New Developments in Deep Hydroconversion of Heavy Oil Residues with Dispersed Catalysts. 2. Kinetic Aspects of Reaction

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This paper discusses the results of hydrocracking experiments performed on a vacuum residue of Belaym crude in the presence of molybdenum naphthenate (MoN) as hydrogenation catalyst precursor and conducted in batch mode within a wide range of operating conditions and catalyst loading. The influence of severity on product distribution and quality is described as well as a kinetic analysis of the data. Results of this work demonstrate that the *in-situ* decomposition of MoN generates micrometer-sized particles of very active hydrogenation catalysts molybdenum disulfide utilizing the sulfur present in the feedstock. The catalyst provides hydrogen in an active form for stabilization of the free radicals produced by the thermal cracking of the petroleum residue so that high conversion to distillate product (500 °C–) can be obtained with minimum coke production. The kinetic analysis of the data shows that the step of MoN sulfidation to generate MoS_2 is very fast compared to feedstock conversion and does not influence the kinetics of distillate production that is thermally controlled (activation energy of 56.7 kcal/mol) and whose apparent over all order of reaction is close to 2.

Introduction

Hydrocracking processes utilizing finely dispersed hydrogenation catalysts are particularly suited to upgrade heavy oils and petroleum residues which generally contain high concentration of heteroatoms, metals, and asphaltenes. These catalysts can be introduced into the feed as finely divided powders, water-soluble or oil-soluble precursors whose thermal decomposition give rise to micrometer-sized particles of the active species, usually metal sulfides. The action of the homogeneous oil-soluble organometallic compounds has been extensively explored in the last decade by Aldridge and Bearden.[1–3] These authors showed that molybdenum-based precursors are extremely effective especially as regards the inhibition of coke generation even at low concentration (e.g., 0.1 g/kg on feed).

More recently, several authors provided an in-depth study of this hydroconversion system with the aim of defining the technical feasibility of this novel approach to upgrade heavy oils and residues. Although a lot of precursors of different nature have been tested and patented,[4] molybdenum naphthenate (MoN) and phosphomolybdic acid (PMA) have been often utilized as reference compounds to study heavy oil upgrading[1,5,6] but also direct coal liquefaction[7,8] and coprocessing.[9,10]

The active species of the catalyst is postulated to be MoS_2 which is formed *in situ* during the first steps of reaction using the sulfur present in the feedstock or added as H_2S, dimethyl disulfide or elemental sulfur. The sulfidation of the molybdenum-containing compounds is generally considered very fast compared to hydrocarbon conversion[1,9,11] but no kinetic data support this statement. Moreover, the physical characterization of solids obtained from hydrocracking tests carried out at CNRS laboratories with MoN and PMA, shows that the sulfidation steps of these two precursors may be substantially different, thus affecting the final hydrocracked product distribution.[12]

Focusing on this problem, we have carried out a series of hydrocracking experiments on both petroleum vacuum residue and model compounds to examine the influence of the MoN sulfidation step on the kinetics of feedstock conversion and typical upgrading reactions such as the hydrodeasphalting.

Experimental Section

Hydrocracking Experiments. The hydrocracking reactions were performed on a vacuum residue of Belaym crude (Table 1) with molybdenum naphthenate (6.0 wt % Mo) as catalyst precursor. The feedstock was prepared mixing the precursor with the vacuum residue at 80 °C. The conversion experiments were conducted in batch mode using a tubing bomb microreactor of 30 mL capacity furnished with a thermocouple for the temperature measurement during reaction.

In a typical experiment, the reactor was charged with 2 g of feedstock, pressurized with 9 MPa of hydrogen, and heated to

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[®] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) Bearden, R.; Aldridge, C. L. *Energy Prog.* **1981**, *1*, (1–4), 44–48.

(2) Bearden, R.; Aldridge, C. L. US Patent 4.066.530, 1978.

(3) Bearden, R.; Aldridge, C. L. US Patent 4.567.156, 1986.

(4) Del Bianco, A.; Panariti, N.; Di Carlo, S.; Elmouchnino, J.; Fixari, B.; LePerchec, P. *Appl. Catal.* **1993**, *A94*, 1–16.

(5) Chen, H. H.; Montgomery, D. S.; Strausz, O. P. *AOSTRA J. Res.* **1988**, *4* (2), 143.

(6) Chen, H. H.; Montgomery, D. S.; Strausz, O. P. *AOSTRA J. Res.* **1989**, *5* (1), 33.

(7) Snape, C. E.; Bolton, C.; Dosch, R. G.; Stephens, H. P. *Energy Fuels* **1989**, *3*, 421–425.

(8) Curtis, C. W.; Pellegrino, J. L. Energy Fuels **1989**, *3*, 160–168.

(9) Kim, H.; Curtis, C. W.; Cronauer, D. C.; Saykowsky, D. J. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1989**, *34* (4), 1431.

(10) Curtis, C. W.; Cassell, F. N. *Energy Fuels* **1988**, *2*, 1–8.

(11) Kim, H.; Curtis, C. W. *Energy Fuels* **1990**, *4*, 206–219.

(12) Le Perchec, P.; Fixari, B.; Elmouchnino, J.; Peureux, P.; Vrinat, M.; Morel, F. *Energy Fuels*, preceding paper in this issue.

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Table 1. Properties of Belaym Vacuum Residue

density 15/4, g/mL	1.028
viscosity at 100 °C, cSt	5230
pour point, °C	63
RCC, wt %	20.8
C5 asphaltenes, wt %	26.2
C7 asphaltenes, wt %	18.6
elemental analysis, wt %	
C/H/N/S	85.03/10.01/0.57/4.2
Ni/V, ppm	130/179

the reaction temperature by immersion into a liquid tin bath for the desired reaction time. The heating system provides a very rapid heat-up of the microreactor (2 min) so that preheating periods can be neglected. During reaction, the reactor was agitated by a pneumatic vibrator to assure the mixing of the products as confirmed by comparative experiments with stirred microautoclaves.

At the end of the run, the microreactor was rapidly quenched to ambient temperature, vented and the gases were recovered into a gas sampling bag. The gas analysis was performed on a Hewlett-Packard gas chromatograph equipped with two TCD detectors by using Poropak Q and molecular sieves columns. The GC analysis resulted in the quantification of H_2, H_2S, CO_x, and C1–C4 hydrocarbons. The hydrogen consumption was calculated by comparison of the initial microreactor pressure and the final gas composition and pressure, both at room temperature. This quantity was expressed in grams of hydrogen per 100 g of residue.

The liquid and solid products of the reactions were recovered with THF. This mixture was stirred in an ultrasonic bath for 15 min and then filtered through a Millipore Teflon filter (0.5 μm) to separate THF-soluble material (THFS) from the residue (coke and metal catalyst). The amount of coke was therefore calculated subtracting the weight of molybdenum as MoS_2 from the residue.

The THFS product was deasphalted by addition of 40 volumes of *n*-pentane to produce a deasphalted oil (DAO) that is then analyzed by GC SIM-DIST (simulated distillation analysis) to obtain the distillation curves of the volatile fractions. The conversion to distillate was therefore calculated by difference from the weight of the various residues (coke, asphaltenes, and DAO 500 °C + fraction).

Model Compound Reactions. The hydrogenation tests with the reference model compound 1-Me-naphthalene were conducted in the microreactor on reactant solutions of 5 wt % 1-Me-naphthalene in *n*-hexadecane.

The catalyst precursor MoN was added at a level of 500, 1000, and 2000 ppm of metal with an excess of elemental sulfur (5 times the stoichiometric) to promote the *in-situ* molybdenum sulfidation. The reactor was pressurized with 7.5 MPa of hydrogen to assure a large excess of reacting gas (H_2/Me-naphthalene mole ratio of about 50) and to maintain most of the substrate (> 95%) in the liquid phase during reaction. The experiments were carried out at temperatures from 340 to 400 °C for various residence times. After reaction, the liquid products were analyzed by GC using a 25 m × 0.32 mm i.d. HP1 column with atomic emission detection.

Results and Discussion

Effect of Severity on Conversion and Product Yield. The results of the hydrocracking experiments carried out at different catalyst concentrations (200–5000 ppm of metal) and various reaction severity by changing residence time and temperature, are reported in Tables 2 and 3. The concentration of three main pseudocomponents, VR (500 °C+), distillate (500 °C−) and coke (THS-insoluble material) was observed during reaction.

The data of Figures 1–4, show the time courses of distillate and coke production at various temperatures and catalyst concentrations as a consequence of the feedstock conversion. Working with a constant catalyst concentration of 1000 ppm of molybdenum, the distillate yield increases regularly with severity while the process of coke formation appears strongly inhibited at any degree of conversion. The amount of THF-insoluble material is always very low ranging from 0.3 to 1.7 wt %.

Table 2. Product Yield (wt %) and Hydrogen Consumption (wt % on Feed) of Hydrocracking Experiments with 1000 ppm of Mo as MoN

temp (°C)	time (min)	coke	distillate	H_2 consumpn
410	15	0.3	10.2	0.3
410	30	1	13.9	0.9
410	60	0.8	19.9	1.2
410	120	1.1	27.5	2.8
410	240	1.2	40.4	3.1
430	15	0.9	16.3	nd[a]
430	30	0.7	24.5	1.1
430	60	1	39.7	1.2
430	120	1	48.6	3.5
430	240	1.1	68.5	3.2
450	15	1	36.1	1
450	30	1.1	50.6	1.9
450	60	1.3	63.6	2.1
450	120	1.7	80.3	3.6
450	240	1.4	84.9	5

[a] nd = not determined.

Table 3. Products Yields (wt %) and Hydrogen Consumption (wt % on feed) of Hydrocracking Experiments at 450 °C with Different Mo Concentrations

Mo concn (ppm)	time (min)	coke	distillate	H_2 consumpn
200	15	0.7	34.9	1.2
200	30	0.6	52	nd[a]
200	60	1	nd	2.5
200	120	0.8	76.6	3.2
200	240	1.5	87.6	3.4
1000	15	1	36.1	1
1000	30	1.1	50.6	1.9
1000	60	1.3	63.6	2.1
1000	120	1.7	80.3	3.6
1000	240	1.4	84.9	5
5000	15	1.5	37.8	nd
5000	30	1.9	49.7	3
5000	60	1.7	69.2	3
5000	120	1.4	85.7	5.1
5000	240	1.3	94.5	5

[a] nd = not determined.

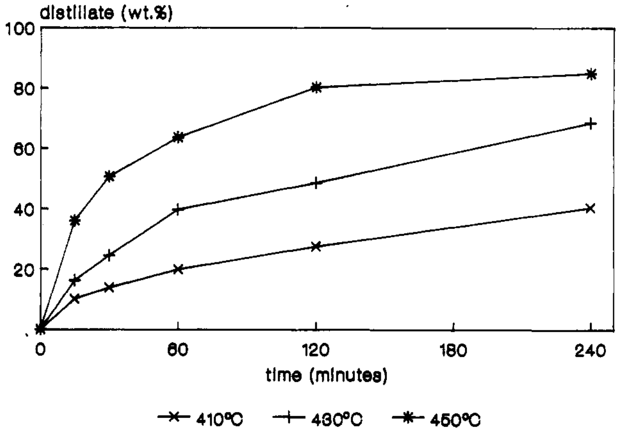

Figure 1. Effect of temperature on distillate production (1000 ppm of molybdenum as MoN).

At 450 °C, the effect of catalyst loading on distillate yield seems to be negligible in the range 200–5000 ppm of molybdenum and the coke production is very well controlled even at the lowest catalyst concentration.

The comparison with data obtained without catalyst at the same temperature shows that the process of VR conversion is initially slowed down by the presence of molybdenum. In fact, this kind of catalyst has no effect

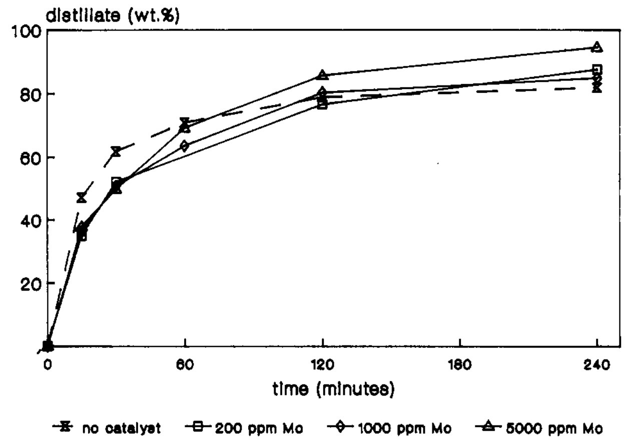

Figure 2. Effect of catalyst concentration on distillate production (isothermal experiments at 450 °C).

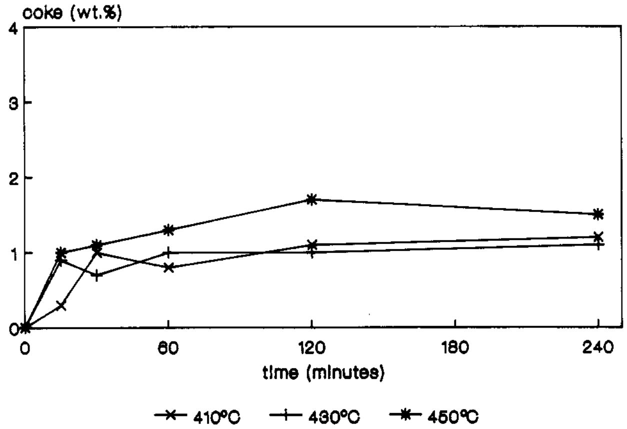

Figure 3. Effect of temperature on coke production (1000 ppm of molybdenum as MoN).

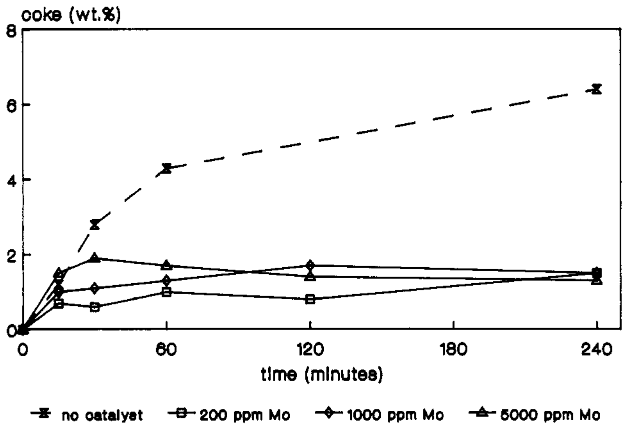

Figure 4. Effect of catalyst concentration on coke production (isothermal experiments at 450 °C).

on C–C bond cracking so that in both cases the driving force for the reaction is thermal activation and the initial free radicals population is determined by the severity of the reaction conditions. The next step of the hydrocracking reaction is the saturation of the reactive fragments which is promoted by the hydrogenation catalyst. If this process is not so rapid as in the presence of molybdenum catalyst, the reactive fragments are not readily stabilized and undergo fast undesirable reactions, such as condensation reactions, which give rise to the appearance of mesophase and then to coke deposition. On the contrary, an efficient hydrogen uptake controls the rate of free radicals propagation and evolution that, via β-scission reaction, favors the process of VR conversion to lighter products.

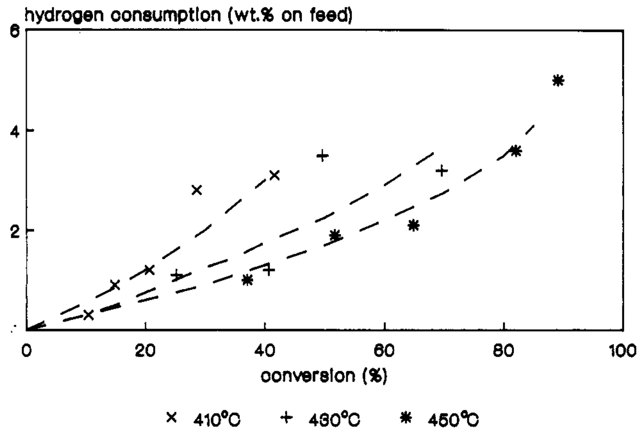

Figure 5. Hydrogen consumption vs. VR conversion.

The trends of hydrogen consumption with conversion qualitatively depicted in Figure 5 show that, at the same conversion level, lower temperatures favor the hydrogen uptake. The amount of hydrogen consumed to achieve distillate yields around 60–80% ranges from 2 to 4 wt % on feed. This is roughly the same order of magnitude as hydrogen consumption required by the ebullated bed technology operating at high conversion (2.5 wt % on feed for the H-oil process[13]).

Kinetic Analysis. *1. Decomposition of Catalyst Precursor.* The VR conversion can be seen to proceed by an initial thermal cracking of the feedstock generating reactive fragments whose evolution to yield distillate and coke is controlled by the hydrogenation reactions. The process of hydrogen uptake is catalyzed by molybdenum disulfide that is simultaneously produced via MoN decomposition and sulfidation. The sulfur compounds present in the feedstock provide the necessary amount of sulfur for a rapid catalyst activation. This finding was confirmed with experiments carried out with a 30-mL stirred microautoclave adding an excess of sulfur (5 times the stoichiometric amount required to produce MoS_2) and recording the reactor pressure during reaction. In a closed system such as the microautoclave, the pressure is the result of two opposite phenomena: the hydrogen consumption which reduces the pressure and the gas production which tends to increase it.

The data of Figure 6 showing the autoclave pressure and temperature profiles as a function of time reveal the same trend for the curves recorded during the hydrocracking experiments carried out both in the absence and in the presence of external sulfur. Moreover, the shape of the curves "pressure vs time" suggests that the MoN activation is very rapid because the hydrogen uptake process starts just after 11 min at the temperature of about 360 °C.

However, in order to measure the rate of the catalyst-precursor sulfidation reaction, separate hydrogenation experiments were performed using 1-Me-naphthalene (MN) as a model reactant. The kinetic analysis was carried out changing the reaction severity (340–400 °C; 15–120 min) and the MoN concentration (500–2000 ppm Mo). In all cases, the main products of the hydrogenation (over 90%) are the tetrahydro derivatives (THMN).

Some tests were also performed without the catalyst to evaluate the action of sulfur and confirming that it has not noticeable effect on MN conversion.

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(13) 1988 Refining Handbook, *Hydrocarbon Process.* **1988**, Sept., 61–91.

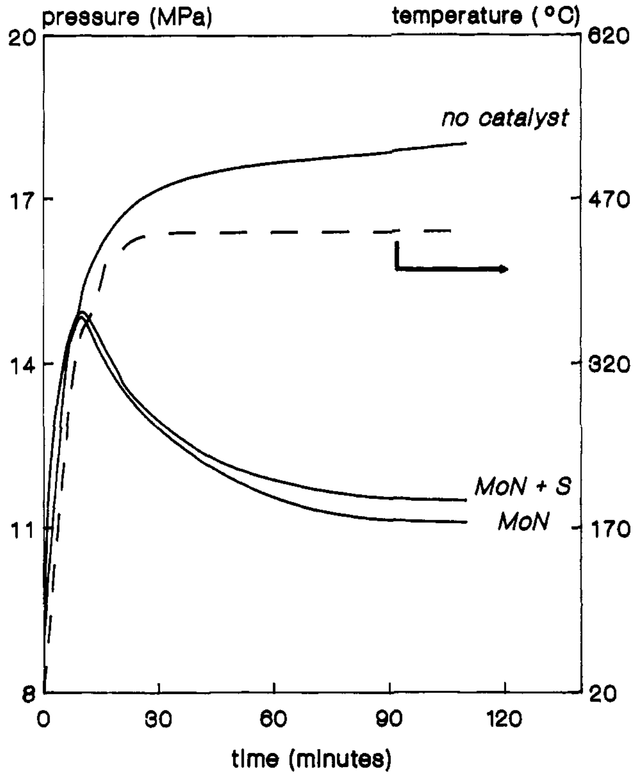

Figure 6. Autoclave pressure and temperature profiles of hydrocracking runs (1000 ppm of molybdenum as MoN).

The S-shaped curves describing the THMN production are probably related to the transformation of the precursor MoN to the hydrogenation catalyst active form (Figure 7). Based on these observations, the following two reactions were studied:

$$\mathrm{MoN} \underset{k_1}{\overset{\mathrm{S,H_2}}{\rightarrow}} \mathrm{MoS_2} \qquad (1)$$

$$\mathrm{MN} \underset{k_2}{\overset{\mathrm{MoS_2}}{\rightarrow}} \mathrm{THMN} \qquad (2)$$

Considering a first-order kinetics for reaction 1 and second-order for reaction 2, the differential equations describing the MoN and MN conversion can be written as

$$\mathrm{dMoS_2}/\mathrm{d}t = k_1 \cdot \mathrm{MoN}$$

$$-\mathrm{dMN}/\mathrm{d}t = k_2 \cdot \mathrm{MN} \cdot \mathrm{MoS_2}$$

and therefore

$$-\mathrm{dMN}/\mathrm{d}t = k_2 \cdot \mathrm{MN} \cdot (1 - e^{-k_1 t}) \cdot \mathrm{MoN_0}$$

which upon integration becomes

$$\ln(\mathrm{MN}/\mathrm{MN_0}) = k_2 \cdot \mathrm{MoN_0}/k_1 \cdot (1 - k_1 t - e^{-k_1 t})$$

This last equation was used to calculate the values of the kinetic parameters performing the minimization of the following objective function F:

$$F = \sum |C_i^{\mathrm{exp}} - C_i^{\mathrm{calc}}|^2$$

where C_i^{exp} and C_i^{calc} represent the experimental and the calculated quantities of MN at various times and temperatures.

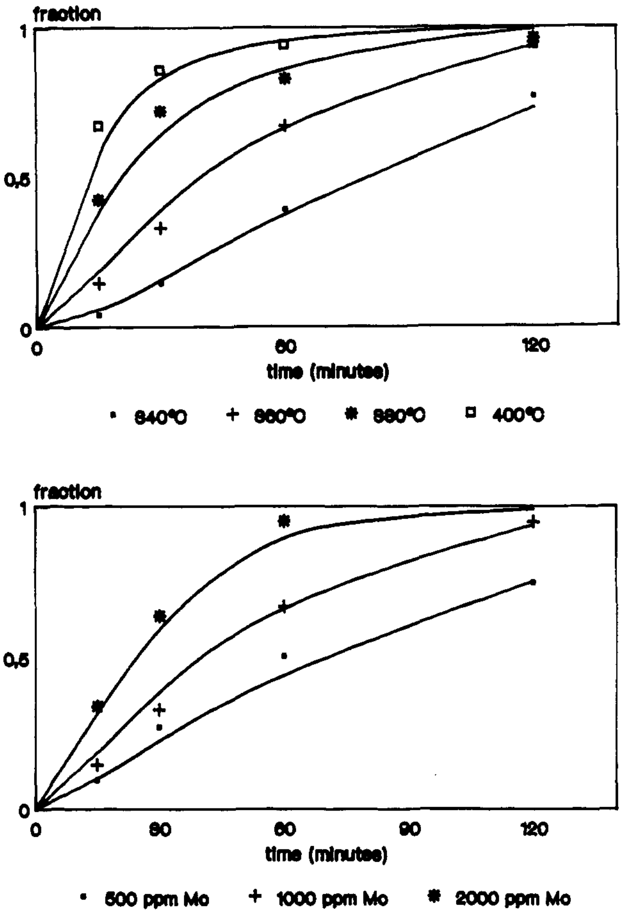

Figure 7. 1-Me-naphthalene hydrogenation. Model prediction vs experimental data.

The values of the rate coefficients for the reaction 1 at 340, 360, 380, and 400 °C are 0.037, 0.107, 0.287, and 0.725 min^{-1}, respectively, with an activation energy of 40.5 kcal/mol and a frequency factor $\ln A = 30.0$ (A in min^{-1}). The validity of the assumed orders and of the calculated kinetic parameters is confirmed by the excellent agreement between the experimental data and the calculated kinetic curves (Figure 7).

2. *Vacuum Residue Conversion.* To obtain kinetic information on VR conversion reaction, in the first approximation, the following assumptions were made.

1. The hydrogen transfer rate to the gas–liquid interface was considered very fast compared to the consumption rate of hydrogen due to reaction in the liquid phase.[14] Under the reaction conditions used, the hydrogen to feedstock ratio assures the excess of reacting gas and an almost constant pressure (20 MPa). For this reason, the hydrogen concentration in the liquid phase was assumed not to change during reaction and therefore the reaction order with respect to hydrogen can be considered zero.

2. Due to the limited coke production, the reaction pathway leading to THF-insoluble material was ignored.

3. The step of catalyst generation was supposed to be instantaneous. In fact, the kinetic analysis achieved for the catalyst sulfidation demonstrates that this reaction (reaction 1) is very fast when compared with the conversion of the VR as shown by the comparison of the half-life periods ($t_{1/2}$, in min) calculated and estimated for the two reactions at the temperatures of 410, 430, 450 °C.

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[14] Versteeg, G. F.; Blauwhoff, P. M. M.; Van Swaaij, W. P. M. *Chem. Eng. Sci.* **1987**, *42*, 1103.

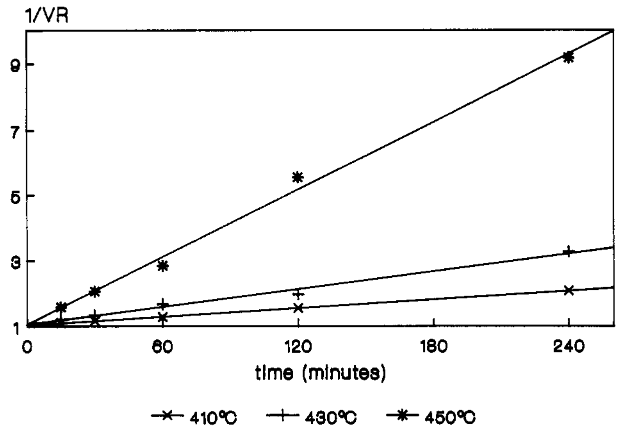

Figure 8. Second-order plot for feedstock conversion reaction.

T (°C)	$t_{1/2}$ (reactn 1)	$t_{1/2}$ (VR conversn)
410	0.61	210
430	0.26	105
450	0.12	30

Thus, the disappearance of the reactant VR can be represented by this simple expression:

$$-\mathrm{dVR}/\mathrm{d}t = k\mathrm{VR}^n$$

The semilog plot of VR conversion versus time ($n = 1$) does not show a satisfactory linearity while the results of Figure 8 might suggest an apparent over all order close to 2. The feedstock is a mixture of compounds of very different reactivities and therefore the kinetics of the VR conversion reaction is complex. As a result, although the individual species of the feedstock probably follow true first-order kinetics, the observed overall VR conversion reaction order is higher. A rationalization of the occurrence of apparent second-order kinetics for a multiplicity of first-order reactions is reported in literature.[15] For the same reason, the disappearance of the asphaltic component of the feed exhibits the same kinetic behavior.

The apparent activation energies (E_a) obtained from Arrhenius plots for VR and asphaltenes conversion are 56.7 kcal/mol (ln A = 35.9) and 38.6 kcal/mol (ln A = 24.4), respectively. The E_a measured for the feedstock conversion is very close to the average value used to calculate the severity in thermal cracking processes operating at similar temperatures, such as visbreaking,[16] confirming the thermal control of this reaction.

The lower value of E_a observed for the second reaction reflects the fact that, in this case, the process of asphaltenes disappearance is the consequence of two kinds of processes, i.e., cracking reaction and hydrogenation reaction (the latter reaction being easier). In fact, asphaltene conversion may also be obtained transforming these heavy molecules into less polar compounds via hydrogenation to generate n-pentane-soluble material. Moreover, although the effect of catalyst concentration on VR conversion is rather poor, the effect on its asphaltic component is much more evident as shown by the data on asphaltene conversion presented in Figure 9. Even this finding agrees with the fact that the processes involving C–C bond cleavage (conversion to distillate) are thermally controlled, while the presence of the catalyst favors the hydrogen uptake reactions, thus affecting the product quality and selectivity (coke inhibition).

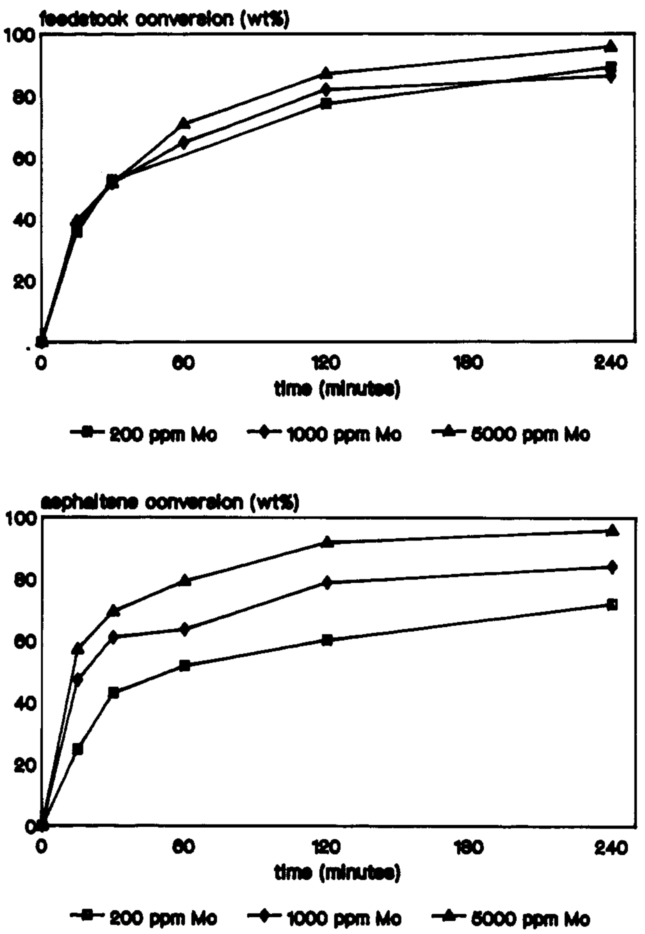

Figure 9. Comparison between feedstock and asphaltene conversion reactions.

Conclusion

The petroleum residue hydrocracking experiments performed at various reaction severities show that the presence of micron-sized catalyst generated *in-situ* from the decomposition of MoN inhibits the condensation reactions providing hydrogen in an active form for stabilization of free radicals so that distillate yields greater than 80% can be obtained with minimum coke production. The amount of hydrogen consumed to achieve this result ranges from 2 to 4 wt % on feed depending on the severity of the reaction conditions.

The catalyst concentration favors the hydrogen uptake and affects the product quality but does not significantly influence the rate of VR conversion, according to a thermal control of this reaction.

The kinetic analysis of the data proves that the step of MoN decomposition to yield molybdenum disulfide is very fast compared to feedstock conversion and does not significantly alter the extent of distillate production.

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(15) Ho, T. C.; Aris, R. *AIChE J.* **1987**, *33* (6), 1050.
(16) Yan, T. Y. *Fuel* **1990**, *69*, 1062.