Thermal Conversion of Heavy Crude Oil in the Presence of Formic Acid as a Hydrogen-donor Solvent

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Abstract. In this study, thermal conversion experiments of heavy oil using steam and formic acid as a hydrogen donor were carried out in a batch reactor at T = 380 °C and P = 165 bar. Material balance and products distribution were calculated after the experiments. Properties of crude oil before and after thermal conversion were analyzed including: viscosity, API gravity, SARA and elemental analysis measurements. It was shown, that application of formic acid as a hydrogen-donor solvent leads to the reduction of coke and gaseous products formation and to the increase of liquid products yield. In addition, the viscosity of upgraded oil was decreased by 23.2% due to addition of formic acid in comparison with thermal conversion without the hydrogen-donor solvent.

1. INTRODUCTION

In last decades, research related to the development of new technologies for the production of heavy hydrocarbons, such as heavy and extra-heavy oils, natural bitumens, oil sands has been extensively conducted [1,2]. This is due to the reduction of the light oil production and the annual increase in the amount of heavy oil involved in recovery processes. Heavy oils have a high content of resins, asphaltenes and other heteroatomic compounds. Many studies were dedicated to the use of unconventional methods that could ensure the production of lighter, so-called synthetic oil from heavy feedstock, which can be further processed according to existing schemes without substantial changes in refinery processes. One of the promising ways to produce synthetic oil is thermal conversion of heavy hydrocarbon feedstock in the presence of water in the form of superheated steam or at critical or supercritical conditions [3]. It was reported that using of superheated steam in the process of cyclic steam stimulation is fostered for the thermal enhanced oil recovery including heavy oils and oil sands, like Athabasca oil sand and Orinoco heavy oil [4-6]. Another research done by Li et al. suggested that thermal conversion of heavy oil takes place in the oil reservoir when injected the superheated steam [7]. In addition, Song et al. offered a new thermal
conversion project for conventional heavy oil by superheated steam. Authors observed [7] that the reaction will reach evenness after a confirmed time and will not be sensitive to reaction time. Katritzky et al. indicated that water in the form of superheated steam participates as a catalyst, reactant, and a good hydrogen-donor solvent in reactions of hydrocarbon compounds with superheated steam [8]. Under these conditions, water has the properties of a non-polar proton-donor solvent. In addition, physical properties of water under these conditions like density, dielectric constant, hydrocarbon solubility and ion dissociation constants, which can speed up the thermal conversion, increased significantly [9]. Consequently, it makes possible to increase the efficiency of thermal processes for the destruction of heavy oil feedstock and, as a consequence, to obtain “synthetic” oil with a low content of high molecular weight heteroatomic compounds and a high content of low-boiling fractions.

The main disadvantage for thermal conversion of heavy hydrocarbon resources in the presence of superheated steam is the significant formation of coke and gaseous products [10], which leads to the loss of the desired components of the liquid products (synthetic oil). However, this issue can be solved by using some additives such as hydrogen-donor solvents or any agent, which prevent the coke and gas formation.

In addition, thermal conversion of heavy oil using hydrogen-donor solvents along with superheated steam lead to an increase in the ratio of hydrogen and carbon, as a result of transfer an additional hydrogen from hydrogen-donor solvents, which participates in hydrogenation reactions (preventing the recombination of the formed radicals). It should be noted that, there are many studies and works showed that using additives such as hydrogen-donor solvents or even different catalysts with steam improve the efficiency of upgrading and conversion of heavy oil and reduce the coke and gas formations. Fan et al indicated that, the coke and gas formations can be decreased by adding hydrogen donor and catalysts [11, 12]. This technology successfully has been applied in the field with good results. For extra-heavy oil (Shengli oilfield, China) the viscosity reduction rate was about 70% after thermal-catalytic upgrading by adding of a hydrogen donor [12].

In Tatarstan region, Russia, there are many heavy and extra-heavy oil fields, which are developed by using steam based method for enhanced oil recovery (SAGD) [13,14]. Using of hydrogen-donor solvents as additive can help to improve the efficiency of their extraction and in-situ upgrading. In this work formic acid is using as hydrogen-donor solvent together with superheated steam, to reduce the formation of coke and gas products, and to prevent the recombination reactions during the thermal conversion process of heavy oil.

2. MATERIALS AND METHODS

Heavy oil (Tatarstan region, Russia) was used in this work. The main characteristics are shown in Table 1.

Table 1. Properties of studied heavy oil
### Results and Discussion

#### 3.1. Material Balance and Products Distributions for the Process of Thermal Conversion

Upgrading experiments were carried out in a stainless-steel 350-ml batch Parr reactor equipped with a heating device and a temperature controller. In a typical experiment, the reactor was loaded with crude oil and water at a weight ratio of 2:1, respectively. The reactor was heated at 5°C/min to 380°C, generating a final pressure of approximately 164 bars for 6 hours (2 bar initial N₂ pressure). The thermal conversion experiment of using steam and hydrogen-donor solvent (2% mas. formic acid) together was conducted at the same conditions as experiment without hydrogen-donor solvent.

Physical-chemical properties including viscosity, API gravity and SARA analysis of oil before and after thermal conversion in the presence and absence of formic acid were studied. Viscosity and API gravity of oil were measured by SVM-3000 Stabinger viscometer. The elemental composition of oil before and after conversion was determined by Analyzer Perkin Elmer 2400 Series II. SARA analysis was done according to ASTM D 4124.

#### 3. RESULTS AND DISCUSSIONS

| Parameter                        | Value | Parameter                        | Value |
|----------------------------------|-------|----------------------------------|-------|
| °API gravity                     | 14.1  | Elemental analysis (wt. %):      |       |
| Viscosity at 25 °C, mPa·s        | 2073  | Carbon                           | 83.68 |
| Saturates, % mas                 | 28.79 | Hydrogen                         | 11.44 |
| Aromatics, % mas                 | 44.32 | Sulfur                           | 4.52  |
| Resin, % mas                     | 20.98 | Nitrogen                         | 0.36  |
| Asphaltenes, % mas               | 5.91  |                                  |       |

where Wi is the weight of component i and WF is the weight of the feed oil (heavy oil downloaded into the reactor) and WA is sum of weights of coke and liquid phase in autoclave after the experiment.
Table 2. Material balance for thermal conversion of crude oil at 380 °C.

| Reaction system | Temperature, °C | Liquid yield (wt, %) | Coke yield (wt, %) | Gas yield (wt, %) |
|-----------------|-----------------|----------------------|--------------------|-------------------|
| oil + superheated steam + N₂ | 380 | 73.04 | 16.63 | 7.33 |
| oil + superheated steam + formic acid + N₂ | 380 | 80.10 | 13.89 | 6.01 |

From table 2 it can be noted high yield of coke and gas after thermal upgrading with superheated steam, due to polymerization and condensation of high molecular weight components. Quite the contrary, adding the formic acid to the reaction system provides decreasing in the yield of the coke and gases and increasing of liquid phase content.

3.2 Viscosity and API gravity of heavy oil before and after thermal conversion at 380 °C

The results of studies of crude oil properties (viscosity, API gravity and SARA analysis) before and after upgrading under superheated steam conditions are given in Table 3.

Table 3. Viscosity, API gravity and SARA composition of oil before and after thermal conversion

| Reaction system | Viscosity at 25 °C, mPa·s | API gravity | Saturates | Aromatics | Resins | Asphaltenes |
|-----------------|----------------------------|-------------|-----------|-----------|--------|------------|
| initial oil     | 2073                       | 14.1        | 28.79     | 44.32     | 20.98  | 5.91       |
| oil + superheated steam | 15.73              | 21.6        | 55.17     | 29.83     | 12.45  | 2.47       |
| oil + superheated steam + formic acid | 12.08              | 22.9        | 57.84     | 31.04     | 9.77   | 1.35       |
From the table 3, we can observe the increase of saturates fraction content and the decrease the amount of resins fraction due to thermal conversion of heavy oil with and without of formic acid as a hydrogen-donor solvent. However, the conversion degree in presence of formic acid is higher. Application of hydrogen donor helps to improve destruction of high-molecular components (resins and asphaltenes) of heavy oil [10,11]. In comparison with the initial oil, the content of saturates significantly increases and the amount of resins and asphaltenes significantly decreases in the same conditions with superheated steam and formic acid. These changes are reflected in the increasing of 0API gravity from 21.6 to 22.9 by adding the hydrogen-donor solvent and reduction viscosity from 2073 to 15.73 without formic acid and 12.08 with it.

3.3 Elemental analysis of oil sample before and after thermal conversion

Table 4 shows the elemental analysis of oil before and after thermal conversion, we can see a noticeable decrease in the heteroatoms, especially sulfur content from 4.52 for initial oil to 2.96 with superheated steam and 2.77 with superheated steam and formic acid. At the same time we can see the decreasing in the percentage of carbon and hydrogen due to their conversion to coke and gas after process of the polymerization and condensation. It should be noted that, adding of formic acid as a hydrogen-donor solvent leads to an increasing the percentage of hydrogen comparing to the upgrading without formic acid.

| System                        | Content, wt % |       |       |       |
|-------------------------------|---------------|-------|-------|-------|
|                               | C             | H     | N     | S     |
| Initial oil                   | 83.68         | 11.44 | 0.36  | 4.52  |
| Oil + superheated steam       | 83.65         | 8.65  | 0.19  | 2.96  |
| Oil + superheated steam + formic acid | 83.01         | 10.87 | 0.34  | 2.77  |

4. CONCLUSION

Thermal conversion of heavy crude oil using a superheated steam together with formic acid as hydrogen-donor solvent gave promising results. The content of high-molecular heteroatom substances such as resins and asphaltenes was decreased in contrast with thermal treatment using just superheated steam. The viscosity of heavy oil was improved by adding formic acid, compared with thermal conversion without the hydrogen-donor solvent (viscosity reduction rate is equal to 23.2%). Additionally, using the formic acid as a hydrogen-donor solvent leads to the reduction of obtained coke and gaseous products, increase the amount of
liquid products (upgraded oil) yield. In addition, the reduction of sulfur content was observed due to adding the formic acid as a proton donor for the thermal conversion process.

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