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Non-thermal plasma enhanced heavy oil upgrading

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HIGHLIGHTS

- A novel process was proposed for upgrading heavy oil using a non-thermal plasma.
- The noticeably high reactivity of plasma was demonstrated by experiments results.
- Loss of the side chain and breakage of the bridged bond were mainly involved.
- Intra-molecular condensation was significant than inter-molecular condensation.

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ABSTRACT

A process was proposed for upgrading heavy oil using non-thermal plasma technology in a conventional thermal cracking system under atmospheric pressure. Results from a comparison of the reactivity of a N_2, H_2 and CH_4 plasma showed that the plasma can increase the trap oil yield significantly. The trap oil yield increased by ~9% when the N_2 plasma was applied and showed a further increase of ~19% when the H_2 or CH_4 plasma was applied. A detailed study on the H_2 plasma-enhanced upgrading process was carried out and the results showed that the trap oil yields of the plasma-on runs can be 8–33% higher than those of the plasma-off runs, depending on experimental conditions. Compared with the plasma-off runs, trap oil from the plasma-on runs had a higher $(H/C)_{atomic}$ but less heteroatoms (S and N). Over-balanced hydrogen in the products from plasma-on runs revealed the H_2 plasma reactivity, which was further demonstrated by an increase in the substitution and condensation indices of trap oil from the plasma-on runs. Although thermal cracking was mainly involved whether the plasma was applied or not, the electrical field for generating the plasma and the generated plasma may assist with hydrocarbon bond cleavage. This was shown by the increased trap oil yield with the N_2 plasma and the hydrogen and carbon residue distribution. Compared with the feedstock, more aromatic and γ-hydrogen (H_A and H_γ, respectively) and less α- and β-hydrogen (H_α and H_β, respectively) were present in the residues, which agrees with the bond dissociation energy data. Similarly, the amounts of saturated (C_s) and alkyl (C_p) carbons in the residues were significantly lower than those in the feedstock while the amount of aromatic carbons (C_a) in the residues was higher than the feedstock. The changes in hydrogen and carbon distribution were more significant for the plasma-on runs. This implies that mainly side chain losses and bridged bond breakage are involved in the processes. This was demonstrated further by the molecular weight distribution. In general, the molecular weight of the residues was lower than that of the feedstock, especially for residues from the plasma-on runs. However, compared with the feedstock, the residues contained less saturated, aromatic and resin fractions but more asphaltene and toluene insoluble fractions. This implies that intra-molecular condensation was more significant than inter-molecular condensation, especially in the plasma-on runs. This should be attributed to the higher stabilization ability of the H_2 plasma for fragments or radicals and gas (plasma) flow by which the fragments or radicals are separated rapidly.

1. Introduction

Worldwide, high-quality light crude oil is becoming depleted and more expensive. The future use of petroleum will likely be centered on heavy oil, including heavy, extra heavy crude and refinery

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residues. Heavy oil differs from conventional crude oil, which has a low hydrogen-to-carbon ratio and a high level of heteroatoms (e.g., nitrogen, sulfur and trace metals) concentrated in the asphaltene fraction [1]. Therefore, the processing of heavy oils by conventional technologies is a challenge.

Typically, two general routes exist for upgrading heavy oil: carbon rejection and hydrogen addition [2]. Carbon rejection processes extract the light products from heavy oil by thermal cracking, such as delayed coking and visbreaking. In general, hydrogen addition processes (i.e. hydrotreating and hydrocracking) add hydrogen to heavy oil with the aid of a catalyst under a high hydrogen partial pressure [3,4]. The quality of light products from the carbon rejection method is usually poor and low-value coke or asphalt-like material are produced. Hydrogenation can suppress coke formation and improve the quality of light products, but it has to face the problem of catalyst deactivation because of carbon and metal deposition on the catalyst surface [5,6].

High plasma reactivity has attracted researchers' attention because of its application in the chemical industry. Plasma is an ionized gas that is defined as the fourth state of matter after solid, liquid and gas. It can be generated by heating a gas or by applying a strong electromagnetic field (or a high voltage electrical field) to a gas. Plasma is an electroneutral mixture and contains electroneutral gas molecules, as well as electrons, ions, atoms, radicals, photons and excited molecules, which are chemically and physically active species [7]. Chemical reactions, such as radical reactions, and physical effects, such as ion bombardment, may be involved when plasma is created.

Plasma technology has been used in many fields, such as gas cleaning, surface treatment and ozone production [8–11]. Studies have been conducted that focus on light oil processing or reforming, which aim to produce hydrogen-rich gas for onboard vehicle fuel cells or syngas [12–15]. Plasma technology can be introduced into the heavy oil upgrading field to reduce hydrogen partial pressure and to avoid the requirements for expensive catalysts in traditional hydroprocessing.

Plasma can be categorized as thermal or non-thermal. The input power required to generate a thermal plasma is relatively high (tens of kilowatts). The thermal plasma temperature is usually higher than 1000 °C. Hence, it is usually used to produce gaseous hydrocarbons, such as ethylene, acetylene and syngas [16–20]. Part of the input power for generating thermal plasma is exhausted by the rise in system temperature. Although high temperatures are required for the reaction, a high consumption of electricity for heating the system is economically infeasible.

In contrast, the input power required for generating a non-thermal plasma is relatively low and does not cause an obvious rise in system temperature. The system can be operated around or slightly higher than ambient temperature. The non-thermal plasma process is energy efficient and has potential for commercial application. It has been studied for coal conversion or heavy oil upgrading. A brown coal was tested using the microwave plasma by Osamu Kamei et al. [21]. A maximum oil yield of 18 wt% was obtained. The coal-liquids that were produced contain mainly C_{13}–C_{34} aliphatic hydrocarbons. Heavy oil was treated in a plate-plate dielectric barrier discharge plasma reactor by Prieto et al. [22]. Products with C_1–C_4 hydrocarbons such as CH_4, C_2H_4, C_3H_6 and C_4H_{10} were detected, with ethylene as the main product. Kong [23] patented a coaxial dielectric barrier discharge (DBD) plasma reactor for co-processing heavy oil and methane. Gasoline and light diesel-like products were identified in the products. Nevertheless the yield of targeted light products is usually low for the non-thermal plasma because of the absence of massive chemical bond cracking of the heavy hydrocarbons.

To take advantage of non-thermal plasma properties (producing and maintaining a high concentration of chemically active species under atmospheric pressure without using a catalyst) and conventional thermal cracking (massive cracking of heavy hydrocarbons), a novel process for upgrading heavy oil has been proposed. In this process, a non-thermal gas plasma is created in a conventional thermal cracking system, in which the reaction is operated at elevated temperature under atmospheric pressure gas flow in a semi-continuous mode. It is expected that gas reactivity can be promoted by exciting to its plasma state (including ions, radicals and atoms), which can accelerate the conversion of heavy oil to light oil. The reactivities of N_2, H_2 and CH_4 plasma were compared in this study and the influence of the H_2 plasma on the product quantity and quality is discussed under different conditions.

2. Experimental

2.1. Feedstock

A petroleum residue from a PetroChina Refinery in China was used as feedstock. The main properties of this feedstock are listed in Table 1.

2.2. Reaction system and experimental procedures

Experiments were carried out in a cylindrical dielectric barrier discharge (DBD) plasma reaction system, which is shown in Fig. 1 [24]. It consists of a stainless steel reactor (51 mm inner diameter, 275 mm long) that is connected to the ground as reaction chamber and ground electrode, a quartz tube (50 mm outer diameter, 46 mm inner diameter and 210 mm long) that is coaxial with the reactor as a dielectric barrier, a stainless steel rod (34 mm diameter) with screw thread located at the center of the reactor as a high voltage (HV) electrode, and an electric furnace (1.5 kW) with a temperature controller. The annular discharge gap was formed between the ground and HV electrodes. The volume of the annular reaction chamber was ~250 cm^3 and approximately 4/5 was filled with feedstock at the beginning of each experiment.

The reaction system was preheated to a designated temperature before ~200 g test sample, which was preheated to 200 °C, was loaded into the reaction chamber. Reaction gas (600 ml/min N_2, H_2 or CH_4) was fed continuously into the reaction chamber from two openings at the bottom of the reactor. The gas stream was bubbled through the heavy oil layer, stirred the heavy oil, increased the gas–liquid interface, and left the reactor continuously from the top whilst entraining the light products. The gas stream then passed through a sequential hot (120 °C) and cold (0 °C) trap, where the condensable products were collected as liquids. The light oil was separated continuously from the heavy oil by the gas flow entrainment. The liquid that collected in the cold and hot traps was termed trap oil and was weighed and analyzed. After each experiment, the heavy oil remaining in the bottom of the reactor as a residue was also collected, weighed and analyzed. All experiments were conducted semicontinuously under atmospheric pressure.

When the experiments were carried out with the plasma, a plasma generator (NanJing Suman Electronics Co., Ltd., China) was used to supply power to the HV electrode. An HV probe Tektronix P6015 (bandwidth: 75 MHz; input impedance: 75 MΩ/3 PF; maximum: 20 kV) and a current probe Tektronix CT-2 (maximum current: 36 A peak, 2.5 A continuous; minimum current: 50 mA; bandwidth: 1.2 kHz–200 MHz; rise time: 500 Ps) with a digital oscilloscope Tektronix DPO3034 (analog bandwidth: 300 MHz; sample rate: 2.5 GS/s; record length: 5 M points; analog channels: 4) were used to monitor the voltage and current between the discharge gap. A high electrical field was formed in the reactor between the HV and ground electrodes (the annular