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Kinetics of thermal hydrocracking of heavy oils under moderate hydroprocessing reaction conditions

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ABSTRACT

Thermal hydrocracking (non-catalytic) of a heavy oil residue was studied in a bench-scale fixed-bed reactor unit. The reaction temperature and the ratio of total mass flow to inert material volume were varied from 380 to 420 °C and from 0.23 to 0.65 $g_T\ cm_{SiC}^{-3}\ h^{-1}$ respectively, at constant hydrogen-to-oil ratio (890 m^3/m^3) and pressure (100 kg/cm^2). The reactor was loaded with silicon carbide as inert material. The results from the simulated distillation of the feed and of the products were used to calculate conversion of vacuum residue and the yield of each specific fraction (vacuum gasoil, middle distillates, naphtha and gases). The lumping approach was used to study the kinetics of the hydrocracking reaction. The results confirm that hydrocracking reactions proceed by cascade mechanism from the heavier fractions to the lighter fractions. Naphtha does not hydrocrack to form gases at the operating conditions studied. The reaction order that better fits the experimental data of vacuum residue conversion is two with activation energy of 42 kcal/mol.

1. Introduction

Hydrocracking reactions are present in a large number of petroleum refining processes [1]. In fact, all fractions of petroleum are able to hydrocrack under certain operating conditions. For instance, in the catalytic reforming process the naphtha fraction suffers hydrocracking to produce liquefied gas and dry gas resulting in a loss of liquid yield [2]. However, the hydrocracking reaction is not always undesirable. For example, when heavy fractions such as vacuum gasoil and residua are hydrocracked the reaction allows for the production of lighter products such as naphtha and middle distillates which have higher market value [3,4]. This hydrocracking is properly controlled by means of suitable catalysts and reaction conditions. The degree of conversion of these heavy feeds depends on the operating conditions (temperature, pressure and contact time) and of course, on the type of feed and catalyst [5]. Most of the hydrocracking reactions proceed via catalytic mechanisms. Many of the industrial catalysts are designed to include active sites and specific promoters to break up hydrocarbon molecules and add hydrogen [6]. The use of different levels and types of acid sites on the catalysts is well-known to achieve these purposes [7].

Depending on the specific characteristics of each process, apart from the catalytic reactions thermal or non-catalytic hydrocracking can also be present [8,9]. The extent of thermal hydrocracking reactions depends strongly on operating conditions [10]. Because they are non-catalytic reactions, they have activation energy larger than the reaction promoted by catalyst, and therefore they are favored by more severe temperature similar to that required at the end-of-run (final life of the catalyst). Moreover, as they are not dependent on active sites of any catalyst they can be carried out in both the gas phase and the liquid phase. The conversion is highly dependent on temperature and on the degree of branching of the hydrocarbon molecules. The thermal hydrocracking reaction is a chain reaction of free radicals. Some researchers have found that the beginning of hydrocracking reactions is determined by temperature [11].

The hydrocracking of heavy fractions involves complex chemical reactions due to the large variety of compounds present in the feed. For this reason it is particularly difficult to study the kinetics and reaction mechanisms of each of the components in the system. Some studies report the use of physicochemical characterization of the hydrocarbon groups by means of NMR spectroscopy and elemental analysis to determine the average molecular parameters, or a wide variety of chemical degradation methods in order to identify families of compounds such as SARA separation [12]. These characterizations are performed before and after reaction so that different path reactions can be studied and the corresponding mechanisms be established. The so-called compositional models describe the changes in oil composition according to different operating conditions through the reactor and the time [13]. Thus, it is possible to determine the reaction kinetics of removal of particular elements as well as of hydrocracking of selected

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Nomenclature

Ea	activation energy (kcal/mol)
Fm_T	total mass flow at the reactor inlet (g h^{-1})
g_i	content of fraction *i* in the product (g)
$g_{i,0}$	content of fraction *i* in the feed (g)
g_T	total amount of stream entering the reactor (g)
g_{VR}	content of vacuum residue (538 °C+) in the product (g)
$g_{VR,0}$	content of vacuum residue (538 °C+) in the feed (g)
k_0	global rate constant for thermal hydrocracking of vacuum residue in Eqs. (2) and (3) ($g_{VR}^{(1-n)}$ cm_{SiC}^{-3} h^{-1})
k_0	global rate constant for thermal hydrocracking of vacuum residue in Eqs. (5)–(9) (g_T cm_{SiC}^{-3} h^{-1})
k_1	rate constant for thermal hydrocracking of vacuum residue to VGO (g_{VR}^{-1} g_T^{n} cm_{SiC}^{-3} h^{-1})
k_2	rate constant for thermal hydrocracking of vacuum residue to middle distillates (g_{VR}^{-1} g_T^{n} cm_{SiC}^{-3} h^{-1})
k_3	rate constant for thermal hydrocracking of vacuum residue to naphtha (g_{VR}^{-1} g_T^{n} cm_{SiC}^{-3} h^{-1})
k_4	rate constant for thermal hydrocracking of vacuum residue to gases (g_{VR}^{-1} g_T^{n} cm_{SiC}^{-3} h^{-1})
k_5	rate constant for thermal hydrocracking of VGO to middle distillates ($g_T cm_{SiC}^{-3} h^{-1}$)
k_6	rate constant for thermal hydrocracking of VGO to naphtha (g_T cm_{SiC}^{-3} h^{-1})
k_7	rate constant for thermal hydrocracking of VGO to gases (g_T cm_{SiC}^{-3} h^{-1})
k_8	rate constant for thermal hydrocracking of middle distillates to naphtha (g_T cm_{SiC}^{-3} h^{-1})
k_9	rate constant for thermal hydrocracking of middle distillates to gases (g_T cm_{SiC}^{-3} h^{-1})
k_{10}	rate constant for thermal hydrocracking of naphtha to gases (g_T cm_{SiC}^{-3} h^{-1})
n	reaction order for the thermal hydrocracking of vacuum residue
r_G	reaction rate of gases (g_G cm_{SiC}^{-3} h^{-1})
r_{MD}	reaction rate of middle distillates (g_{MD} cm_{SiC}^{-3} h^{-1})
r_N	reaction rate of naphtha (g_N cm_{SiC}^{-3} h^{-1})
r_{VGO}	reaction rate of VGO (g_{VGO} cm_{SiC}^{-3} h^{-1})
r_{VR}	reaction rate of vacuum residue (g_{VR} cm_{SiC}^{-3} h^{-1})
V_{SiC}	total amount of inert material (cm_{SiC}^{-3})
x_{VR}	vacuum residue conversion
Y_i	yield of fraction *i* (%)
y_i	composition of fraction *i* in the product
$y_{i,0}$	composition of fraction *i* in the feed
y_{MD}	composition of middle distillates
y_G	composition of gases
y_N	composition of naphtha
y_{VGO}	composition of VGO
y_{VR}	composition of vacuum residue

Subscripts

SiC	silicon carbide
VR	vacuum residue
VGO	vacuum gasoil
MD	middle distillates
N	naphtha
G	gases

hydrocarbon groups when initial and final concentrations of them are known in spite of dealing with heavy hydrocarbons [14,15].

Most of the kinetic studies for hydrocracking of petroleum-derived samples have been developed in the presence of catalyst, severe reaction conditions and using vacuum gasoil as feed. However, the non-catalytic hydrocracking has received less attention, particularly for heavy residues. Schweitzer and Kressmann [16] reported a four-lump kinetic reaction scheme for catalytic and thermal hydrocracking; however only the kinetic constants and activation energy for the catalytic hydrocracking were given. It is well recognized that temperature has a great impact on the extent of hydrocracking, but also other process variables affect it, e.g. pressure and hydrogen-to-oil ratio, thus not working at severe conditions, i.e. at mild conditions, will considerably affect the reaction kinetics [17,18]. In other words, the reaction kinetics at severe conditions will be different to that at moderate conditions.

In a previous paper, we studied the thermal removal of sulfur and metals during non-catalytic hydrotreating of an atmospheric residue from heavy crude (13 °API) [19]. The present contribution uses the same experiments, but now the thermal hydrocracking is analyzed by means of the effect of reaction conditions on product distribution. A lumped kinetic model already reported in the literature for catalytic hydrocraking of heavy oil was also used for non-catalytic hydrocracking [20].

2. Experimental

Thermal hydrocracking tests were conducted in a fixed-bed bench-scale reactor. Details of the experimental set up and procedure were given elsewhere [19]. The operation of the reactor was carried out in isothermal regime at a pressure of 100 kg/cm^2 and a H_2-to-oil ratio of 890 m^3/m^3 (5000 ft^3/bl). The reactor was loaded with 200 ml of silicon carbide (SiC). Silicon carbide has a density of 3.2 g/cm^3 and it is highly chemically inert. It possesses high thermal conductivity, strength and low thermal expansion coefficient (4.0×10^{-6} K^{-1}) and does not experience phase transitions that would cause discontinuities during thermal expansion. The reactor temperature was varied from 380 to 420 °C and the ratio of the total mass flow (Fm_T) respect to the silicon carbide volume (V_{SiC}) was varied from 0.23 to 0.65 g_T cm_{SiC}^{-3} h^{-1}.

An atmospheric residue was used as feed for all the experiments. This sample was obtained from the fractionation (ASTM D-1160) of a 13 °API heavy crude oil. Table 1 shows the main properties of the feed. Simulated distillation according to ASTM D-7169 method was used to determine the mass composition of the feed and of the hydrocracked products.

3. Results and discussion

3.1. Effects on the API gravity

Fig. 1 shows the changes in API gravity of the product as a function of Fm_T/V_{SiC} ratio and temperature. The total increase in API gravity at the most severe operating conditions (0.23 g_T cm_{SiC}^{-3} h^{-1} of Fm_T/V_{SiC} ratio and 420 °C) is about 7 units with respect to feed value (3.2 °API). It is also observed that the effect of temperature on API gravity is less pronounced than that of Fm_T/V_{SiC} ratio. Although at the highest temperatures (400–420 °C) the API gravity increases more as compared with lower temperatures. The changes observed in the API gravity are directly related to the hydrocracking extent, that is the higher the API gravity the higher the hydrocracking degree. The effect of Fm_T/V_{SiC} ratio at all temperatures follows a tendency quite close to linear, which means that kinetics of hydrocracking can be represented by simple power-law model.