Kinetics of Conradson Carbon Residue Conversion in the Catalytic Hydroprocessing of a Maya Residue

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A residue from a Maya crude was hydroprocessed in a continuous hydroprocessing unit provided with a continuous stirred-tank reactor. The kinetic study of Conradson carbon residue (CCR) conversion was carried out, and the data of CCR conversion fit half-order kinetics, with the activation energy being 277.58 kJ/mol. No dependence of the rate constants on hydrogen pressure was observed. The relationship between CCR and different parameters was studied, and it was found that asphaltenes, hydrogen content, H/C atomic ratio, and residue content (350 °C) were linearly related with CCR content. Gas yield was also found to be linearly related with CCR conversion. A structural analysis was carried out by ^{13}C NMR and ^{1}H NMR, and a linear relationship was found between CCR and aromatic carbon contents for the products obtained at 415 °C, when the products obtained at the same temperature are compared. However, a general relationship for all temperatures was not found.

Introduction

Over the past few years there has been an increase in petroleum vacuum residue processing due to the decrease in the fuel oil demand and the increase in distillate fuels market. These low-quality vacuum residues are characterized by high metal, high Conradson carbon residue (CCR), and high asphaltenes contents.

The specifications of all petroleum products are dictated by their application and by environmental constraints. For this reason, various industrial processes have been developed to convert heavy crude oils into transport fuels, and the methods used vary from refinery to refinery (Quann et al., 1988; Speight, 1990; O'Connor et al., 1991). Most of the processes in use are based on residual cracking or hydroprocessing over catalyst. Although residue cracking is becoming increasingly popular, the bulk of heavy oils processing still involves hydrotreating.

A critical factor that limits the maximum conversion of heavy residues to light cuts in a commercial residue hydroprocessing unit is the formation of coke. This is usually deposited inside the reactor and downstream vessel as well as on the catalyst surface and causes both operability and catalyst deactivation problems.

A way to predict the yield of coke which would be produced from a coking process is by measuring the CCR. A large number of studies have shown that an important variable in determining coke yield is CCR in the feed. Kirchen et al. (1989) have found a linear relationship between coke make and microcarbon residue, MCR. The numerical values of MCR and CCR have been reported to be identical (ASTM D4530).

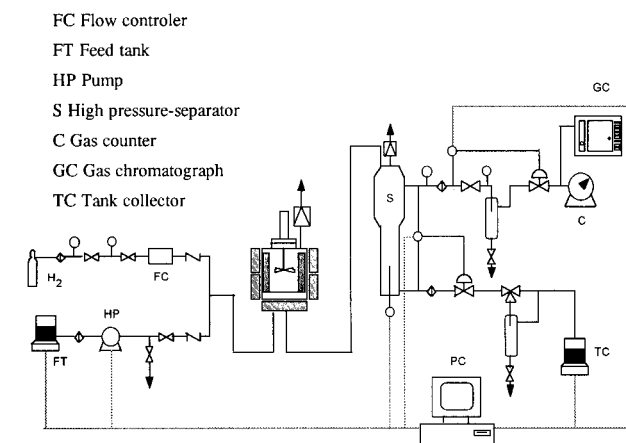CCR conversion is a critically important reaction in residue hydroprocessing. This conversion minimizes the amount of petroleum coke produced in a refinery, and coke is the least valuable product obtained in a refinery.

Beaton and Bertolacini (1991) have investigated the relative contributions of the catalytic and thermal reactions. Miki et al. (1983) reported that the catalyst plays an important role in hydrogenation, decomposition, desulfurization, and denitrogenation of the residue but has little effect on the cracking. Sanford (1991) studied the influence of the catalyst in the hydrocracking of Athabasca bitumen and calculated that the CCR is largely converted in a catalytic process, with the 540 °C boiling material conversion being largely a thermal process.

Sanford and Chung (1995) has proposed a general reaction scheme for the conversion of a residue into distillate. This scheme is centered around two classes of residue molecules; one of which forms residue in the test CCR and the other, non-CCR residue, does not. In this scheme the rate-determining step is the thermal breaking of a carbon-to-carbon bond to give an aliphatic radical and an aromatic radical. This first step is independent of whether hydrogen is present or not. The aliphatic radical can undergo rapid fragmentation to produce gases and distillate, whereas the aromatic radical can either undergo condensation reactions leading to coke formation or react with molecular hydrogen to produce a carbon-to-hydrogen bond and a hydrogen atom. The hydrogen atom can react with condensed aromatic centers, leading to the decomposition of these centers and again giving distillates and gases.

There are several studies which indicate that CCR is related to certain parameters. Gray et al. (1991) have shown that the MCR content of a residue can be correlated with the aromatic carbon content in the sample. It is believed that CCR conversion is due to aromatics saturation and that CCR reduction comes about through catalytic hydrogenation of the aromatic rings followed by thermal cracking of the naphthenic rings produced by hydrogenation (Beaton and Bertola-

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FC Flow controler
FT Feed tank
HP Pump
S High pressure-separator
C Gas counter
GC Gas chromatograph
TC Tank collector

Figure 1. Schematic diagram of a hydroprocessing unit provided with a continuous stirred-tank reactor.

cini, 1991), and that this is an indirect way of studying aromatic saturation. Roberts (1989) found that the CCR is a linear function of either hydrogen to carbon atomic ratio or hydrogen content and that this linear function is independent of crude source and process history.

In this paper, the CCR conversion kinetics and the relationship of CCR with different factors, H/C ratio, hydrogen, aromatic carbon, asphaltenes and residue contents, and gas yields, in the catalytic hydroprocessing of a Maya residue will be studied.

Experimental Section

A residue from a crude Maya was hydroprocessed in a continuous hydroprocessing unit provided with a continuous stirred-tank reactor (Figure 1).

The Maya residue has high asphaltenes content (8.6 wt %), high CCR (11.2 wt %), and high metals content (45.17 ppm of nickel and 242.12 ppm of vanadium). The main characteristics of the feed are shown in Table 1.

A commercial catalyst, Topsoe TK-711, was used. It is a specially-developed demetalation catalyst for pretreatment of residual oils for reduction of metals, asphaltenes, and Conradson carbon. It is utilized for guard beds, for guard reactors, or as a first-stage catalyst in composite fillings. The characteristics of this catalyst are indicated in Table 1.

The kinetic study of CCR conversion was performed in a continuous stirred-tank reactor (CSTR) which has a capacity of 1000 cm^3 provided with a "kinetic basket" for 185 cm^3 of catalyst. The reactor is equipped with three furnace control thermocouples. The inside temperature is measured by two thermocouples, one at the bottom of the reactor and the other at the top.

Hydrogen feed was measured by a mass flow controller which consists of a flow sensor and a control valve. Liquids were fed by a high-pressure pump and measured by a balance located at the feed tank. At the reactor outlet, gases and liquids were conducted to a high-pressure gas/liquid separator. Liquid level was measured by a differential pressure transducer, and liquid output was regulated by a control valve. The reaction pressure was measured by a pressure transducer and regulated by a control valve located at the gas outlet.

The utilization of a CSTR in the kinetic study provides a tool for working in the absence of intrareactor gradients, but another type of gradient, those at the boundary between different phases (gas/liquid/solid) in the reac-

Table 1. Maya Crude Residue and Catalyst Characteristics

characteristics	
Maya Crude Residue Properties	
IBP, 540 °C (vol %)	63.30
sulfur (wt %)	3.45
nitrogen (wt %)	0.28
nickel (ppm)	45.17
vanadium (ppm)	242.12
asphaltenes (wt %)	8.60
Conradson C. (wt %)	11.22
density (g/mL), 50 °C	0.9245
kinematic viscosity (cSt)	
50 °C	111.5
100 °C	16.5
120 °C	9.2
dynamic viscosity (cP)	
50 °C	103.1
100 °C	14.73
120 °C	8.11
surface tension (K s^{-2})	31.04×10^{-3}
B.P. > 540 °C Cut Properties	
asphaltenes (wt %)	15.39
Ramsbottom C (wt %)	30.4
sulfur (wt %)	4.84
nickel (ppm)	142
vanadium (ppm)	562.4
Catalyst Characterization	
NiO (wt %)	2.0
MoO$_3$ (wt %)	6.0
surface area (m^2/g)	140
pore volume (cm^3/g)	0.60
pore diameter (Å)	150
bulk density (kg/L) (sock loaded, $^1/_{20}$ in. threelobes)	0.58

Table 2. Operating Conditions for Kinetic Experiments and CCR Analysis of Feedstock and Products

run	temp (°C)	pressure (MPa)	liquid flow (g/h)	CCR (wt %)	CCR conv
feed				11.22	
1	375	10.0	46.06	6.41	42.8
2	375	10.0	88.91	7.66	31.7
3	375	10.0	38.52	8.56	23.7
4	375	12.5	56.72	6.48	42.2
5	375	12.5	89.75	7.94	29.2
6	375	12.5	116.56	8.20	26.9
7	375	15.0	27.58	6.00	46.5
8	375	15.0	82.04	8.56	26.0
9	375	15.0	109.86	8.86	21.1
10	400	12.5	43.84	1.98	82.3
11	400	12.5	78.99	4.06	63.8
12	400	12.5	118.73	6.69	40.4
13	415	12.5	63.3	0.20	98.2
14	415	12.5	71.6	0.27	97.6
15	415	12.5	135.57	0.87	92.2

tion medium and gradient within the catalyst particle, can also be present.

In our kinetic study, working conditions in the absence of interphase gradients were investigated by Martínez et al. (1996). The stirring speed was varied from 2000 to 3500 rpm and the gas flow rate from 6000 to 10 000 std.ft^3/bbl. From the results, a kinetic study was carried out at 10 000 std. ft^3/bbl gas/liquid ratio and 3500 rpm stirring speed. The conditions of temperature, pressure, and liquid flow used are indicated in Table 2.

In order to avoid intraparticle gradients, the kinetic runs were carried out with the catalyst crushed at a range of particle size between 53 and 530 μm. Twenty grams of presulfured Topsoe TK-711 catalyst were located inside bags of metallic mesh of 35 μm of sieve aperture in order to avoid misleading results caused by

losses of catalyst by attrition and plugs in the reactor output. After 180 h of running the hydroprocessing unit, steady-state conditions for the catalyst were reached and the runs indicated in Table 2 were started.

The CCR was determined by the D189-81 ASTM standard test method on products from kinetic runs from hydroprocessing. This test determines the amount of carbonaceous residue left after destructive atmospheric distillation of the sample.

The high-molecular-weight and complex nature of petroleum fractions make analysis of the individual components difficult so a structural analysis scheme has been devised that enables average chemical structures to be derived for the aromatic petroleum fractions.

^{1}H NMR was performed in a Unity 300 Varian at 293 K, with resonance frequency 299.863 MHz, acquisition time 3.7 s, pulse angle 45°, spectral width 40 000 Hz, deuterated chloroform 95 wt %, and wave of width band with 2 canals. ^{13}C NMR spectra were recorded with a Fourier transform NMR spectrometer (Bruker, AC80). The spectrometer is equipped with a 1.8 T electromagnet locked by means of deuterium resonance. The resonance frequency for ^{13}C is 20.15 MHz. The samples (150−500 mg) were dissolved in 1 cm^3 CDCl$_3$ (99% D), which also served as an internal standard. Cr(CACA)$_3$ (5 × 10^{-5} mol/cm^3) was added to the sample as a paramagnetic relaxation agent. Inverse-gated decoupling was used with a 90° radio-frequency pulse length of 6.8 μs. For each spectrum 4000−32 000 scans were accumulated with a relaxation delay of 5 s.

Results

Kinetic Study. The results from CCR determination and percentages of CCR conversion are indicated in Table 2. The range of CCR conversion is 21.1−98.2 wt %. Sanford (1995) obtained a range of CCR conversion from 20.7 to 74.6 wt % in hydrocracking of Athabasca bitumen in a batch stirred-tank reactor and a wide range of experimental conditions. The CCR conversion increases as the liquid flow decreases as Gray et al. (1991) found for hydrocracking of residues from Alberta bitumen. The CCR conversion also increases as the reaction temperature increases.

In our experimental study, for a heterogeneous perfectly mixed system working continuously and after steady-state conditions had been reached, the rate equation assuming constant density is

$$\frac{C_0 - C}{-r} = \frac{1}{\text{LHSV}} \tag{1}$$

where C_0 is the initial concentration, C outlet concentration, LHSV liquid hourly space velocity, and r the rate of reaction.
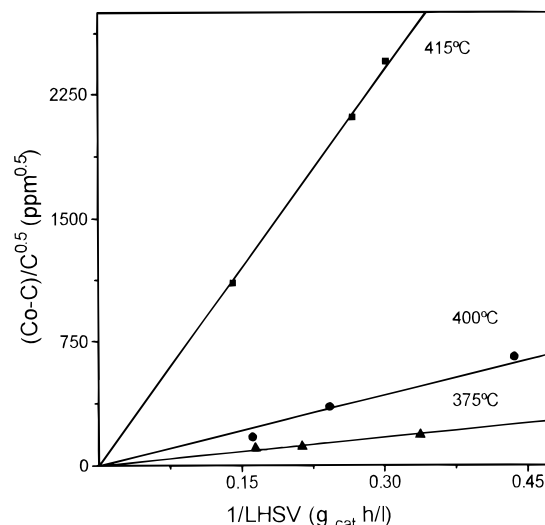
CCR removal rate can be expressed by

$$-r = KP_{H_2}{}^m C^n \tag{2}$$

K^* is the intrinsic rate constant, m is the order dependence on H$_2$ pressure, n is the kinetic order, and P_{H_2} is the hydrogen pressure.

From eqs 1 and 2

$$C_0 - C = K^* C^n P_{H_2}{}^m/\text{LHSV} \tag{3}$$

Figure 2. Half-order kinetic plot for CCR conversion reactions in the hydroprocessing of Maya crude with Topsoe-TK-711 crushed catalyst in a CSTR.

In order to obtain the kinetic order n, the process was carried out at constant pressure, 12.5 MPa, and a pseudokinetic rate constant K was defined.

$$K = K^* P_{H_2}{}^m \tag{4}$$

Then eq 3 can be rewritten as

$$C_0 - C = KC^n/\text{LHSV} \tag{5}$$

For calculating m from the expression (4), a series of experiments at 375 °C and different pressures and liquid flows (Table 2) were carried out. A log−log plot of K versus hydrogen pressure would have a slope m and ln K^* as the intersection with the ordinate axis.

The data of CCR conversion (Table 2) fit half-order kinetics, and the equation which describes the behavior of the system in this case is

$$\frac{C_0 - C}{C^{0.5}} = \frac{K}{\text{LHSV}} \tag{6}$$

Figure 2 represents a half-order kinetic plot for CCR conversion.

No pressure dependence on the rate constant, as defined by eq 4, has been observed as the constant kinetic values found at different pressures show (Table 3). Beaton and Bertolacini (1991) found that the reaction of Ramsbottom carbon conversion is roughly first order with respect to hydrogen partial pressure for hydroprocessing of a typical vacuum residue in a commercial plant with three trains of three backmixed reactors in series.

The influence of temperature has been assumed to follow the equation of Arrhenius

$$K = K_0 e^{-E_a/RT} \tag{7}$$

Figure 3 shows the Arrhenius plot of ln K versus $1/T$. The values of the rate constants ln K_0 and E_a/R are indicated in Table 3. The activation energy was 277.58 kJ/mol.
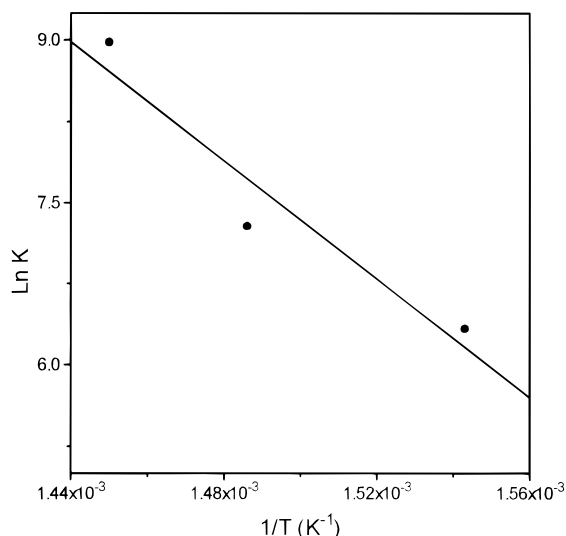
Figure 3. Arrhenius plot for the rate constants of CCR conversion reactions.

Table 3. Kinetic Order, Rate Constants, and Activation Energy for the CCR Conversion in the Hydroprocessing of Maya Crude Residue

CCR conversion	375 °C (std. err)	400 °C (std. err)	415 °C (std. err)
K_{10MPa} (ppm$^{0.5}$ L/h g$_{cat}$)	500.71 (72.02)		
correl. coeff	0.87		
std err of estimation	35.1		
$K_{12.5MPa}$ (ppm$^{0.5}$ L/h g$_{cat}$)	563.98 (32.48)	1459.24 (120.81)	8003.14 (113.53)
correl. coeff	0.97	0.98	0.99
std err of estimation	14	63.31	48.48
K_{15MPa} (ppm$^{0.5}$ L/h g$_{cat}$)	327.56 (48.23)		
correl. coeff	0.93		
std err of estimation	36.25		
ln K_0	49.47 (13.66)		
$-E_a/R$	−28 070.67 (9139.43)		
correl. coeff	0.95		
std. err of estimation	0.59		
E_a (kJ/mol)	227.58		

Structural Analysis. The carbon residue data are intended to indicate the quantity of coke which will be formed under thermal stress.

Coke formation from oils is produced by thermolysis (Levinter et al., 1967) by a sequence of polymerization and condensation steps from the lightest to the heaviest fractions:

maltenes → resins → asphaltenes →
carbenes → coke
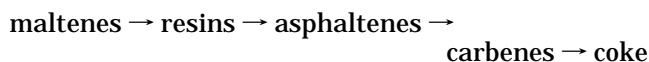
Wiehe (1992) showed that this reaction pathway results from an aromaticity increase, oligomerization, and a combination of both. Sanford (1995) and Gray et al. (1991) have shown that the CCR content of a residue can be correlated with the aromatic fractions in the sample. The removal of compounds which contribute to CCR is thought to be due to aromatics saturation and is an indirect way of studying aromatics saturation.

Roberts (1989) and Wiehe (1994) have related the CCR content to the hydrogen content or H/C ratio. Wiehe (1994) proposed a model which indicates a linear relationship between CCR content and hydrogen weight percent for residues with molecular weights of more than 700 amu.

Therefore, in our study a structural analysis was carried out in order to find the possible relationship between CCR content and aromatic fractions in the sample.

The hydrogen atom distribution and molecular weight are indicated in Table 4, and the carbon atom distribution is shown in Table 5. With the values indicated in these two tables, the structural parameters were calculated. The numerical values of these parameters are also indicated in Table 5.

In Table 4, it can be observed that the aromatic hydrogen content is lower in the feed that in the obtained products. However, the aromatic carbon content (Table 5), is higher in the feed than in the products. The decrease in aromatic carbon is greater at 375 and 400 °C than at 415 °C. The condensation degree (H_a/C_a) also decreases in the hydroprocessing, with the lowest values (higher H_a/C_a) being those corresponding to the products obtained in runs 10, 11, 12 (400 °C), and 14 (415 °C).

The increases in aromatic carbon, aromaticity, f_a, and condensation degree in the products obtained at 415 °C compared to those obtained at 375 and 400 °C seem to indicate the existence of condensation and coking reactions which are favored at high temperature. Nevertheless, the aromatic hydrogen increase and molecular weight decrease during the processing at 415 °C, compared to results obtained at 375 and 400 °C, do not indicate an increase in the condensation reactions which would produce larger molecules but rather that an increase of cyclation reactions could have been produced. The decrease in AG, the number of alkyl and hydroaromatic groups per molecule, seems to suggest that cyclation reactions are being carried out during the hydroprocessing. At the same time, there could be dehydrogenation reactions of alkylcyclohexane to produce cyclohexene and benzene or toluene structures.

The products from processing at 415 °C show increasing aromatic carbon and CCR when the LHSV increases. Nevertheless, when the values of CCR and aromatic carbon in the products from processing at 375, 400 and 415 °C are compared, it can be seen that the aromatic carbon of the products obtained at 415 °C is higher than that of the products at 375 and 400 °C, with the CCR being lower (Figure 4).

The products from processing at 400 °C have CCR values intermediate between those obtained at 375 and 415 °C, and these values increase as the LHSV increases. However, the aromatic carbon content was found to be approximately constant while the values of liquid flow and CCR increased. This seems to indicate that, at 375 and 400 °C, the hydrogenation of aromatics, cracking reactions, and stabilization of forming radicals are produced, while at 415 °C these reactions are overlapped by cyclation and dehydrogenation of alkylcyclohexane reactions. The increase of cyclation and dehydrogenation reactions is supported by the increase in condensation and aromaticity.

A linear relationship between CCR content and hydrogen content was found (Figure 5). These findings coincide with those of Roberts (1989) and Wiehe (1994). The CCR value increases as the hydrogen content decreases, and a relationship between the H/C ratio and CCR content was found (Figure 6). The highest value corresponds to the lowest CCR value for the run done at the most severe conditions.

Asphaltenes have been considered as being coke precursors. In addition to the mechanism postulated by Levinter (1967), some authors (Savage et al., 1985; Speight, 1994) have reported that coke formation is
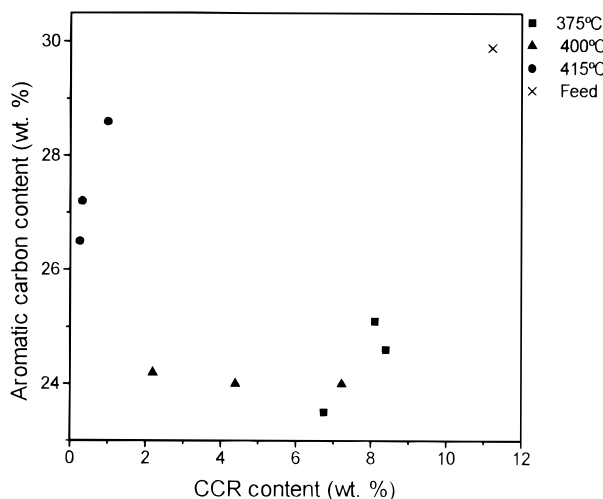
Table 4. Distribution of Hydrogen Atom by ^{1}H NMR and Molecular Weight

run	H_{aro} %	H_α % [δ(1.9−3.3 ppm)]	H_β % [δ(1−1.6 ppm)]	H_F % [δ(7.2−8.5 ppm)]	H_γ % [δ(0.5−1 ppm)]	MW (amu)
feed	5.74	11.15	55.20	0.50	21.57	402
1	5.8	10.99	55.63	0.46	21.32	351
2	5.85	11.90	55.34	0.52	21.35	378
3	5.78	11.05	55.31	0.45	21.55	385
4	5.89	11.16	55.22	0.70	21.06	348
5	5.77	10.79	55.39	0.45	21.84	313
6	5.88	10.92	55.13	0.46	21.84	259
7	5.86	10.70	55.34	0.44	21.93	360
8	5.78	11.23	55.28	0.50	21.19	378
9	6.32	11.28	54.19	0.89	21.64	
10	6.36	9.35	55.16	0.14	23.82	289
11	6.52	10.06	54.77	0.30	22.88	275
12	6.50	11.03	54.69	0.69	21.23	327
13	6.25	10.52	54.23	0.49	22.63	207
14	7.68	8.65	54.14	0.15	24.55	275
15	6.91	10.83	54.56	0.54	21.43	282

Table 5. Carbon Distribution and Structural Parameters Obtained by ^{13}C NMR[a]

| run	C_{aro} % (100−210 ppm)	C_{sat} % (10−100 ppm)	H_a/C_a	f_a	AG	CL	RJG
feed	29.9	70.1	0.33	0.30	2.31	8.47	0.72
1	26.3	73.7	0.38	0.26	2.05	8.8	0.56
2	25	75	0.41	0.25	2.21	8.93	0.62
3	26.4	73.6	0.38	0.26	2.23	8.84	0.67
4	23.5	76.5	0.43	0.24	2.05	9.05	0.55
5	25.1	74.9	0.4	0.25	1.79	9.13	0.48
6	24.6	75.4	0.39	0.25	1.43	9.71	0.29
7	26.1	73.9	0.4	0.26	2.08	8.94	0.48
8	26.4	73.6	0.38	0.26	2.25	8.64	0.64
9	25.3	74.7					
10	24.2	75.8	0.47	0.24	1.47	10.51	0.2
11	24	76	0.48	0.24	1.51	9.72	0.25
12	24	76	0.47	0.24	1.93	9.01	0.47
13	26.5	73.5	0.44	0.27	1.26	8.49	0.20
14	27.2	72.8	0.51	0.27	1.32	10.77	0.18
15	28.6	71.4	0.43	0.29	1.67	8.52	0.30

[a] H_a/C_a, ratio between aromatic hydrogen atoms and aromatic carbon atoms. f_a, the fraction of aromatic carbon or aromaticity. AG, the number of alkyl and hydroaromatic groups per molecule, AG = H_α/a where $a = 2.3$CL. CL, the average size or chain length of the alkyl and hydroaromatic group. RJG, the number of ring-joining groups per molecule.

Figure 5. Linear relationship between CCR content and hydrogen atom content at 12.5 MPa. The equation obtained is $Y = 118.43 - 9.29X$ ($r = -0.91$).

Figure 4. CCR versus aromatic carbon content at 12.5 MPa. The equation obtained is $Y = 26.124 + 2.5X$ ($r = 0.97$) at 415 °C.
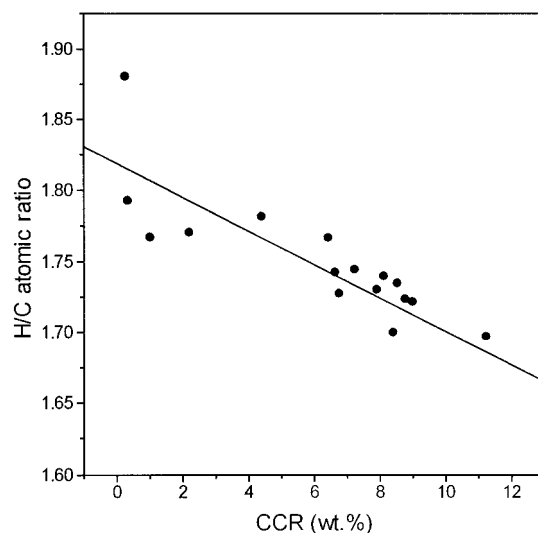
Figure 6. Linear relationship between CCR content and H/C atomic ratio at 12.5 MPa. The equation obtained is $Y = 1.8186 - 0.012X$ ($r = -0.76$).

triggered by the phase separation of asphaltenes, with an induction period existing that has been described by some authors (Wiehe, 1993; Takatsuka et al., 1989; Martínez et al., 1997) as resulting from a phase-separation step of asphaltenes in thermolysis and in residua hydroconversion.

Asphaltenes are the major precursors to sludge and sediments. Asphaltenes are very large polyaromatic compounds, with molecular weight ranging from 1000 to about 20 000 and generally possessing a boiling point
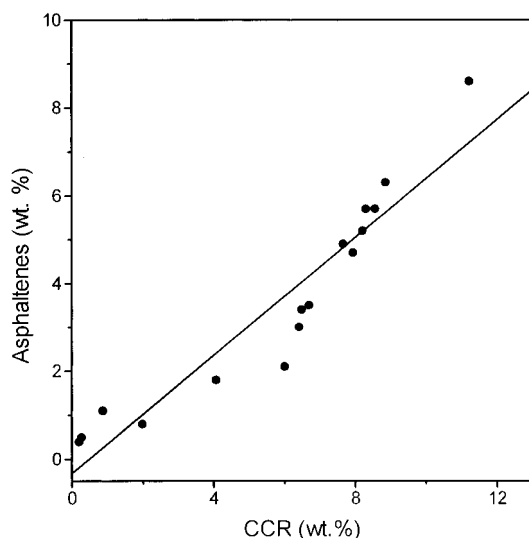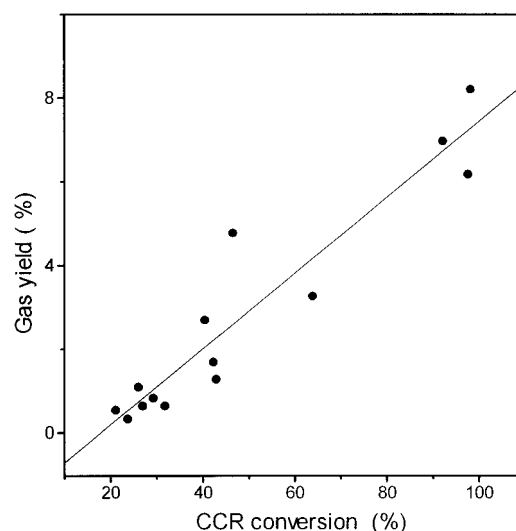
Figure 7. Linear relationship between asphaltenes content and CCR content at 12.5 MPa. $Y = -0.393 + 0.659X$ ($r = 0.93$).

Figure 8. Linear relationship between gas yield and CCR conversion at 12.5 MPa. $Y = -1.6137 + 0.0905X$ ($r = 0.94$).

above 1000 °F. Bitumens, heavy oils, and residua are characterized by a large amount of asphaltenes which consist of large molecules of condensed polyaromatic rings. Asphaltenes are important in catalytic processes since a high percentage of heteroatoms and coke precursors reside in the asphaltenic fraction (Quann et al., 1988). Consequently, this asphaltenic fraction will limit the efficiency of the refining process, leading to a quicker catalyst deactivation and higher coke yields (Sheu et al., 1992). Since the asphaltenes make catalytic hydrotreating very difficult, a better understanding of the properties and changes during the processing is important for the development of upgrading technology for asphaltene-containing heavy feedstocks.
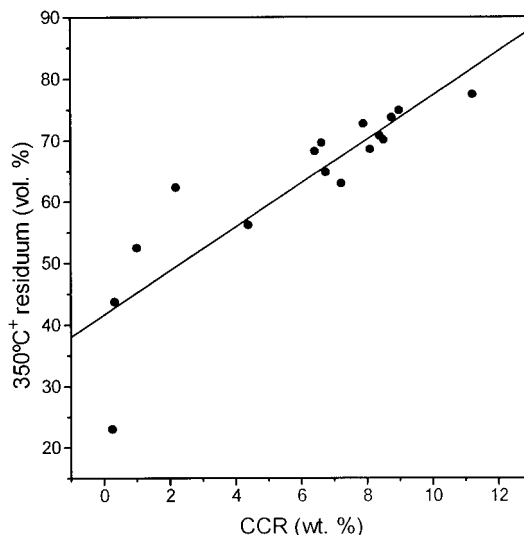
The possible relationship between CCR content and asphaltenes content was studied (Figure 7), and a linear relationship was observed. The highest asphaltenes and CCR values were obtained in the feed. The CCR content decreases as the asphaltenes content decreases, with the lowest value being obtained at 415 °C and the lowest liquid flow.

Asphaltenes conversion occurs through gases and oils formation, with the coke formation being strongly inhibited (Schucker and Keweshan, 1980; Savage et al., 1988; Martínez et al., 1997). A relationship between CCR conversion and gas yield was found (Figure 8). The lowest CCR conversion and gas yield were obtained at 415 °C and the lowest liquid flow.

Several studies had been done to show the relationship between CCR and 525 °C residuum content. Ternan and Kritz (1990) found that there was a correlation between pitch content and CCR in the feeds and products from hydrocracking reactions, both with hydrotreating catalysts and hydrogen transfer additives in continuous pilot-plant reactions. Sanford (1991) did not find a clearly linear relationship for batch catalytic hydrocracking, but a linear tendency was found. In our experimental conditions, a linear relationship between CCR content and 350 °C residuum content was found (Figure 9), with the lowest value of 350 °C residuum and CCR contents for the product being obtained at the most severe conditions, 415 °C and the lowest value of liquid flow.

Figure 9. Linear relationship between residue content ($T > 350$ °C) and CCR content at 12.5 MPa. $Y = -41.60 + 3.567X$ ($r = 0.87$).

Conclusions

The data of CCR conversion fit half-order kinetics, and no pressure dependence on the rate constants as defined by the equation $K = K^* P_{H_2}{}^m$ has been observed. The activation energy of the process is 277.58 kJ/mol.

The CCR conversion ranges from 21.1 to 98.2 wt%, and the products obtained at 415 °C meet the CCR specifications for FCC (fluid catalytic cracking) feeds.

The NMR data indicate that at 375 and 400 °C the hydrogenation of aromatics, cracking reactions, and stabilization of forming radicals are produced while at 415 °C these reactions are overlapped with cyclation and dehydrogenation of alkylcyclohexane reactions. A linear relationship between CCR and aromatic carbon contents was found in the processed products obtained at 415 °C. A general relationship for all temperatures was not found.

The relationship between CCR and different parameters was studied, and it was found that asphaltenes, hydrogen contents, H/C atomic ratio, and 350 °C residue content were linearly related to CCR content. Gas yield was also found to be linearly related to CCR conversion.

The linear relationship found between CCR and asphaltenes and 350 °C fraction indicates that it is in

the asphaltenes and in the higher boiling fractions where the coke precursors reside. The most accepted model for the asphaltene molecules describes them as consisting of large, pericondensed polynuclear aromatic centers with attached alkyl and alicyclic systems. These centers are the coke precursors and not the smaller aromatic molecules as is deduced from the nonexistence of a general correlation between aromatic carbon and CCR. The systematic variation in the composition of petroleum as a function of boiling point, reported by Quann et al. (1988), makes this conclusion extensive to fractions of similar boiling point to other crudes.

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