Fuel 154 (2015) 152–160

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

An efficient treatment of ultra-heavy asphaltic crude oil using electron beam technology ☆

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HIGHLIGHTS

- Electron beam improves the viscosity reduction process during heavy oil upgrading.
- Different analytical techniques used to analyze physical and chemical changes.
- Irradiation provides an efficient energy transfer means to large hydrocarbons.
- High aromatic content alters the reaction mechanism of radiation thermal cracking.
- Electron irradiated samples exhibit a stable viscosity over time.

ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 4 March 2015
Accepted 10 March 2015
Available online 26 March 2015

Keywords:
Electron beam irradiation
Heavy oil
Asphaltene
Viscosity reduction
Cracking

ABSTRACT

Electron beam technology, as a promising energy-efficient process, is used as a new treatment for ultra-heavy asphaltic petroleum fluids. Over the past few decades, heavy oil resources have been recognized to be among the most abundant sources of energy. However, extraction, transportation, and processing problems of these fluids still remain to be a challenge in the petroleum industry. The contribution of these hydrocarbon resources to the energy market has been impacted by the fact that the conventional upgrading and visbreaking methods demand a considerable energy investment. In this paper, we coupled electron beam irradiation with conventional thermal processing methods to find an energy-efficient way of improving unfavorable properties of heavy asphaltic hydrocarbons. Electron irradiation was observed to improve the viscosity reduction process by a factor of 30% compared to thermal treatment. Energy transfer process becomes more efficient in radiation-induced reactions, which results in an intensified cracking process. The role of complex asphaltene structures on radiation thermal cracking was investigated by using hydrocarbons with high and low asphaltene content. Our results showed that in samples with high asphaltene content, electron radiation impacts the reaction mechanism of the thermal cracking process. In fact, high energy electrons interact with aromatic structures of asphaltene molecules, resulting in products with a different hydrocarbon component distribution and time-stability properties, as opposed to the simple thermal cracking case. On the other hand, experiments showed thermal and radiation thermal cracking processes follow a similar reaction mechanism for hydrocarbons of low asphaltene content.

1. Introduction

During the past few years, the amount of conventional hydrocarbon reserves worldwide was considered to be on a decline, as predicted by the "peak oil" scenario, due to the limited incidence of significant discoveries of such reservoirs. Indeed, while production from conventional acreage declines, global demand rises steadily. Although concerns regarding ways to fulfill the world's need for fuel are definitely not new, the ever-increasing global population and subsequent mounting energy demands on limited traditional resources make the subject more pressing. Looking at the bright side, new technical advances in drilling, completion, production, reservoir characterization, and enhanced recovery techniques have introduced "unconventional resources" as viable alternatives that not only help satisfy growing energy demands but do so in a more secure way. Unconventional reservoirs are reservoirs that contain fossil fuel but are uneconomical

☆ *Abbreviations*: DAO, deasphalted oil; HAO, heavy asphaltic oil; RTC, radiation thermal cracking; TC, thermal cracking.

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http://dx.doi.org/10.1016/j.fuel.2015.03.040
0016-2361/

to produce (typically have recoveries less than 5%) at prevailing market rates when conventional recovery processes are applied. Among these unconventional resources, heavy oils can play an instrumental role in extending and/or replacing the world's energy reserves. Although found in all parts of the world (e.g., Russia, U.S.A., Middle East, Africa, Cuba, Mexico, China, Brazil, Madagascar, Europe, and Indonesia), the largest heavy and extra-heavy oil reserves are concentrated in Venezuela and Canada [1,2]. Regardless of the extraction method (mining, or cold or thermal in situ recovery), producing heavy oils requires a series of processing techniques based on complex and innovative technologies to yield a commercial-grade product.

As an example of these innovative technologies, electron irradiation provides an efficient way of delivering energy to molecular levels of hydrocarbons, while minimizing any probable energy loss in other forms. Electrons give out small portion of their energy to the surrounding molecules while passing through a media, resulting in an almost continuous energy loss mechanism with a substantial deflection in their track due to their small mass [3]. Depending on the factors such as the velocity of the collision and the distance between the closest approach of the particles and the target atoms or molecules, the electron particles interaction with the electrons of atoms or molecules in the material can be inelastic or elastic [4]. The collision is known as inelastic if the individual electrons in the atomic structure of the molecule or atom gain enough energy to be excited into higher energy levels or be ejected into an unbound state. Inelastic scattering results in energy transfer to the molecules producing excited molecules, secondary and Auger electrons, photons, or X-ray. For cases in which the exerted energy is less than the smallest molecular energy level difference, energy and momentum are conserved and the collision is assumed to be elastic. Elastic scattering causes angular deflection in the electron track without any energy loss. Appearance of electric charges is one of the most obvious consequences of exposing materials to ionizing irradiation. Ionizing incidents result in abstraction of electrons from the molecules and creation of positive ions in a so called "ionization" process. The electrons abstracted from the irradiated molecules will be strongly pulled by ions of positive charge, resulting in "charge recombination". The recovered ionization potential generates highly excited molecules (C_n^{**}) with energy levels much higher than bond strength (Eqs. (1a) and (1b)).

$$C_n \rightsquigarrow C_n^+ + e^- \tag{1a}$$

$$C_n^+ + e^- \rightarrow C_n^{**} \tag{1b}$$

The remaining energy that is deposited by ionizing irradiation causes "excitation" for the molecules exposed to irradiation (Eq. (2)) [5–7].

$$C_n \rightsquigarrow C_n^* \tag{2}$$

A highly probable consequence of this excitation and energy transfer to the atomic structure of molecules will be C–C or C–H bond rupture in liquid and gas hydrocarbon radiation as reported by some authors [8–10]. According to Skripchenko et al. [11] radiation is capable of promoting destructive reactions in heavy petroleum fluids, coal samples, and their mixtures. Covalent bond rupture in excited (C_n^*) or highly excited species (C_n^{**}) generates highly reactive free radicals that are capable of initiating chain reactions. Depending on the experimental conditions, this series of chain reactions can result in cracking of larger hydrocarbon molecules into smaller species. Energy deposited into the material through irradiation process (dose) is usually reported as joules per kilogram of the material or gray (Gy).

Application of different irradiation techniques in hydrocarbons includes, but not limited to, gaseous hydrocarbon reactions [12,13], heavy oil upgrading [14–22], and coal processing [23–25]. Yang et al. [14,15] investigated electron beam upgrading of heavy oil samples. They were the first to use Monte Carlo simulation to model energy deposition during electron beam irradiation of petroleum samples. Their laboratory scale investigation showed that C–H bond cleavage occurred during radiation thermal cracking of C_{16} samples. In an effort to introduce a new method to decrease viscosity of heavy oil to overcome its transportation problems, Alfi et al. [16–19] observed that coupling thermal cracking with electron irradiation intensifies the heavy oil cracking process (chemical and physical changes of the products were analyzed). This reinforced cracking is reflected in the lower viscosity of the irradiated fluids.

In this paper, we have analyzed the effect of electron beam irradiation on cracking of Heavy Asphaltic Oil (HAO). Our HAO sample has around 10 wt% asphaltene with a very high viscosity of 5.5×10^6 cp at 20 °C. To assess the influence of radiation on asphaltene molecules, some complementary experiments were performed while the HAO sample was deasphaltened (this fluid is named Deasphalted Oil (DAO)) and the results were compared to the original HAO experiments. Radiation Thermal Cracking (RTC) and Thermal Cracking (TC) were two types of experiments conducted in this research and the products were analyzed in terms of their physical and chemical properties. To author's knowledge, the current paper is the first work to provide a systematic approach to investigate the effect of asphaltic structures on radiation thermal cracking of heavy petroleum samples and the consequent changes in physical and chemical properties of the products.

2. Experimental methodology and material

In this section, we will describe our experimental setup, analytical tools used in this research, petroleum fluids characteristics, and the electron irradiation facility.

2.1. Analytical tools

We have used different analytical techniques to study the physical and chemical changes occurring as a result of electron irradiation of highly asphaltic petroleum samples. The viscosity of the liquid products was measured using Brookfield HBDV-IIIUCP and RVDV-IIIUCP viscometers. Density measurements were performed using the Anton Paar SVM 3000 densitometer. To investigate the boiling point distribution of the liquid products, we performed simulated distillation analysis (ASTM D7169) using high temperature gas chromatography (GC). This test is designed to determine the boiling point distribution of the hydrocarbons up to n-C_{100} and elution temperature of 720 °C, applicable for samples with very heavy nature like atmospheric and vacuum residues. GC analyses were performed at an initial oven temperature of −20 °C with no hold time. The oven is then heated to the final temperature of 425 °C at the rate of 15 °C/min where the final temperature was kept for 10 min. Helium was used as the carrier gas (mobile phase) and its flow rate was set to 20 mL/min. Eluting components were detected using a Flame Ionization Detector (FID). The column used in this test was 5 m long with an inner diameter of 0.53 mm (stationary phase thickness was 0.15 μm). Similar GC techniques were also used to analyze lighter fraction of the liquid products with boiling points less than 250 °C (called *light liquid fraction*), which can be used as a fingerprint for investigation of reaction mechanism.

2.2. Petroleum fluid characteristics

The *Heavy Asphaltic Oil* (HAO), is the atmospheric residuum remaining from atmospheric distillation of crude oil. This fluid is