction)
Th	0.0087	0.0080
BT	0.0087	0.0080
DBT	0.1	0.1000
4,6-DMDBT	0.0	0.0200
n-C_{11}	0.4966	0.4890
n-C_{12}	0.3166	0.3160
n-C_{13}	0.0089	0.0080
n-C_{14}	0.0015	0.0010
n-C_{16}	0.0589	0.0500

First a reference steady state is defined to achieve a target conversion of 99% mol for both DBT and 4,6-DMDBT, considering the feed composition that includes all components and the reaction scheme where both reaction routes are carried out (i.e. Case 3). Then, the influence of the RDC design over the DBT and 4,6-DMDBT conversions is shown for case 2. Finally bifurcation diagrams are constructed to find the SSS and MSS regions under several operation variables, such as: holdup, reflux ratio, HC feed stage and HC feed flow. In particular, to show the effect of the kinetic reaction rate, two different reaction rates for the DBT conversion are studied for Case 1, using kinetic expression given by: *i)* Broderick and Gates (1981), and *ii)* Froment et al. (1994). All this steady state analysis was performed using Aspen Plus 11.1^{TM}.

5. Reference steady state

As above mentioned, the reference steady state is obtained considering the design specifications given in the Table 1, the composition B given in Table 2 and the complete reaction scheme (i.e. Case 3), achieving good elimination of the organo-sulfur compounds for both DBT and 4,6-DMDBT conversions with target conversions over 99% as given in Table 3 (Case 3). In same Table 3, conversions achieved for Cases 1 and 2 are presented.

Table 3 Design composition targets for the RDC.

Case study	*DBT conversion (% mol)*	*4,6-DMDBT conversion (% mol)*
Case 1	99.99	-
Case 2	99.54	66.16
Case 3	99.90	99.35

As it can be seen, the DBT conversion is practically no affected by the reaction scheme nor by the presence of 4,6-DMDBT in the feed composition. But the same does not happen for the 4,6-DMDBT conversion as it is drastically reduced (from 99.35% to 66.16%) when only the hydrogenolysis reaction route is considered. Concluding, that the hydrogenation route of 4,6-DMDBT is very important and for it should not be excluded for a realistic RDC design.

A way of increasing the 4,6-DMDBT conversion is by modifying the RDC design by increasing the total number of stages of the RDC (either reactive or non-reactive stages) or changing the operating conditions (feed stages, feed flowrates, reflux ratio, etc.). For instance, some combinations that improve the 4,6-DMDBT conversion for Case 2 are given in the Table 4, by increasing the total number of reactive stages.

Table 4 Combinations to improve the conversion (Case 2).

Total number of stages	*Reactive stages*	*HC feed stage*	*H_2 feed stage*	*DBT conversion (% mol)*	*4,6-DMDBT conversion (% mol)*
13	5-7, 10-12	9	12	99.23	58.34
*14	5-7, 10-12	9	12	99.54	66.16
15	5-7, 10-14	9	13	99.97	80.21
16	4-8, 10-15	9	14	99.86	91.42

* Reference design specification.

Figures 4, 5 and 6 show the liquid composition of H_2 and organo-sulfur compounds (Th, BT, DBT, and 4,6-DMDBT), consumption of the organo-sulfur compounds and temperature profiles along the RDC for the three case studies. It can be noted that the maximum compositions are located at the HC feed stage (stage 9). The highest concentration of DBT is due to the amount of DBT in the feed stream and its high boiling temperature. Also, it can be observed that as the organo-sulfur compounds go into the reactive zones (stages 5-7 and 10-12), the concentrations of the three or four (according it is the case) species fall sharply to zero. In addition, the composition profile (higher concentration at the reactive zone I) suggests that the H_2S vaporization rate is larger at the stripping section. Therefore, the catalyst activity inhibition may be reduced at this section increasing the conversion of the heavier organo-sulfur compounds.

Regarding the organo-sulfur compounds consumption, the species are mainly consumed at stage 7 and 10, which are the incoming stages to the reactive zones. It should be pointed out that between the reactive zones there are two non-reactive stages (8 and 9) performing the separation and distribution of the organo-sulfur compounds. An interesting case is when both hydrogenolysis and hydrogenation routes are considered (Case 3). It can noted in Figure 6, that the hydrogenation route increases substantially the consumption of DBT and 4,6-DMDBT, which is also reflected in the final achieved conversions (as above shown in Table 3).

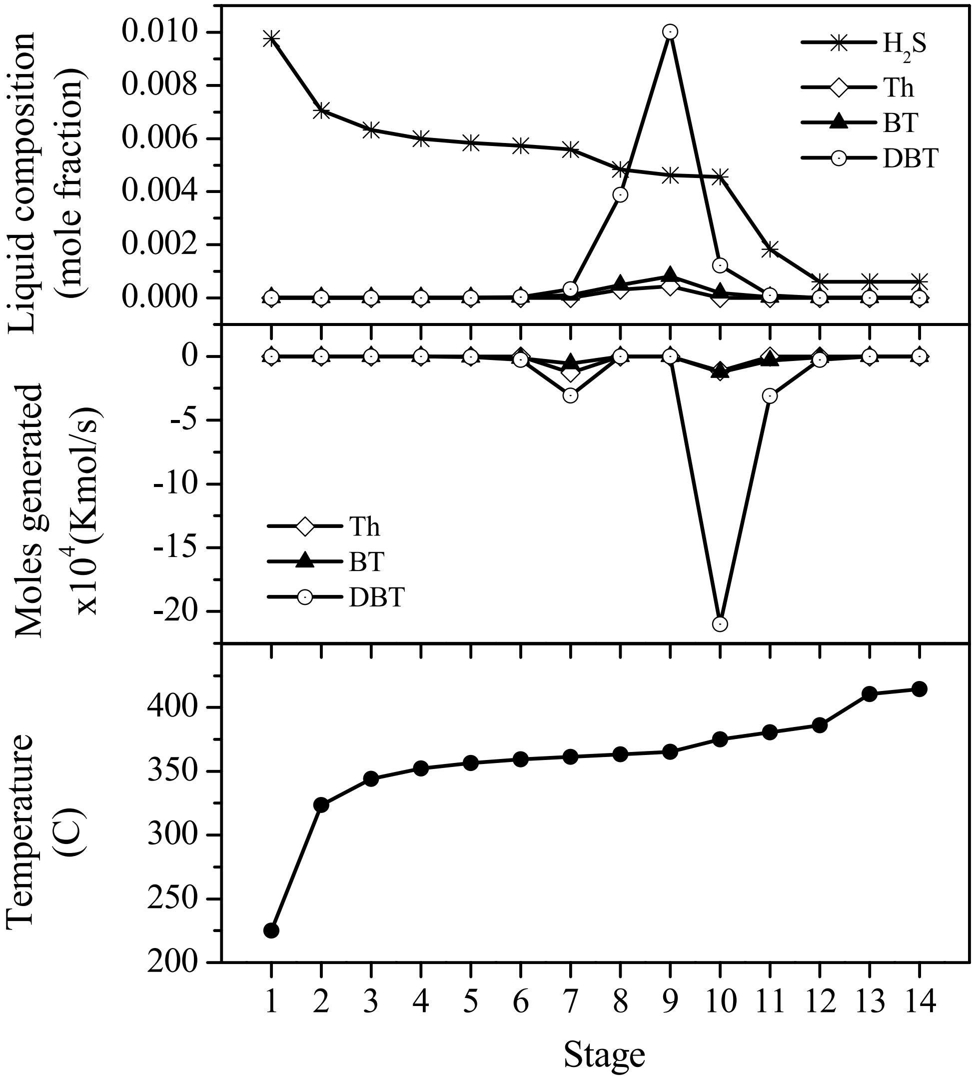

Fig. 4 Liquid composition, temperature and consumption profiles for Case 1.

The temperature profiles for all cases show that the reactive zone I operates close to isothermal conditions, while in the reactive zone II the temperature increases around 15 C. The isothermal behavior of zone I can be explained due to the solvent presence in the fuel diesel and the neglect of the heat released by the chemical reaction in the modeling. While the temperature increment in zone II may be explained due to the concentration increase of the heavy hydrocarbons and the moles generated in this reactive zone.

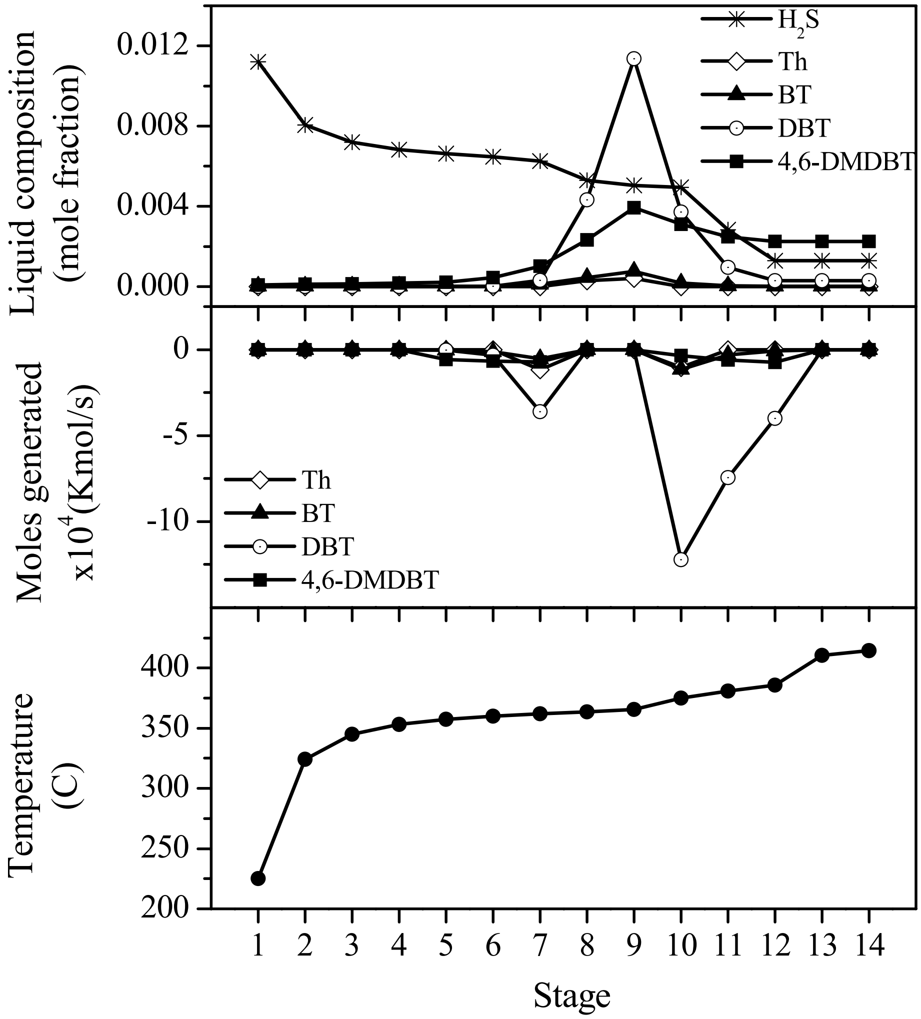

Fig. 5 Liquid composition, temperature and consumption profiles for Case 2

6. Analysis of Steady State Multiplicity

As mentioned in the introduction, RDCs are highly nonlinear, and MSS solutions have been reported by many researches, i.e., Güttinger and Morari (1999a, 1999b). In this work, the MSS is analyzed through bifurcation diagrams, which are built using a continuation method (Guckenheimer and Holmes, 1983), raking the steady state of the model when the value of a bifurcation parameter is increased or decreased. In fact, two multiplicity types can be found: input multiplicity and output multiplicity. Input multiplicity is associated with unusual, unexpected or inverse columns responses. It occurs when two or more unique sets of input variables produce the same out condition.

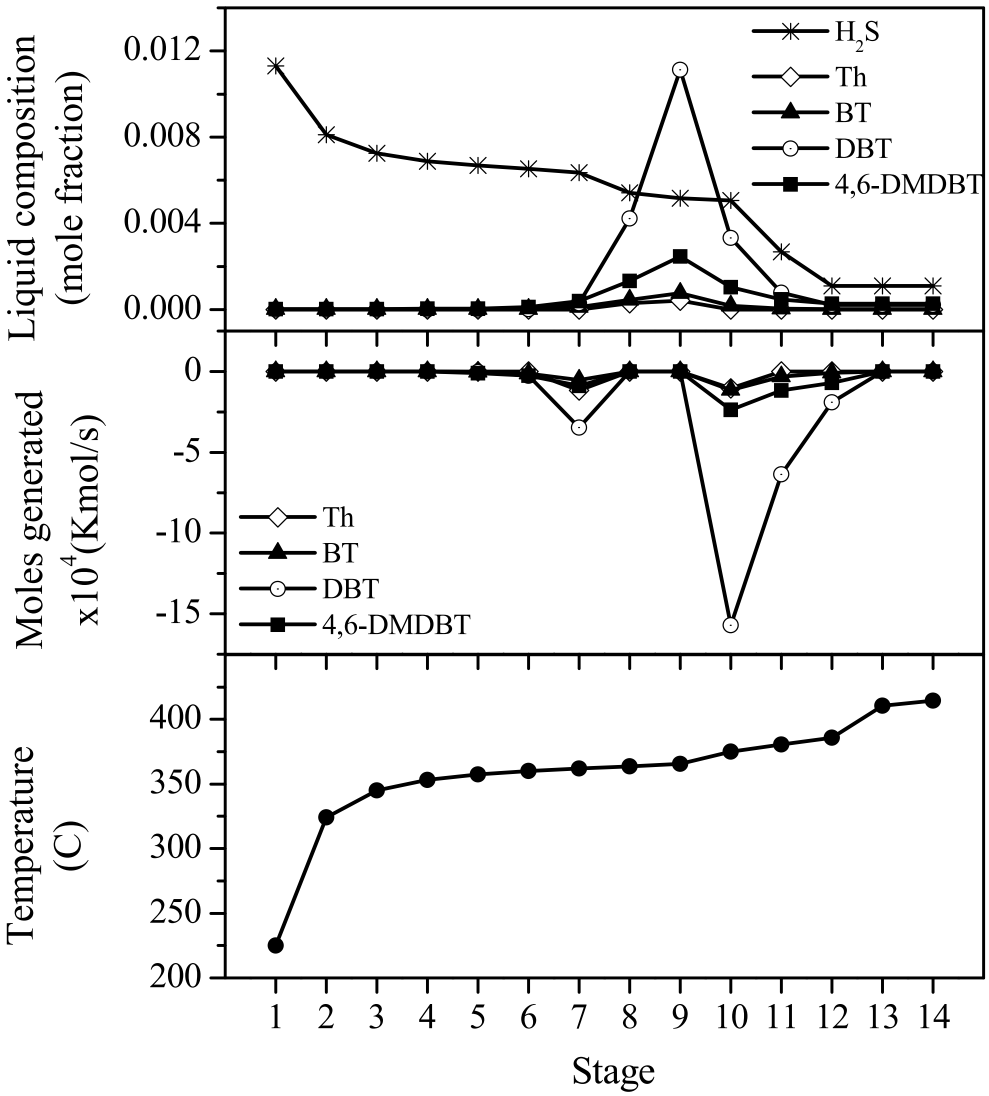

Fig. 6 Liquid composition, temperature and consumption profiles for Case 3

Output multiplicity occurs when one set of input variables results in two or more unique and independent sets of output variables. Moreover, a combined input-output multiplicity may be also encountered.

Next the effect of the DBT kinetic reaction rate and some operating conditions (holdup, reflux ratio and HC feed stage) are discussed in the generation of SSS or MSS. A summarize of the results found about the type of MSS is presented in Table 5.

Table 5 Summarize: Analysis of Steady State multiplicity.

	MSS type					
	Case 1		*Case 2*		*Case 3*	
Bifurcation parameter	DBT	4,6-DMDBT	DBT	4,6-DMDBT	DBT	4,6-DMDBT
Holdup	X	-	O	I-O	O	I-O
Reflux ratio	X	-	O	I-O	O	I-O
HC feed stage	X	-	O	O	O	O

X: No multiplicity, I: Input multiplicity, O: Output multiplicity

6.1. Effect of the DBT kinetic reaction rate

In order to study this effect, Case I (where 4,6-DMBDT does not interfere) is considered. The two following kinetic expressions for the hydrogenolysis reaction of DBT are studied:

$$r_{3,\sigma} = \frac{k' K_{DBT} K_{H_2} C_{DBT} C_{H_2}}{\left(1 + K_{DBT} C_{DBT} + K_{H_2S} C_{H_2S}\right)^2 \left(1 + K_{H_2} C_{H_2}\right)} \tag{3}$$

$$r_{3,\sigma} = \frac{k_1 K_{DBT,\sigma} K_{H_2,\sigma} C_{DBT} C_{H_2}}{\left(1 + K_{DBT,\sigma} C_{DBT} + \sqrt{K_{H_2,\sigma} C_{H_2}} + K_{H_2S,\sigma} \dfrac{C_{H_2S}}{C_{H_2}}\right)^3} \tag{4}$$

The kinetic constants for these expressions are given in Broderick and Gates (1981) and Froment et al. (1994), respectively.

Bifurcation diagrams were built using both kinetic expressions and for most of the operating conditions (as bifurcation parameters): holdup, reflux ratio, HC feed stage, HC feed flow, H_2 feed flow, distillate ratio, condenser temperature and DBT feed composition.

The main variables that affect the steady state behavior changing drastically the final elimination of sulfur compounds were: holdup, reflux ratio, HC feed stage, and HC feed flowrate (as shown in Figures 7a-7d); while the other variables do not modify significantly the final conversion. Moreover, all the bifurcation diagrams exhibited no evidence of multiplicity (i.e. only SSS). According to Figures 7a-7d, the DBT kinetic reaction does not affect significantly the final DBT conversion; excluding the HC feed flow (Figure 7d).

From the results, it can be observed that the holdup (Figure 7a) must be greater than 1,000 Kg to keep a DBT conversion around 99%; while below 1,000 Kg there is a strong decline of the conversion. Something similar happened with the reflux ratio (Figure 7b), its value must be greater than 0.4, otherwise with lower values there is a decrease in the DBT conversion. For the HC feed stage (Figure 7c), the HC feed must be done between the stages 4-12 (i.e. in the reactive stages or the non-reactive stages that are located in the middle) to maintain a 99% DBT conversion; if not, the DBT conversion can drop up to 90%. On the other hand, the variation of HC feed flow presented a dependence of the DBT kinetic expression (Figure 7d), so that to reach the 99% of DBT conversion, the HC feed flow must be kept below: (a) 440 Kg/h when using Eq. (3) (Broderick and Gates, 1981), or (b) 330 Kg/h when using Eq. (4) (Froment et al., 1994); above these values there is a constant decrease of the DBT conversion (more rapidly when using Eq. 4).

However there is a region below 200 Kg/h where the prediction of both expression coincide, meaning that the RDC should be operated with HC feed flows in this region to assess a good conversion of DBT.

6.2. Effect of the holdup

Figures 7a, 8a and 9a show the effect of varying the holdup in the RDC for the three case studies, respectively. As aforementioned Case 1 does not present MSS, but

Cases 2 and 3 reveal the existence of MSS in the HDS system: output multiplicity for DBT conversion and input-output multiplicity for 4,6-DMDBT conversion.

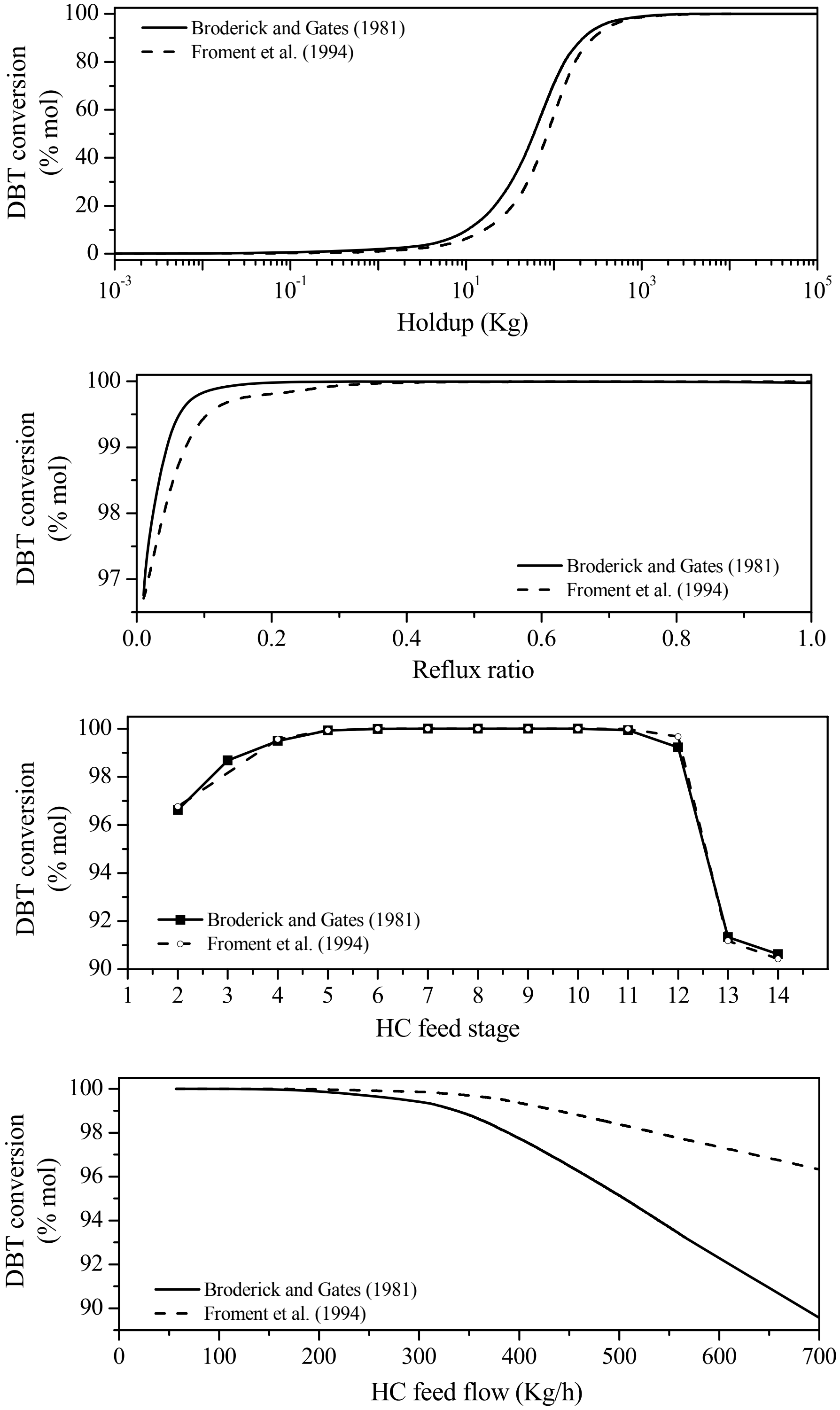

Fig. 7 Bifurcation diagrams using two kinetic expressions for DBT for Case 1: (a) holdup, (b) reflux ratio, (c) HC feed stage, (d) HC feed flow.

For Case 2 (Figures 8a) at holdups between 7,150 and 8,500 Kg and for Case 3 (Figure 9a) at holdups between 4,300 and 6,650 Kg, there are three steady state solutions that for a same value of the holdup, and each solution corresponds to different conversions of DBT and 4,6-DMDBT. In addition, as 4,6-DMDBT conversion presents both input and output multiplicity, this implies that a same 4,6-DMDBT conversion can be obtained at two different values of the holdup. When only a SSS is present, such steady state is stable. On the other hand, when three steady states are present, the ones corresponding to low and high conversion are stable; while the other one corresponding to middle conversion 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. Meaning that the stable steady states of the upper branch (i.e. with high conversion) outside the MSS region are better to be selected as operating points (set points). According to this, the holdup should be kept in a value greater than: (a) 1,000 Kg for Case 1, (b) 8,500 Kg for Case 2, and (c) 6,650 Kg for Case 3. Of course, it must keep in mind that the more realistic case study is Case 3, as it considers a diesel composition with all four organo-sulfur compounds and a complete reaction scheme.

6.3. Effect of the reflux ratio

The variation of the reflux ratio as bifurcation parameter is shown in Figures 7b, 8b and 9b the three case studies respectively. A similar behavior to the holdup variation is obtained: Case 1 does not present MSS, while Cases 2 and 3 present output multiplicity for DBT conversion and input-output multiplicity for 4,6-DMDBT conversion. The MSS region is found between reflux ratio values of 0.435 and 0.35 for Case 2, and 0.22 and 0.345 for Case 3. Meaning that stable steady states with high conversion outside the MSS region are located in reflux ratio values greater than: (a) 0.4 for Case 1, (b) 0.435 for Case 2, and (c) 0.345 for Case 3; which are values very close.

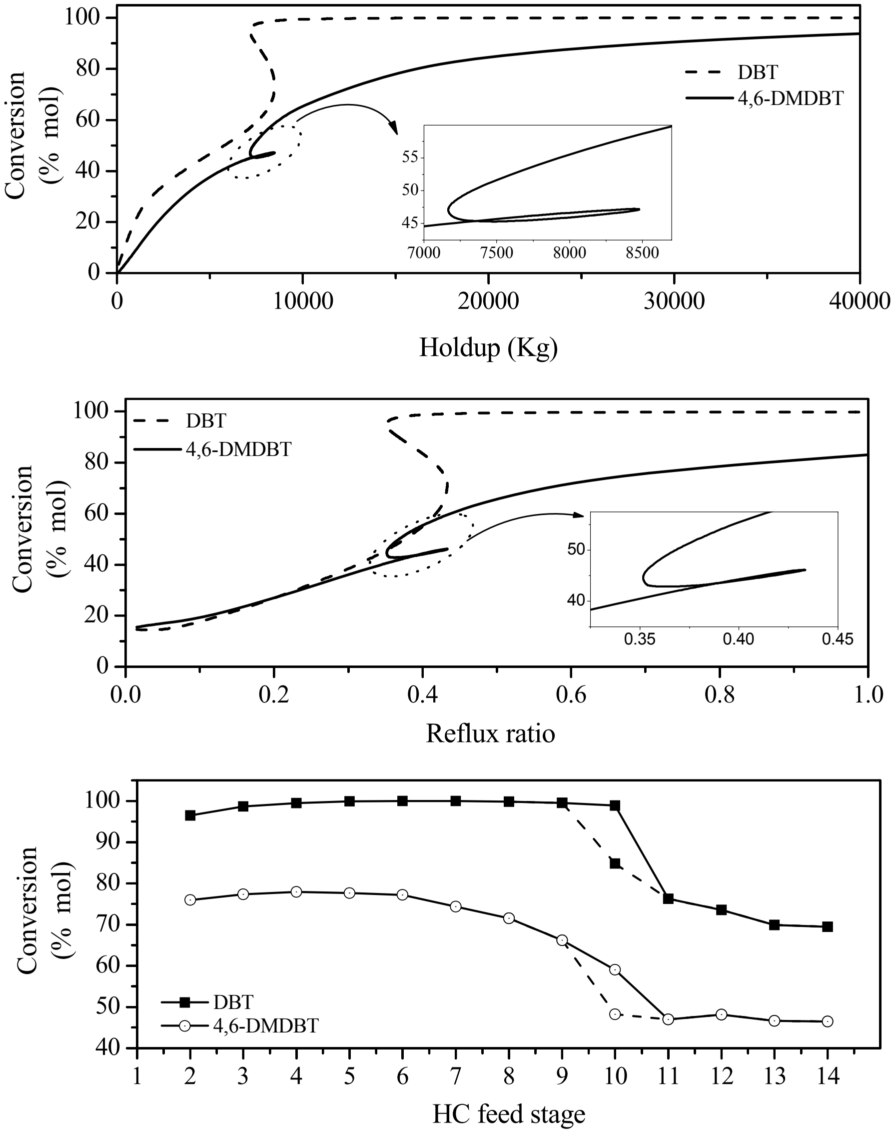

Fig. 8 Bifurcation diagrams for Case 2: (a) holdup, (b) reflux ratio, (c) HC feed stage.

6.4. Effect of the HC feed stage

Finally the effect of varying the HC feed stage is shown in Figures 7c, 8c and 9c-d. In particular for Case 3, two holdup values are considered (Figures 9c and 9d) to show its combined effect in the multiplicity analysis (where the reference value for the holdup is 10,000 Kg as stated in Table 1). As the values of the HC feed stage are integer numbers, then the results from bifurcation analysis are different to the previous ones. According to the results when the reference holdup (10,000 Kg) is used: (a) Case 1 has only SSS (Figure

7c), (b) Case 2 present output multiplicity but with only two stable branches (Figure 8c), and (c) Case 3 presents also SSS (Figure 9c), with a similar behavior to Case 1 as described in Section 6.1. However for Case 3, we found that the output multiplicity exists for lower holdup values, as it can be seen in Figure 9d for a holdup value of 5500 Kg.

For Case 2 with holdup of 10,000 Kg and Case 3 with holdup of 5,500 Kg, the output multiplicity is due to a hysteresis behavior: (a) when the direction of change starts from feed stage 2, high conversions (ignition reaction zone) are obtained until feed stage 10, then when arriving to feed stage 11 there is a drastic decrease of the conversion (extinction zone); and (b) when the direction of change starts from feed stage 14, same values for the low conversions are obtained until stage 10, but then a new branch with stable steady states appears (dashed lines). Once again to avoid the MSS region and keep high conversions, the HC stream should be fed between stages: (a) 4-12 for Case 1, (b) 4-9 for Case 2, and (c) 4-11 when the holdup is 10,000 Kg or 4-8 when the holdup is 5,500 Kg for Case 3.

7. Conclusions

The rigorous analysis of steady state multiplicity of a RDC for deep HDS of diesel has been presented. First the corresponding profiles were obtained, achieving good elimination of sulfur compounds with 99% conversions of DBT and 4,6-DMDBT. Then the effect of several operation conditions were analyzed, for instance changes in holdup, reflux ratio, HC feed stage and HC feed flowrate. According to the analysis, feasibility regions to obtain high conversions can be guaranteed selecting those operation conditions outside of the multiplicity region (i.e. in the upper stable branch of the bifurcation diagrams), for example: with high values of holdup, moderate values of reflux ratio and the HC feed stage located in the reactive zones or between them.

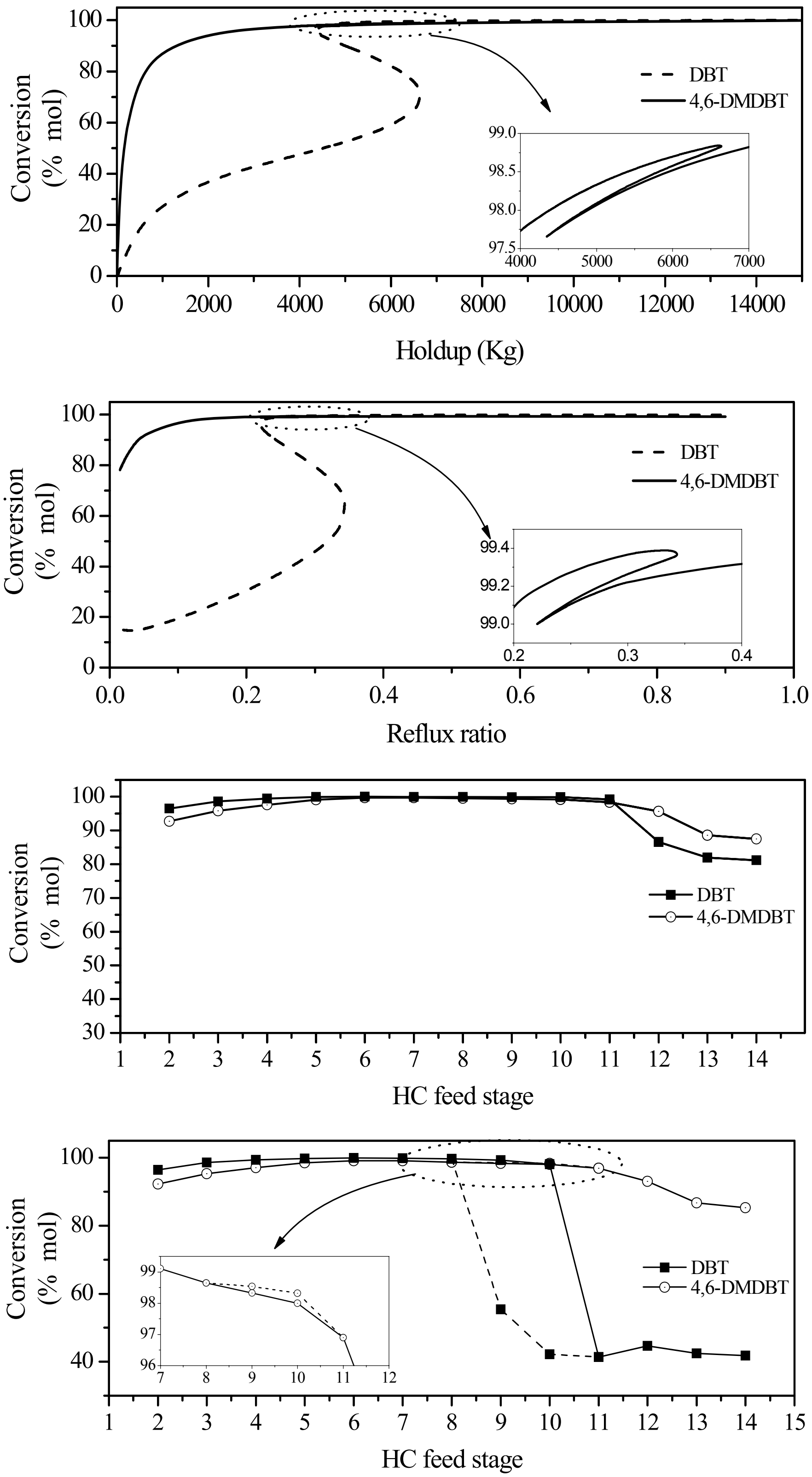

Fig. 9 Bifurcation diagrams for Case 3: (a) holdup, (b) reflux ratio, (c) HC feed stage (Holdup _+ 10,000 Kg), (c) HC feed stage (Holdup = 5,500 Kg).

However, from an industrial point of view, frequently is desirable to operate the process in the region of unstable multiplicity, since the reaction rate can allow high conversion and productivity, guaranteeing moderate temperatures that prevent the secondary reactions or the deactivation of the catalyst. Therefore, the implementation of a control is necessary to reach the unstable steady state, implying the selection of input and output control. In this case, the analysis of multiplicity is outstanding for control purposes, since the possible inputs (HC feed flow, reflux ratio, condenser temperature, etc.) have been studied in this work as bifurcation parameters.

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The conceptual design of the RDC considers two reactive zones operating with different catalysts, where the HDS of the diesel is carried out by means of two paths (hydrogenolisis and hydrogenation).

Posteriormente, Pérez-Cisneros y col. [42] presentaron un análisis de la aplicabilidad de los conceptos de destilación reactiva para el proceso de HDS. Estos autores obtienen un diseño conceptual de una columna de destilación reactiva a través de mapas de curvas residuales reactivas (basadas en el concepto de composición de *elemento*) a diferentes presiones de operación para el DBT y H_2, utilizando la cinética propuesta por Broderick y Gates [9]. El cálculo del equilibrio de fases fue determinado con la ecuación de estado de Peng-Robinson modificada por Stryjek y Vera [52]. En los mapas de curvas residuales reactivas se definieron tres regiones, cada una conectada a los nodos estables de los componentes Org-S-H_2S, lo que indica que esta zona debiera evitarse para eliminar el H_2S de la mezcla líquida, ya que reduce la actividad del catalizador. Las otras dos regiones presentan nodos estables entre Org-S – Org-3H_2 y Org-3H_2 – H_2. Esto indica la posibilidad de diseñar una columna de destilación reactiva con una zona reactiva, donde la eliminación del compuesto orgánico azufrado se realiza simultáneamente con la producción de H_2S en la fase líquida y la subsiguiente vaporización del H_2S, y otra zona reactiva donde pueden manejarse los compuestos de azufre más difíciles de hidrotratar (como el 4,6-DMDBT), con una mayor concentración de H_2. Este análisis condujo a los autores a realizar un diseño preliminar de una columna de destilación reactiva con dos zonas reactivas: *i)* una en la parte alta de la columna con catalizador Co-Mo y *ii)* otra en el fondo de la columna con catalizador Ni-Mo. Con esto, seis diferentes configuraciones de CDR fueron validadas a través de simulaciones numéricas logrando un 99.6% de conversión de DBT.

En un trabajo posterior, Aguilar-Escalante y col. [3] mostraron la factibilidad de la eliminación de tiofeno (T), benzotiofeno (BT) y DBT en una sola columna con dos zonas reactivas para obtener diesel ultra-limpio. El tiofeno y el benzotiofeno se excluyen preferentemente en la zona reactiva superior, mientras que el DBT se consume en la zona reactiva inferior. El análisis esta basado en el cálculo de mapas de curvas residuales no reactivas y reactivas para la eliminación del DBT. La presión de operación de la columna de destilación reactiva fue considerada de 30 atm. Se encontró que la concentración del solvente (n-hexadecano) es muy importante en la determinación de la solubilidad del H_2 y H_2S en la mezcla reactiva; además, se analizó el efecto de dos expresiones cinéticas considerando solamente la ruta de reacción de hidrogenólisis [9, 15], concluyendo que debe tenerse mucho cuidado con la selección de la expresión cinética.