THERMODYNAMIC ANALYSIS OF THE DEEP HYDRODESULFURIZATION OF DIESEL THROUGH REACTIVE DISTILLATION

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ABSTRACT

A thermodynamic analysis for the deep hydrodesulfurization of diesel through reactive distillation has been performed. The analysis is based on the computation of reactive and non-reactive residue curve maps for elimination of dibenzothiophene. It was found that the solvent concentration is very important in determining the solubility of hydrogen and hydrogen sulfide in the reactive mixture. From the reactive residue curves, it could be observed that, there is a high temperature region were the vaporization effects favor the elimination of dibenzothiophene. Based on this, a conceptual reactive distillation column design considering two reactive zones was developed. Due to the volatility differences, thiophene and benzothiophene are preferentially eliminated at the reactive zone I, located above the hydrocarbon feed stream, while dibenzothiophene is consumed mainly in reactive zone II, located below the feed stream. Rigorous steady state simulations using two different reaction rate expressions for elimination of dibenzothiophene were performed. The results show that extreme caution should be taken in using reaction rates expressions reported in the open literature, since despite a specified conversion is achieved, untrustworthy results could be obtained.

INTRODUCTION

The worldwide regulations concerned to improve the quality of diesel transport fuel are increasing the pressure on the oil industry. The European Union agreed on specifications for the future quality of diesel. These specifications consider that a maximum permissible sulfur content of diesel will be 350 wppm from the year 2000, and 50 wppm from the year 2005. This required reduction is promoting 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 reactor configuration to increase the sulfur-compounds conversion, are needed. Specifically, the diesel produced in Mexican (PEMEX) refineries contains around 500 wppm of sulfur and is though that the reduction to 50 wppm will require an investment of 195.5 MMUSD. Therefore, the study and analysis of the different technological alternatives are considered to be high priority.

The conventional HDS process (see Furimsky,1998) uses several types of commercial catalytic reactors (fixed-bed, moving-bed, LC-fining, etc) operating under a similar principle, but with technical differences, that is, the fixed-bed reactor is preferred to process light feeds, while the moving-bed reactor is selected for hydroprocessing of heavy feeds. The catalysts employed are chosen depending of the feed properties and usually include supported molybdate and tungstate catalysts promoted by either Ni or Co. γ-alumina, zeolites, silica and silica aluminates are among common supports. Recently, Knudsen *et al*. (1999) have pointed out that the reactivity of the most common catalysts (Ni-Mo and Co-Mo) are different depending on two main factors: i) the pressure (high pressure favors Ni-Mo) and, ii) the amount of heterocyclic compounds (low amount of heterocyclic compounds favors Co-Mo). Also, they stated the influence of the operating conditions in a conventional reactor for deep desulfurization, this is, how the residence time, hydrogen partial pressure, hydrogen sulfide partial pressure, recycle gas-oil ratio and improved vapor/liquid distribution, affect the process.

In another excellent work, Van Hasselt et al. (1999) pointed out that a countercurrent operation of a trickle-bed reactor could lead to a higher reduction of sulfur content than the conventional cocurrent operation. They also show that the flooding limits (i.e., commercial flow rates) are attained by using a finned monolith catalyst packing. Advances in the development of new catalysts for cleaning diesel have been carried out in Argonne National Laboratories (2001). Argonne scientists recently identified several new diesel fuel desulfurization catalysts with improved HDS activity and selectivity. The researchers synthesized and tested the new catalysts at 400° C and 400 psig, and believe it may be possible to achieve optimal HDS processing at lower temperatures and/or pressures – even for heavier crude oils.

There are few papers addressing the application of reactive distillation to the deep HDS of diesel. Taylor and Krishna (2000) revealed why it could be possible the application of reactive distillation concepts to hydrodesulfurization of heavy oils. Hidalgo-Vivas and Towler (1998) presented several alternative flowsheets for reducing the sulfur content below 500 wppm without a significant increase in the process hydrogen requirement and with energy integration. Their simulation results, however, do not show how such processes were designed, that is, number of

reactive and non-reactive stages, feed locations, etc. On the other hand, CdTech company (2000) claims to have the complete development of the reactive distillation technology for ultra-low sulfur diesel production, but that information is not open to the public domain.

The detailed analysis of the operating conditions to obtain ultra-low sulfur diesel in a conventional HDS process stated by Knudsen *et al*. (1999) and Van Hasselt et al. (1999) suggest that reactive distillation could be an interesting technological alternative for deep hydrodesulfurization of diesel. In a reactive distillation process the countercurrent operation is the natural operation mode and the flooding requirement can be obtained through, both, the catalyst packing arrangement or by manipulating the reflux and/or boiling ratio variable. A comparison between the deep HDS in a conventional reactor and the operational and design alternatives offered by a reactive distillation process are presented in table 1.

Table 1. Deep Hydrodesulfurization of Diesel. a) conventional process, b) reactive distillation alternative

a) Requirements for deep-HDS of diesel in a conventional process	b) Operating and design options in a reactive distillation operation
Counter-Current operation	• The nature of the reactive distillation process offer a counter-current operation
High Residence times	• Increased Condensed Recycle
Increased H_2 partial pressure	• Fresh H_2 feeds located in appropriate places along the column
Reduced H_2S partial pressure	• Elimination of H_2S through vapor side streams.
Catalyst Co-Mo based: higher activity at low temperatures and it follows the direct route of sulfur elimination.	• A reactive catalytic zone could be located over the HC feed with this type of catalyst, considering the temperature profile of the column.
Catalyst Ni-Mo based: higher activity at high temperatures and it follows the hydrogenation route with high partial pressures of H_2	• A reactive catalytic zone could be located below the HC feed with this type of catalyst, considering the temperature profile of the column (higher temperature at the bottom of the column).
Appropriate distribution of liquid/vapor	• Selection of the appropriate plate design for the non reactive stages and the height and type of packing (i.e., monolith)

Despite the above, the application of the reactive distillation concepts to deep hydrodesulfurization of diesel requires a careful analysis of the reactive system in terms of –at least- three main items. i) thermodynamics; ii) reaction kinetics and iii) transport phenomena. The thermodynamic analysis plays a crucial role in the application of the reactive distillation technology. The appropriate knowledge of the behavior of the phases and the different components in the reacting mixture determine the separation feasibility. The visualization of this behavior through reactive phase diagrams and/or reactive residue curve maps is needed to indicate the trend of the reaction and separation of the phases. The certainty of correct

reaction kinetics expressions is very important, since the effect of inappropriate reaction kinetics for any reaction may lead to non-sense results and unreliable process designs. Therefore, careful planning of the experiments for determining the reaction kinetic expressions under boiling conditions should be carried out. The transport phenomena point of view is, perhaps, the most complicated. Since, most of the catalytic reactions are affected by the rates of heat and mass transfer and the size and geometry of packing, transport coefficients are necessary and its the experimental determination is rather quite hard. Besides, in reactive distillation one deals with concentrated multi-component systems where the Fickia'n approach is not necessarily correct. Nevertheless, very important advances on this area have come out from Taylor and Krishna (2000).

The objective of the present work is to perform a thermodynamic analysis of the deep hydrodesulfurization of diesel in terms of reaction-separation feasibility. The analysis considers the computation of reactive residue curve maps for the elimination of dibenzothiophene. Based on this analysis, a conceptual design of a reactive distillation process is developed and rigorous numerical simulations for the production of ultra-low sulfur diesel are performed to validate such design.

THE HDS REACTIVE SYSTEM AND THE *ELEMENT* APPROACH

In general, there are two possible reaction pathways for removal of sulfur from dibenzothiophene, as shown in figure 1. The first pathway is direct extraction (hydrogenolysis) of the sulfur atom from the molecule. The second pathway is pre-hydrogenation of one aromatic ring followed by extraction of the sulfur atom.
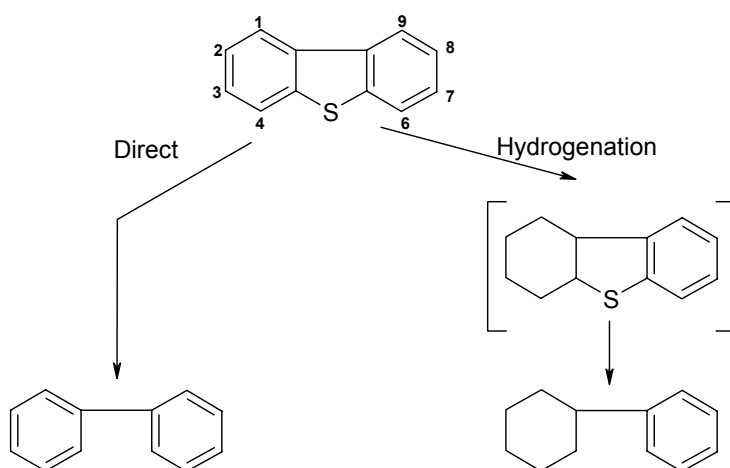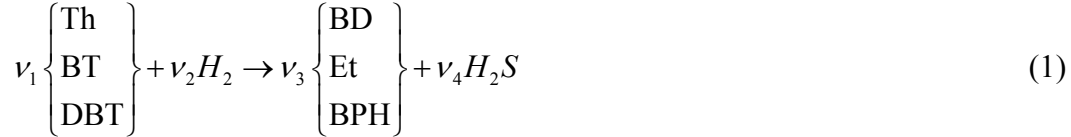

Fig. 1 Reaction pathways for HDS of DBT

Model compound tests have shown that the HDS reaction for dibenzothiophene (DBT) preferentially progresses via the direct extraction route. When alkyl substituents are attached to the carbon atoms adjacent to the sulfur atom, the rate for direct sulfur extraction is diminished whereas the rate for sulfur removal via prehydrogenation route is relatively unaffected. Co-Mo catalyst desulfurizes primarily via the direct desulfurization route, while the Ni-Mo catalyst via hydrogenation route. The extent to which a given catalyst desulfurizes via one route or the other is

determined by the effect of H_2 partial pressure, H_2S partial pressure and feed properties.

In the present work, only the hydrogenolysis reaction route is considered. In fact, modeling kinetics of desulfurization of actual hydrocarbon streams is quite complex due to the presence of a wide variety of sulfur compounds, which all have different reactivity. For practical purposes, desulfurization of various species may be lumped into the following reaction:

$$\nu_1 \begin{Bmatrix} Th \\ BT \\ DBT \end{Bmatrix} + \nu_2 H_2 \rightarrow \nu_3 \begin{Bmatrix} BD \\ Et \\ BPH \end{Bmatrix} + \nu_4 H_2 S \tag{1}$$

where Th represents thiophene; BT: benzothiophene; DBT: dibenzothiophene; BD: butadiene; Et: ethylbenzene; and BPH is biphenyl. ν_i are the appropriate stoichiometric coefficients. It can be noted that the hydrogenolisys reactions involve four species and usually are carried out in a mixture of many hydrocarbons as solvent medium, i.e., a paraffinic blend of C_{10}–C_{16}. The calculation of the phase behavior of this reactive mixture is complex itself, this is because of the complexity of any multicomponent stream containing H_2 and H_2S. However, by using the appropriate thermodynamic model and binary interaction parameters, the calculation can be safely carried out. Using the *element* concept proposed by Michelsen (1995) a reduction of the composition space is possible, and reaction (1) can be written in terms of *elements* as

$$\nu_1 \mathbf{AB} + \nu_2 \mathbf{C} \rightarrow \nu_3 \mathbf{A}(\nu_2 - \nu_4)\mathbf{C} + \nu_4 \mathbf{BC} \tag{2}$$

where *element* **A** is the organic part of the sulfur compounds, **B** is the sulfur atom, **C** is the hydrogen molecule and **D** is a inert solvent. The *element* matrix can be written as:

	Th, BT, DBT	H_2	BD, Et, BP	H_2S	$C_{16}H_{34}$
$A = Org$	ν_1	0	ν_3	0	0
$\mathbf{B} = S$	ν_1	0	0	ν_4	0
$\mathbf{C} = H_2$	0	ν_2	$\nu_2 - \nu_4$	ν_4	0
$\mathbf{D} = C_{16}H_{34}$	0	0	0	0	1

The element fractions (amount of *element j*/total amount of *element*) can be defined as

$$W_A = \frac{\nu_1 x_1 + \nu_3 x_3}{2\nu_1 x_1 + \nu_2 x_2 + (\nu_3 + \nu_2 - \nu_4)x_3 + 2\nu_4 x_4 + x_5} \tag{3}$$

$$W_B = \frac{\nu_1 x_1 + \nu_4 x_4}{2\nu_1 x_1 + \nu_2 x_2 + (\nu_3 + \nu_2 - \nu_4)x_3 + 2\nu_4 x_4 + x_5} \tag{4}$$

$$W_C = \frac{\nu_2 x_2 + \nu_3 x_3 + (\nu_2 - \nu_4)x_3 + \nu_4 x_4}{2\nu_1 x_1 + \nu_2 x_2 + (\nu_3 + \nu_2 - \nu_4)x_3 + 2\nu_4 x_4 + x_5} \tag{5}$$

$$W_D = \frac{x_5}{2v_1 x_1 + v_2 x_2 + (v_3 + v_2 - v_4)x_3 + 2v_4 x_4 + x_5}$$ (6)

If we select the stoichiometric coefficients (DBT case without solvent) as $v_1=1$, $v_2=2$, $v_3=1$, $v_4=1$, the triangular reactive diagram shown in figure 2 can be obtained. It should be noticed that, with the above definition of *element* fractions, the different species participating in the reaction can be located in the reactive diagram shown in figure 2. The coordinates for the pure species in the diagram are: DBT (0.5,0.5,0.0), H$_2$ (0,0,1), BPH (0.25,0.0,0.75), H$_2$S (0.0,0.5,0.5) respectively.
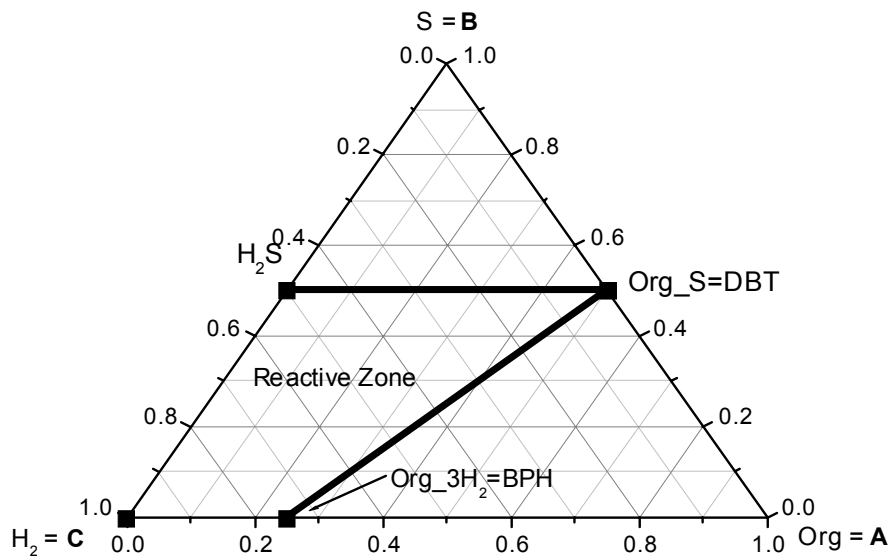
Fig. 2 Triangular reactive composition diagram for the hydrogenolysis of DBT.

REACTIVE RESIDUE CURVES MAP FOR THE HDS PROCESS

The thermodynamic analysis considers the computation of non-reactive residue curves, in order to understand the combined effect of the solvent concentration on the hydrogen and hydrogen sulfide solubility. The computation of the non-reactive residue curves at different solvent (C$_{16}$H$_{34}$) concentrations and a pressure of 30 atm was performed (see figure 3). The phase equilibrium calculations must be carried out carefully, because the interactions between H$_2$ and H$_2$S with the hydrocarbon mixture and the appropriate binary interaction coefficients must be used for the Peng-Robinson equation of state.

From figure 3, it can be observed that if the solvent concentration increases (from 0.6 to 0.8) the hydrogen solubility is augmented, as the element residue curve for this solvent composition is larger than the other residue curves. The initial point for the calculation of the residue curves was $x_{DBT}^0 = 0.110, x_{H_2}^0 = 0.019, x_{BPH}^0 = 0.110, x_{H_2S}^0 = 0.101, x_{C_{16}H_{34}}^0 = 0.660,$ which corresponds to a boiling temperature of T=300 K at P=30 atm. This behavior can be clearly seen in figures 4 and 5. In figure 5, (with x$_{C16H34}$=0.8), in the range of temperature 550-700 K,

the liquid mole fraction of hydrogen is practically the same as hydrogen sulfide, while in figure 4, for the whole temperature range the liquid mole fraction of hydrogen is below it. The continuous dashed lines are the respective vapor mole fractions.
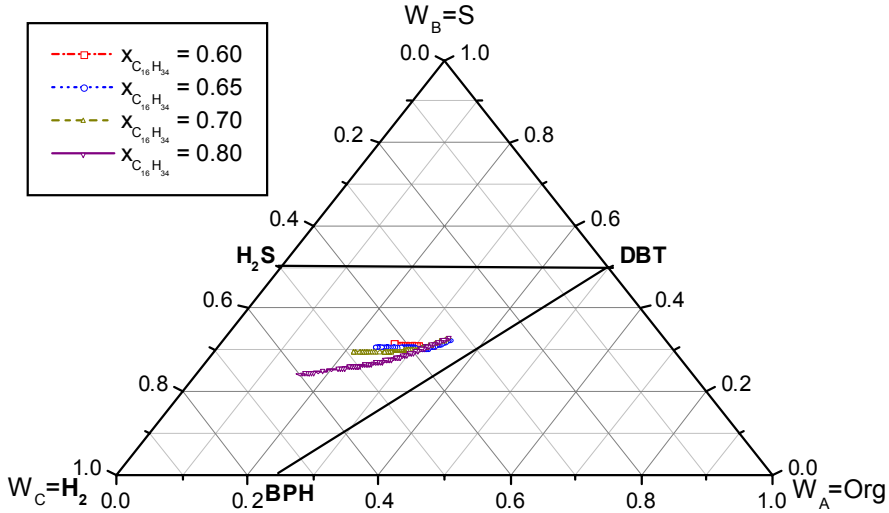

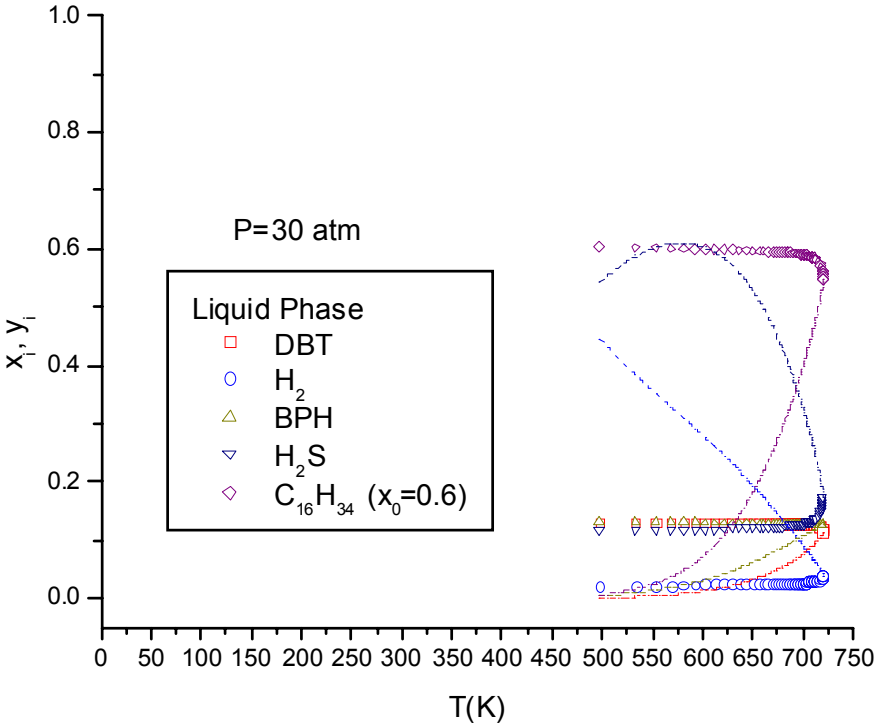*Fig. 3 Non-reactive residue curves for DBT reactive system with $C_{16}H_{34}$ as solvent.*

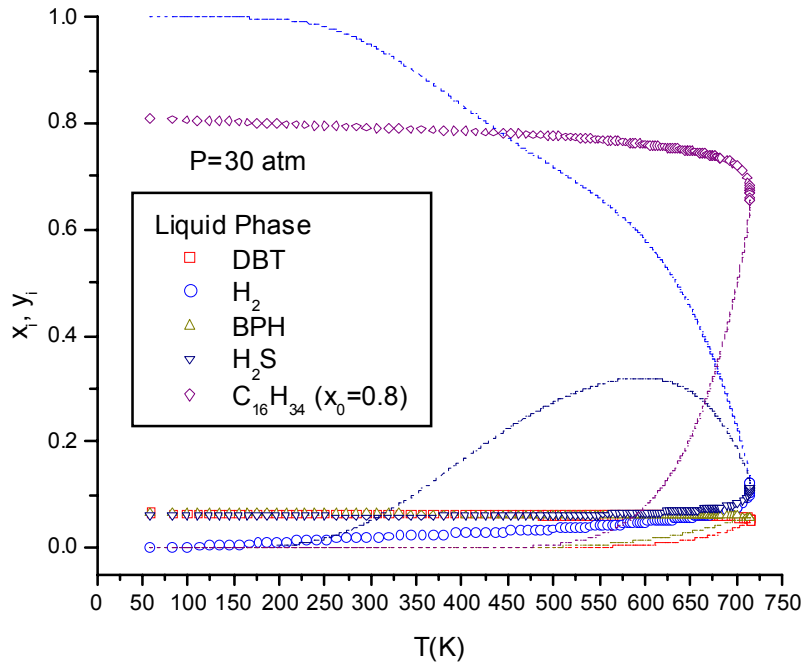*Fig. 4 Phase behavior of the non-reactive residue curve for DBT reactive system with x_{C16H34}=0.6.*

Fig 5. Phase diagram x-y-T for DBT reactive system with x_{C16H34}=0.8. (non-reactive residue curve)

It should be pointed out that this difference in hydrogen solubility is an important finding in terms of the application of reactive distillation concepts, since it is known that for complete elimination of the sulfur compounds, high hydrogen solubility, at the boiling conditions of the reactive mixture, is required.

The <u>reactive</u> residue curves for the elimination of dibenzothiophene with x_{C16H34}=0.8, are shown in figure 6. The reaction kinetic expression proposed by Broderick and Gates (1981) has been used. The equations to compute the reactive residue curves are:

$$\frac{dx_i}{d\tau} = x_i - y_i + (\nu_i - \nu_T x_i)\frac{Da}{k_{ref}} \frac{kK_{DBT}K_{H_2}x_{DBT}x_{H_2}\rho_L^2}{(1+K_{H_2}x_{H_2}\rho_L)(1+K_{DBT}x_{DBT}\rho_L + K_{H_2S}x_{H_2S}\rho_L)^2} \qquad (7)$$

Where

$$Da = \frac{M_{cat}}{V_0}k_{ref}; \quad d\tau = \frac{H_0}{V_0}dt \qquad (8)$$

and k_{ref} is evaluated at 300 K. It can be observed in figure 6 that at low Damkhöler numbers ($Da = 1X10^{-7}$) the reactive residue curve behavior is not too different from the non-reactive curve. However, as the hydrogen concentration and the Damkhöler number value increase ($Da = 1X10^{-5}$), the residue curves separate each other. This indicates that the trend of the reactive residue curves, as Da increases, is pointing to the BPH pure component. The effect of the chemical reaction on the phase behavior is more clearly seen in figure 7.
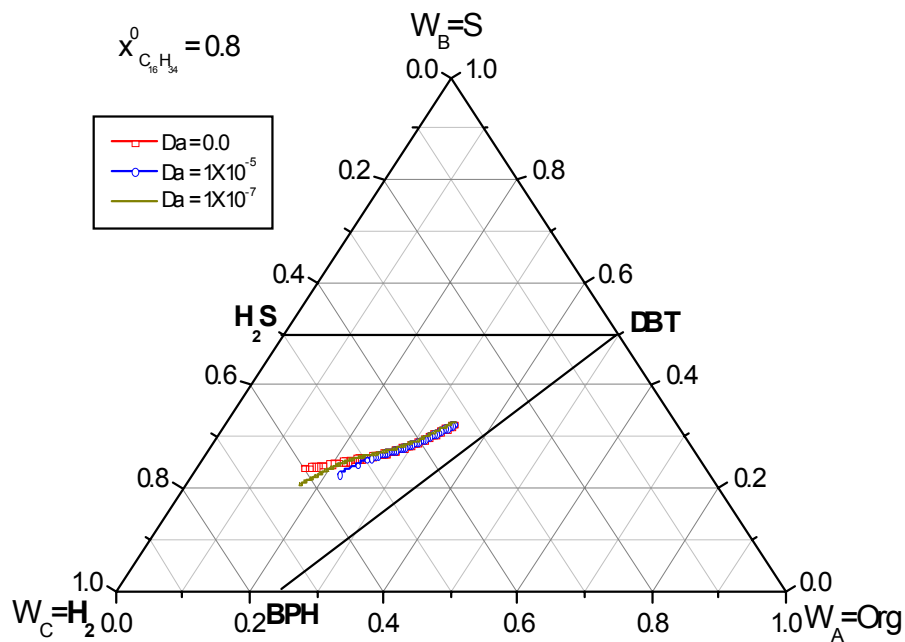
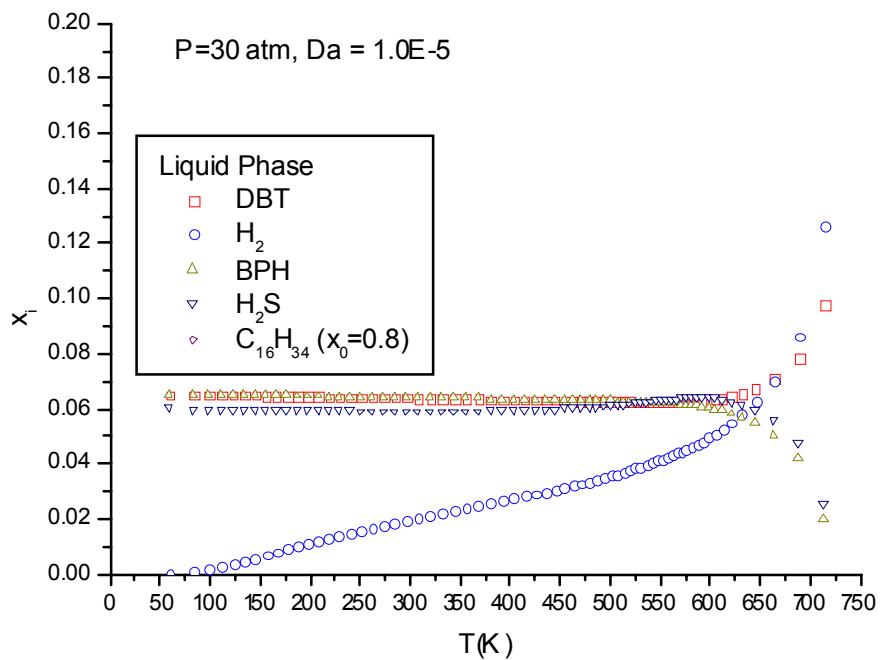*Fig. 6 Reactive residue curves for DBT reactive system with $C_{16}H_{34}$ as solvent*

Fig. 7 Effect of the chemical reaction on the liquid composition for the reactive DBT system.

It can be noted in figure 7 that, from 600 K to 750 K, the liquid composition of BPH and H_2S decreases and the concentration of DBT and H_2 increases. The explanation of this behavior may be stated as follow: there is a certain temperature region where the boiling conditions favor the vaporization of BPH and H_2S species, reducing their concentration in the liquid phase and, with this, promoting their production, through

the reaction of DBT and H_2. Therefore, this high temperature region should be considered as an optimal reactive section in a reactive distillation column design.

CONCEPTUAL DESIGN OF A REACTIVE DISTILLATION COLUMN FOR HDS

With the above information, it may be possible to develop a conceptual design of a reactive distillation column with the following considerations: i) 5% weight of the total HC fed to the reactive distillation column corresponds to the organo-sulfur compounds; ii) the organo-sulfur compounds considered are: Thiophene, benzothiophene and dibenzothiophene; iii) the operating pressure of the column is 30 atm. Also, it is well known that the order of reactivity for the compounds containing sulfur is: Thiophene> benzothiophene> dibenzothiophene and that the normal boiling temperatures follow the opposite sequence. From the residue curves computation is clear that the elimination of DBT will be favored at high temperatures, whereas the elimination of Th and BT may be carried out at lower temperatures due to their lower volatilities. The above leads directly to figure out a reactive distillation column consisting of two reactive zones: one zone of high temperature (bottom) where preferentially the elimination of DBT occurs and, another reactive zone (Top) where Th and BT are eliminated at lower temperature. Figure 8 shows the schematic diagram of such reactive distillation column.
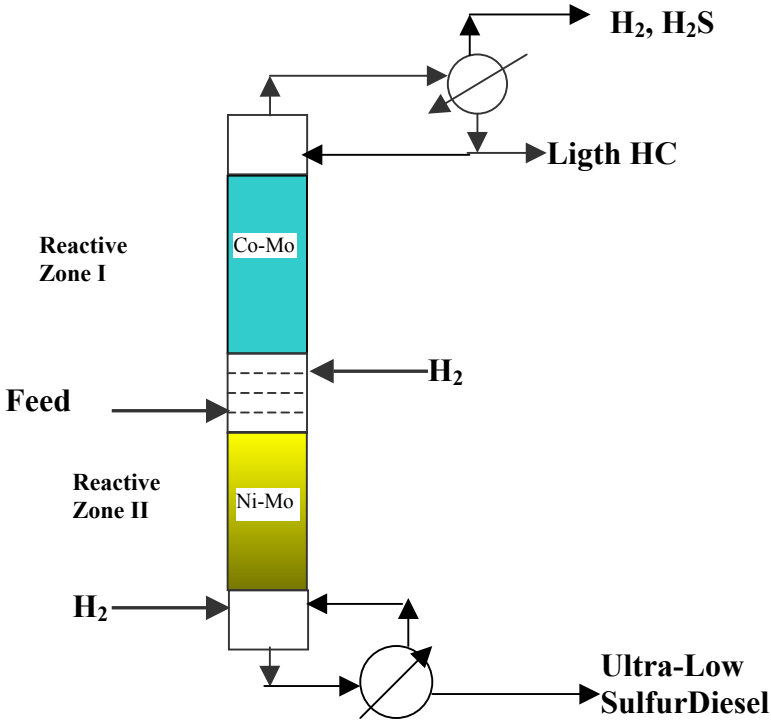

Fig. 8   Conceptual basic design of a reactive distillation column for ultra-low sulfur diesel production

RIGUROUS SIMULATION OF THE REACTIVE DISTILLATION COLUMN FOR DEEP HDS OF DIESEL

After a basic conceptual design has been obtained, that is, a reactive distillation column comprising two reactive zones and non-reactive stages, several different column configurations were proposed and validated through numerical simulations (Pérez-Cisneros *et. al*, 2002). The optimal column configuration found considers 15 stages, with 6 reactive stages. The hydrocarbon mixture fed to the column was a paraffinic mixture with the following composition (mole fraction): $Th=0.0087$, $BT=0.0087$, $DBT=0.1$, $C_{11}=0.4966$, $C_{12}=0.3166$, $C_{13}=0.0089$, $C_{14}=0.0015$, $C_{16}=0.0589$. The operation pressure of the reactive column was set to 30 atm and a H_2/HC feed relation of 3 was used. Two kinetic expressions for the hydrogenolysis of DBT were used: Broderick and Gates (1981) and Froment *et. al* (1994). Table 2 shows the details of the column configuration used for the simulations.

Table 2. Reactive distillation column configuration

	COLUMN SPECIFICATION
Reactive Stages [(1)]	5-7,10-12
Non-Reactive stages	1-4, 8-9, 13-15
HC Feed Stage)	9
H_2 Feed stage	12
Distillate Flow (kmol/hr)	340
Reflux Ratio	0.5
Top Temp. °C	225
Th Kinetic expression	Van Parijs and Froment, 1986
BT Kinetic expression	Van Parijs *et. al*, 1986
DBT Kinetic expression 1	Broderick and Gates, 1981
DBT Kinetic expression 2.	Froment *et. al*, 1994

(1) Stage 1 is a non-reactive partial condenser.

RESULTS AND DISSCUSION

Rigorous steady state simulations of the reactive distillation column described in table 2 were performed. Figure 8 shows the temperature profile along the reactive distillation column using the kinetic expression 1 for DBT. It can be observed that, reactive zone I operates almost isothermally, while in reactive zone II, there is a temperature difference of 15 degrees. This temperature profile may be explained by considering the heat released by the chemical reactions. In reactive zone I is consumed preferentially thiophene and benzothiophene with lower exothermic heat of reaction than dibenzothiophene, which is consumed preferentially in reactive zone II. This statement can be verified in figure 9, by observing the conversion or generation of the different organo-sulfur compounds in the reactive zones. Figure 10 shows the liquid composition profile of Th, BT and DBT along the column. It can be noted that the maximum compositions are located at the HC feed stage, and the higher DBT concentration is because of DBT feed composition. Also, it can be observed that as the organo-sulfur compounds pass across the reactive zones (stages 5-7 and 10-12), the concentrations of the three species diminishes sharply to zero.
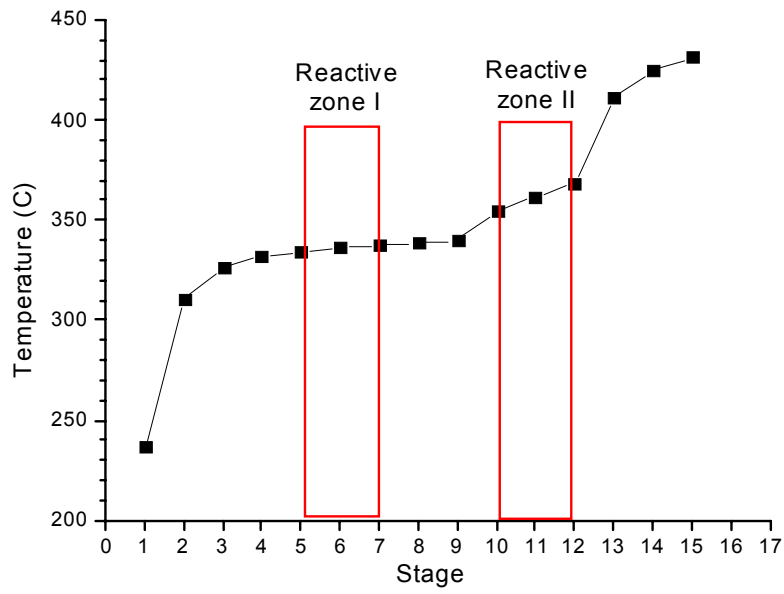
Fig. 8 Temperature profile along the reactive distillation column for deep HDS of diesel. Kinetic expression 1.
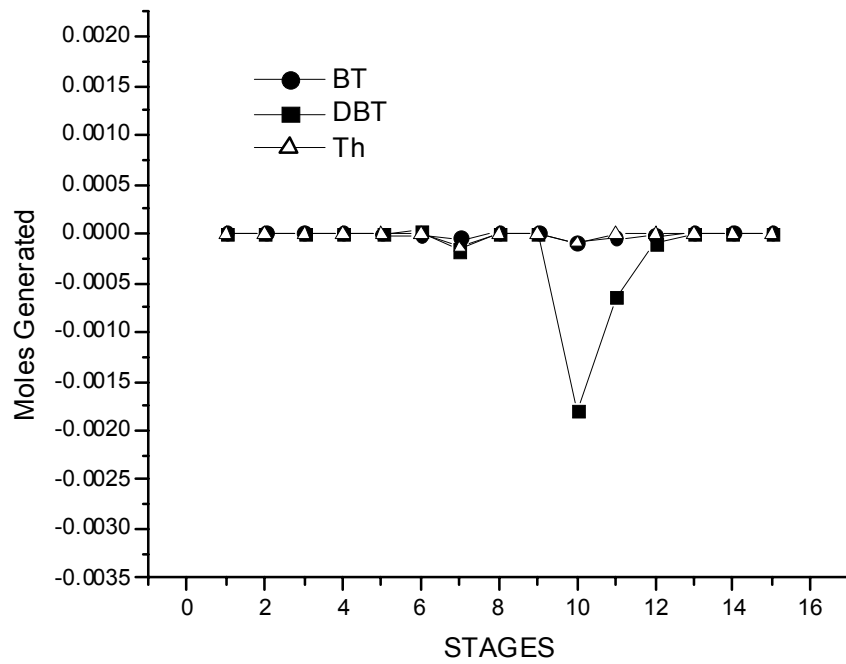

Fig. 9 Moles generated of Th, BT, and DBT along the reactive distillation column. Kinetic expression 1.
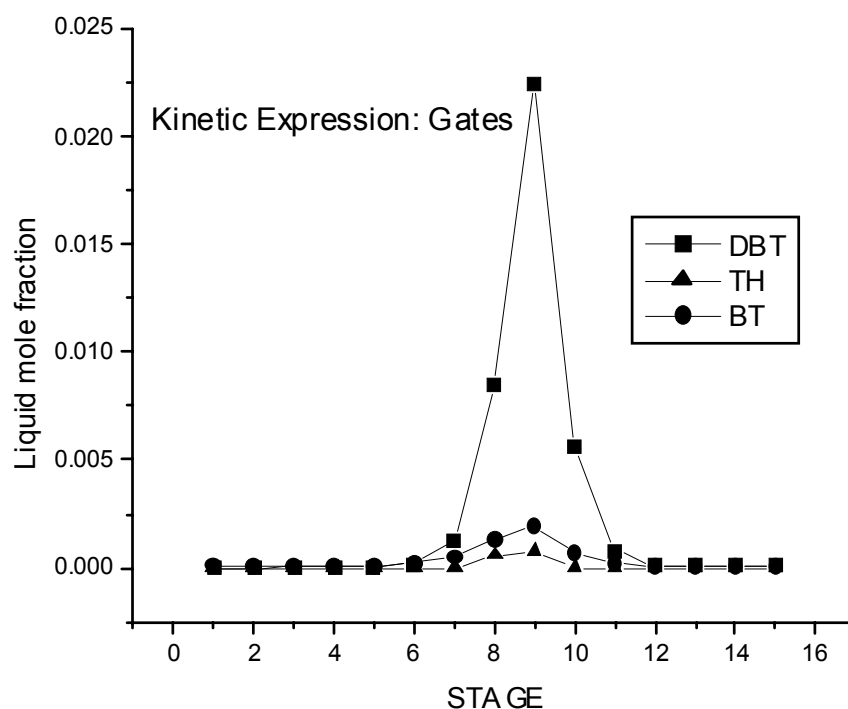
Fig 10 Liquid composition profile for Th, BT, and DBT along the reactive distillation column. Kinetic expression 1.

Figure 11 shows the DBT liquid composition profile along the reactive column using three different thermodynamic models. As was stated before, in order to obtain satisfactory results, the appropriate binary interaction coefficients must be used in the equations of state. In this simulation case, for SRK equation of state, such binary coefficients were set to be zero, but the conversion was kept to eliminate completely the sulfur compounds. However, when an activity coefficient liquid model is used (UNIQUAC), an unreliable behavior of the reactive system is obtained.

Figure 12 shows the effect of different rate of reaction expressions for the elimination of DBT. If we keep the conversion of DBT constant, that is 99.9%, and the same reactive distillation column configuration, a large difference in the amount of catalyst required to achieve the specified conversion is observed. Unless some parameter values for the reaction rate expression proposed by Froment *et. al* (1994) are inaccurately reported, the amount of catalyst required is definitely unreliable. Therefore, extreme caution should be taken in using the reaction rate expressions, and it is highly recommended to verify them through careful experiments.

Figure 13 shows the H_2S liquid composition along the reactive distillation column. It can be observed that for the two kinetic expressions there is not great difference in the composition values. The composition profile (higher concentration at the reactive zone I) suggest that in order to avoid catalyst activity inhibition, the operating conditions at the non-reactive stages, such as temperature, could be increased or a vapor side stream could be placed at the reactive zone I. Kinetic expression 1 shows higher concentration of H_2S at the reactive zone II due that the rate of generation is larger that kinetic expression 2.
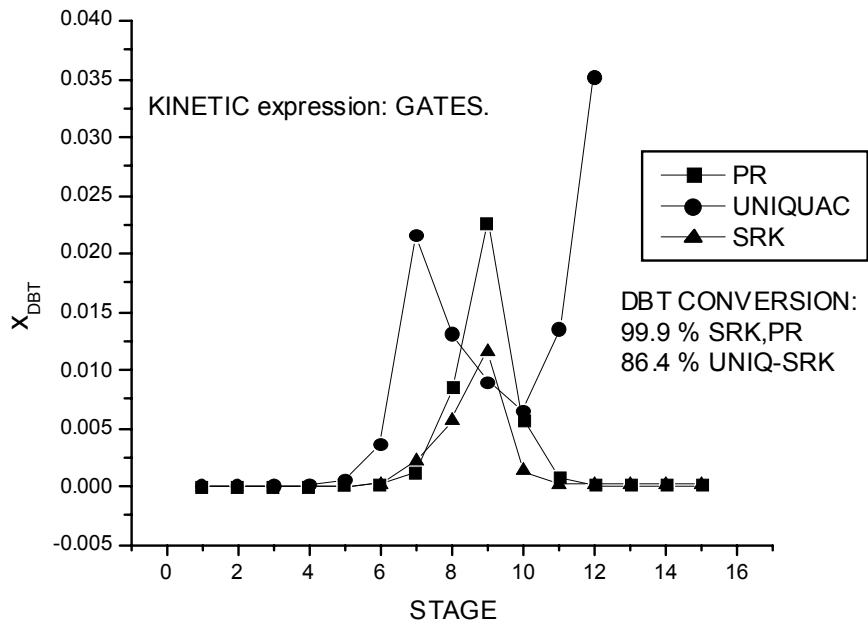
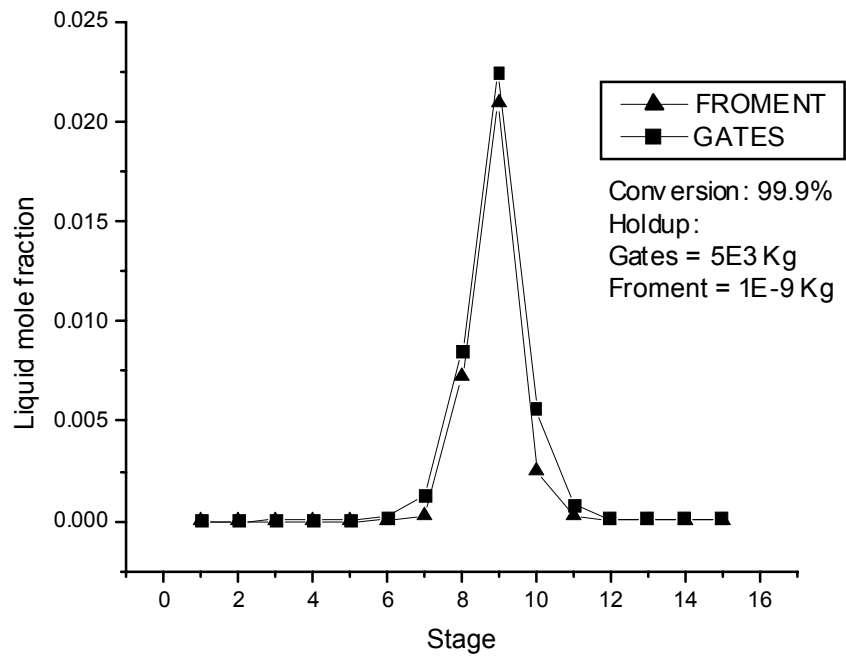*Fig. 11 Effect of the thermodynamic model on the DBT liquid composition profile along the reactive column.*

Fig. 12 Effect of the different reaction rate expressions on the DBT liquid composition profile.
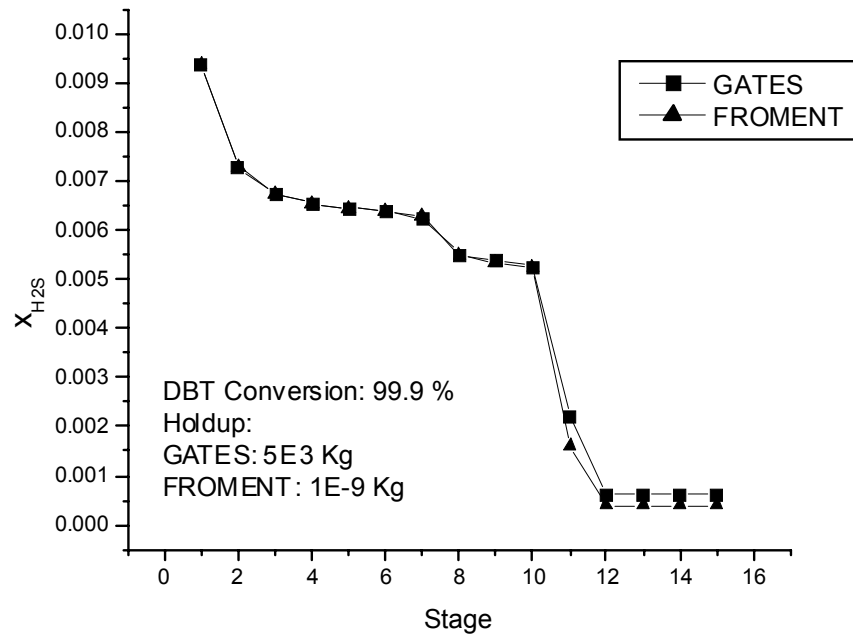
Fig. 13 H_2S liquid composition profile along the reactive distillation column.

CONCLUSIONS

A thermodynamic analysis for the deep hydrodesulfurization of diesel through reactive distillation has been performed. The analysis is based on the computation of reactive and non-reactive residue curve maps for the DBT reactive system. It was observed that the solvent concentration –or non-reactive hydrocarbon species (n-hexadecane)- is very important in determining the solubility of hydrogen and hydrogen sulfide in the reactive mixture. For the computation of the reactive residue curves the Peng-Robinson equation of state, with the appropriate binary interaction coefficients, and the reaction rate expression proposed by Broderick and Gates (1981) were used. From the reactive residue curve evaluated at $Da = 1X10^{-5}$ it could be observed that there exist a high temperature region were the vaporization effects favors the elimination of dibenzothiophene. Based on the residue curves analysis, a conceptual reactive distillation column design was developed. The design considers two reactive zones. At the reactive zone I, located above the HC feed stream, due to the volatility differences, thiophene and benzothiophene are preferentially eliminated, while dibenzothiophene is consumed mainly in reactive zone II. Rigorous steady state simulations using two different reaction rate expressions were performed. The results show that one must have extreme caution in choosing the reaction rate used. Despite the specified conversion of the organo-sulfur compounds is achieved, the amount of catalyst required to evaluate each reaction rate expression is very different, which leads to reject the expression producing untrustworthy results. This definitely indicates that, in order to obtain reliable results, experimental work to obtain the appropriate kinetic expressions should be carried out. Current work is addressed to the experimental determination of the "real" reaction rate expression for heavier organo-sulfur compounds, i.e., 4-6 DMDBT for the specific hydrocarbon mixture

obtained in the Mexican wells. Also, experiments on a bench reactive distillation column to elucidate the phase behavior of the reactive system are initiating.

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