



Studies on thermal cracking behavior of vacuum residues in Eureka process

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HIGHLIGHTS

- ▶ Thermal cracking of VR in Eureka process results in cracked oil, off-gas, and pitch.
- ▶ The quality of the products and yield distribution were investigated.
- ▶ Result analysis revealed that the thermal cracking follows first order kinetic.
- ▶ Significant increase in the saturate fraction was observed in the cracked oil.
- ▶ The stability and compatibility of cracked oils were evaluated.

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ABSTRACT

Vacuum residues derived from three Kuwaiti crude oils, both conventional and heavy, were thermally cracked in a pilot-scale semi-batch reactor that simulates the cracking operation performance in the Eureka process. The thermal cracking of the vacuum residues resulted in three products: cracked oil, off-gas, and pitch. The effect of operating conditions (i.e. reaction temperature and residence time) on the quality of the products and yield distribution has been investigated. The study also determines the kinetic parameters from the experimental data and compares them with the ones predicted from a previously developed five-lumps discrete kinetic model [1]. The stabilities of the thermally cracked oils were also evaluated using the oxidation stability test while their compatibility with the crude oils were assessed using the Oil Compatibility Model of Exxon.

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1. Introduction

Residual oils are playing an increasingly important role in meeting world demand for hydrocarbon-based energy resources. Utilization of residual oils requires upgrading them to petroleum products that are compatible with the prevailing specifications of petroleum products. The upgrading technologies for residues and heavy petroleum fractions are mainly classified into two categories: hydrogen addition processes and carbon rejection processes. The hydrogen addition route requires the heavy oil to react with hydrogen from an external source, which results in an overall increase in H/C ratio, while the carbon rejection route is based on thermal treatment to redistribute hydrogen among the various components, which results in increasing the H/C ratio in some fractions and lowering it in others. In general, thermal cracking route is more commonly employed in processing vacuum residues, as compared to hydrogen

addition route, because vacuum residues typically have high content of heteroatoms, metals and asphaltene that pose problems for hydrogen addition processes. Examples of thermal cracking processes used in the refining industry for the cracking residual oils include delayed coking, flexi-coking, visbreaking, and Eureka.

The Eureka process is a commercially proven thermal cracking process that produces valuable cracked oil and aromatic petroleum pitch from vacuum residues [2,3]. Unlike conventional coking processes, Eureka is designed to prevent oil from over-cracking by continuously stripping the products. This results in a relatively high liquid yield and a low gas yield. The residual product from the process is in the form of pitch, which flows easily out of the reactor at the reaction temperature.

AlHumaidan et al. [1] recently developed a kinetic model that describes the cracking operation performed in the Eureka process. The model is based on the discrete lumping approach, which is commonly utilized to overcome the modeling complexity associated with heavy hydrocarbon conversions [4–12]. Their cracking kinetic model assumed five discrete lumps. The first lump represented the

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total amount of crackable oil in vacuum residue, while the other four lumps represented the cracked products, which are progressively stripped out of the reactor. The product lumps were selected based on the four cuts mainly produced from the Eureka process and these are: the off-gases (<150 °C), cracked light oil (150–370 °C), cracked heavy oil (370–538 °C), and demister oil (>538 °C). The study revealed that thermal cracking of Kuwaiti vacuum residues in the Eureka process followed first order kinetics, which is dominated by parallel pathways.

Thermal cracking kinetics of vacuum residues in other thermal cracking processes have also been studied by various groups of researchers. Reported investigations included visbreaking process [13–26] and delayed coking [27–31]. Most of these studies concluded that the thermal cracking of vacuum residue followed a first-order kinetics [15,19–25,32–38], while Yan et al. [26] reported second-order kinetics.

Thermally cracked oil fractions are known for their low stability and some attempts have been made to enhance product quality and hinder coke formation in certain processes such as the visbreaking process [39,40]. The cracked oils obtained from Eureka process are unique as they normally contain insignificant amount of asphaltene [3]. Therefore, their stability cannot be determined by the commonly used *P*-value parameter, which indicate the ability of an oil to maintain the asphaltene in a peptized state and prevent their flocculation upon heat and storage [41,42]. Instead, the stability of these cracked oils is commonly evaluated by the oxidation test (ASTM 7545), which is a measure of the resistance of the oil to oxidation reaction. The oxidation reactions normally take place through chain reactions, which normally start slow and then rapidly speed up. The time for the oxidation reaction to happen is called the “induction time”, and it is repeatable under identical conditions. The higher the induction time, the higher is the oxidation stability.

In addition to cracked oil stability, the blend compatibility of cracked oil with crude oils is a very important factor in the petroleum industry for producing synthetic crude oils. The compatibility in petroleum industry is defined as the ability to blend two or more oils, within specified ratios, without evidence of flocculation or precipitation of asphaltenes. An incompatible blend normally results in catastrophic fouling and coking in processing equipment, which is considered an expensive problem in petroleum industry [43]. For this reason various oil compatibility tests and models have been proposed to predict the mixing ratios and the blending order of oils that would prevent incompatibility [44–50]. One of the most commonly employed blending model in the petroleum industry is the Oil Compatibility Model of Exxon [46–50], which presents a way to blend two or more processed or unprocessed crude oils in a manner that minimizes fouling and coking in refinery process equipment. The technical viability and the economical profitability of producing different grades of synthetic crude oils by blending thermally cracked oils from Eureka with the heavy crude oils has been assessed by Ramadhan et al. [44].

Most of the studies reported in literature are related to thermal cracking that takes place in delayed coker and visbreaker [13–31]. Very limited work is reported about the Eureka process. The main focus of this work is on the characterization of the product obtained from the thermal cracking of vacuum residue performed in the Eureka process. As previously stated, the thermal cracking in Eureka process is unique, as compared to other thermal cracking processes, because the products are continuously stripped after their formation, which prevents over-cracking and increases cracked-oil yield [2,3].

2. Experimental

The feedstocks of the thermal cracking experiments are vacuum residues that have been prepared by two successive distillations of crude oils. First, the crude oils were atmospherically distilled in a GECIL MVD 30 L distillation unit (ASTM D-2892 method). The

atmospheric residues (AR) were then distilled in a GECIL POTSTILL 5 L vacuum distillation unit (ASTM D-5236 method). Vacuum residues (VRs) were obtained from three Kuwaiti crude oils: Ratawi–Burgan (RB), Eocene (EC) and Lower-Fars (LF). RB is a conventional crude oil with an API gravity of 27, while EC and LF are heavy crudes with API of 18 and 16, respectively. The properties of the three vacuum residues that were used in this study are shown in Table 1.

The vacuum residues were thermally cracked at three cracking temperatures (400, 415, 430 °C) and three reaction times (30, 50, 60 min). The thermal cracking tests were carried out in a 2 L semi-batch pilot-scale reactor, emulating the commercial Eureka process. The schematic diagram of the thermal cracking pilot plant is shown in Fig. 1. The reactor is loaded with 500 g of vacuum residue and heated using a two-zone electrical furnace (bottom and side heaters) that can be controlled using the skin and bed temperatures of the reactor. The reactor is equipped with a mixer and a nitrogen-injector. The speed of the mixer is fixed at 300 rpm to provide a uniform reaction temperature. Pre-heated nitrogen stream is injected at a constant flow rate (1 NL/min) into the reactor to strip the products immediately after formation (nitrogen pre-heater is set at the required cracking temperature). Continuous stripping of the products prevents over-cracking and reduces the hydrocarbon partial pressure in the reactor, which shifts the reaction equilibrium toward product formation. The cracked oil, in vapor state, is stripped out of the reactor by the nitrogen stream to a condenser, where most of the cracked oil is separated from the non-condensable gas. The temperature of the condenser is set at 50 °C, which is the minimum temperature required to prevent wax deposition and plugging of the heat exchanger. The condensed cracked oil is collected in a round-bottom flask, while the non-condensed vapor is passed through a 2 °C condenser to recover the light fractions of the cracked oil. The non-condensable gas, which is mainly composed of light hydrocarbons and inert carrier gas, is passed through a mist trap and a dry gas counter before being collected in a 150 L gas sampling bag for analysis.

Each experimental run produces three products: cracked oil, off-gases, and pitch. The cracked oil was characterized by measuring fundamental physical properties such as the density (ASTM D5002) and kinematic viscosity (ASTM D445). The metal content (i.e. Nickel and Vanadium) in the cracked oils was determined using Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry (ASTM D5708-Test Method A). The cracked oils were also analyzed by simulated distillation (ASTM D7169), CHNS elemental analysis (Dynamic flash combustion with GC-column separation and TCD; Thermo Scientific FLASH 2000), and SARA analysis (ASTM D6560). The cracked oils obtained from our experimental work have insignificant amount of asphaltene, therefore, their stability was assessed by the oxidation stability test (ASTM D7545) rather than an asphaltene precipitation test. The blend compatibility of these cracked oils with Kuwaiti crude oils, on the other hand, was evaluated by the Porla Analyzer (ASTM D7112), which involves an automatic procedure for oil titration and optical detection of asphaltene precipitation. The off-gases were analyzed using Refinery Gas Analyzer (RGA, UOP 539 Method) to determine its composition and to get the material balance. The pitch, on the other hand, was analyzed for softening point using Capillary Rheometer Shimadzu Flow Tester (CFT 500 D), CHNS elemental analysis, and SARA analysis. Material balance was carried out using the measured quantities of the cracked oil, pitch and gas, with reasonably high accuracy in the range of 97–99%.

Measurement of the reaction residence time starts the moment the liquid temperature in the reactor reaches 380 °C, the temperature at which thermal cracking of vacuum residue starts [20,33].

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