



Full Length Article

Direct crude oil cracking for producing chemicals: Thermal cracking modeling



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ABSTRACT

The direct cracking of crude oil is an interesting option for producing cheaply large amounts of petrochemicals. This may be carried out with catalyst and equipment similar to that of catalytic cracking, but at a temperature range between that of standard catalytic cracking and steam cracking. Thermal cracking will play a role in the conversion, but is rarely disclosed in experimental or modeling work. Thus, a crude oil and its fractions were thermally cracked and the products yields were modeled using a 9 lumps cracking scheme. It was found that heavy fraction cracks twice as fast as diesel fraction and ten times faster than gasoline fraction, with activation energies in the 140–200 kJ/mol range. Selectivity to ethylene, propylene and butenes were found similar in the operating range explored.

1. Introduction

Most petrochemical feedstocks, namely light olefins (ethylene, propylene, butenes, butadiene) and aromatics (benzene, toluene, xylenes) are produced today as valuable by-products from petroleum refining. Their markets are expanding and new producing technologies have to be implemented [1]. A large part of the olefin production is ensured today through steam crackers [2], where the ratio between the two main olefins, ethylene to propylene, is not very flexible and usually produces more ethylene than propylene. As a consequence, propylene has been increasingly sourced from catalytic cracking, and on-purpose propylene processes such as propane dehydrogenation and olefin metathesis. In terms of catalytic cracking, a number of high temperature and high catalyst to oil ratio processes have been developed [3–6]. As a refinery product, petrochemicals production is dependent on the refinery feedstock. Crude oil would be an ideal feedstock for directly producing olefins and aromatics. Then, direct steam cracking of crude oil has to deal with coking issues, which can be tackled by separating the heavy fraction or using solid heat carriers to retain coke [7–9]. Also, the limited flexibility in the ratio of the produced olefins calls for a different process, which could be inspired from Fluid Catalytic Cracking process [10].

Numerous models have been used to model catalytic cracking of Vacuum Gas Oil [11–17], and some were directed to high temperature cracking for olefins dedicated processes [18–21]. Lumps are usually

used for modeling distillates (gasoline and higher boiling point compounds), while the gas fraction description may be more detailed, with the sought olefins sometimes modeled as a separate component. In most of the models related to catalytic cracking, thermal cracking is not modeled, as the thermal contribution to the final yields is considered as negligible compared to the much faster catalytic process. While this is a very legitimate assumption for traditional catalytic cracking, which operates at temperatures below 550 °C, this is no longer accurate when the temperature increases above 600 °C, where the thermal contribution begins to be important [22]. A number of models were developed for steam cracking of light feeds and naphthas, with a great detail of reaction scheme and resulting gas compositions for a wide range of feeds, for example the SPYRO model [23]. Models for (thermal) pyrolysis of crude oil that include the vacuum gas oil fraction were however not reported, as this feed is not used in steam cracking due to coking issues. We also sought for a model easily compatible with simple catalytic cracking models.

By keeping in mind a process that would involve the direct high temperature cracking of crude oil using a solid carrier/catalyst to produce olefins, while removing coke, the current study reports the thermal cracking of a crude oil, in a temperature range that covers from high end catalytic cracking (560 °C) to high temperature olefins oriented processes (640 °C). The full crude oil was processed. After splitting into a light and a heavy fraction, the response to thermal cracking of these fractions was also examined. A 9 components model

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was then developed to describe thermal cracking.

2. Experimental

2.1. Materials

2.1.1. Solid heat carrier

An inert solid was used as a heat carrier in the setup to provide heat for vaporization and thermal cracking. While the wall may transfer some heat to the gas media, it is preferable to have a solid in the unit acting as thermal mass and providing efficient heat transfer for feed vaporization and compensate for heat of reaction. Sand is often used, but has poor flowing properties. In our case a solid was prepared from an Equilibrium catalyst (E-Cat) which was impregnated with Na and then steamed at 900 °C for 10 h. The obtained particles have shown a surface area below 1 m²/g and no acidity could be measured through pyridine adsorption. Yet the solid retained the microsphere shape and density of an equilibrium catalyst, which allowed smooth flowing through the unit. Inertness of the solid was checked comparing the obtained activity with that of carborundum in a Microactivity test at 545 °C using a standard VGO. Identical results were obtained for the two solids: very low conversion due to thermal cracking.

2.1.2. Feed characterization

The properties of the crude oil used in this study are listed in Table 1. The crude was further fractionated into a light and a heavy fraction, with a cut point set at 350 °C. Properties of the crude oil fractions are listed in Tables 2 and 3.

As for crude oil, the boiling point curve was determined by Simulated Distillation (SIMDIS) following ASTM D-2887 specifications. The relative amount of the fractions in the crude oil was determined as 61 wt% light fraction and 39 wt% of heavy fraction. Some butane present in the crude oil was lost during the distillation and as a result gasoline composition in the light cut is slightly different from the gasoline composition in the crude oil. Analysis showed that n-butane for crude oil is about 0.9 wt% and 0.3 wt% for light fraction.

2.2. Cracking setup

Hardware and detailed operation of the Microdowner unit has been described previously [24,25]. Main features of the unit comprises a solid preheater where said solid is stored before the test, an once-through reactor where the feed and the preheated solid are fed continuously during the test while their residence time is very short, ranging from 0.3 to 5 s, and a separator which separates hydrocarbons and collect spent solid for further regeneration and coke determination. The unit simulates a steady state regime during the length of the test, which usually takes between one and two minutes. The solid separated from the reaction products is continuously stripped during the reaction and for 60 s more after the end of the reaction. Liquids and gaseous products are recovered by cold traps and water displacement burette while the coke deposited on the solid is burned in-situ after the test with a

Table 1
Properties of the crude oil.

Density @15 °C (g/cm ³)	0.828	
Sulfur (wt%)	1.1	
CCR (wt%)	1.4	
Distillation curve (D-1160 from SIMDIS, °C)		
10	50	90
134	284	487
SIMDIS cut, wt%		
Gasoline (ibp-216 °C)	38.8	
Diesel (216–359 °C)	30.6	
Bottoms (359-fbp)	30.6	

Table 2
Properties of the crude oil light fraction.

Density @15 °C (g/cm ³)	0.750	
CCR (wt%)	–	
Distillation curve (D-1160 from SIMDIS, °C)		
10	50	90
122	215	299
SIMDIS cut, wt%		
Gasoline (ibp-216 °C)	58.2	
Diesel (216–359 °C)	41.8	
Bottoms (359-fbp)	0.0	

Table 3
Properties of the crude oil heavy fraction.

Density @15 °C (g/cm ³)	0.920	
CCR (wt%)	3.9	
Distillation curve (D-1160 from SIMDIS, °C)		
10	50	90
391	458	590
SIMDIS cut, wt%		
Gasoline (ibp-216 °C)	0.0	
Diesel (216–359 °C)	6.3	
Bottoms (359-fbp)	93.7	

500 ml/min. of air at 850 K during 3 h. Alternatively, the coked solid can be withdrawn from the unit after the stripping step, and coke is determined by Elemental Analysis. A flow of nitrogen is used for solid transportation and feed dispersion.

For this study a constant feed rate of 2.5 g/ min of oil was used for all the tests. Total flow of nitrogen diluent towards the reactor was 156 Nml/min, including flow for oil dispersion and solid carry-over. Three different reactors were used to attain different gas residence time ranges during operation. The gas residence time can be estimated from experimental data in the reactor with a correlation taking into account inlet composition, outlet composition, temperature and pressure in the reactor. Gas residence time shortened significantly at constant reactor volume when increasing the reaction temperature due to large increase in gas yield. Reactor diameter was maintained constant at 9 mm, while length was 15, 45 or 110 cm, resulting in volumes of 10, 30 and 70 cm³ approximately. Residence time varied in the range of 0.4–0.8 s for the short reactor, 1–2 s for the intermediate reactor and 2.5–5 s for the long reactor, depending on feed and processing temperature. Total pressure was kept at 0.5 bar above atmospheric pressure.

2.3. Analysis of the cracked products and mass balance

Gases were analyzed using a Varian 3800-GC equipped with three detectors, two Thermal Conductivity Detectors (TCD) for analysis of H₂ and N₂ after separation on a 15 cm column filled with 5 A and a 8 cm column filled with 13X molecular sieves respectively, and a Flame Ionization Detector (FID) for C₁ to C₆ hydrocarbons separated in a 30 m Plot/Alumina column. Simulated distillation of the liquids was carried out with a Varian 3800-GC following ASTM-D2887 procedure. Cuts were made at 216 °C for gasoline and 359 °C for diesel. The fraction with a boiling point above 359 °C was defined as Bottoms. Coke was burned in situ and the resulting CO₂ weight measured using adsorbents. Mass balances were considered acceptable in the range 100 ± 5% of the feed introduced.

A conversion was defined as the sum of gases, gasoline, and coke. It has to be reminded here that this conventional definition is not very relevant when applied to the cracking of light fractions or crude oil that includes a significant amount of gasoline.

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