



Upgrading of petroleum vacuum residue using a hydrogen-donor solvent with acid-treated carbon



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ARTICLE INFO

Keywords:

Upgrading
Vacuum residue
Hydrogen-donor solvent
Activated carbon
Supercritical tetralin

ABSTRACT

Hydrocarbon/carbon systems can be used to perform the hydrogen transfer reaction in heavy oil upgrading, as alternatives to metal catalysts and molecular hydrogen. In this study, a system comprising a hydrogen-donor solvent (tetralin) and acid-treated activated carbon was established to evaluate its ability as a hydrogen transfer agent to upgrade a vacuum residue (VR). The use of tetralin substantially decreased coke formation from 32.7 wt % to a negligible amount in VR upgrading at 450 °C because the solvent could act as a hydrogen donor and diluent for the coke precursors. The acid-treated activated carbon accelerated dehydrogenation of tetralin through hydrogen transfer in the upgrading, resulting in a higher residue conversion and moderate coke formation. In view of the phase behavior, the hydrogen transfer reaction could also be promoted by increasing the contact between the hydrogen acceptor and donor in the supercritical medium. In the VR upgrading using the activated carbon in supercritical tetralin, complete residue conversion was achieved with 47 wt% light fractions (gas and light oil) and 6 wt% coke at 450 °C and 5.33 MPa. The results indicate that the streams available in oil refinery processes, which are rich in hydrocarbons with hydrogen-donor abilities, have great potential for use in heavy oil upgrading.

1. Introduction

Depletion of light crude oils and the high demand for transport fuels have forced the global refining industry to pay attention to heavy oil upgrading [1–3]. Among the heavy feedstocks, vacuum residue (VR), the heaviest fraction of crude oil, contains high proportions of asphaltenes, sulfur, nitrogen, and ash-forming metallic constituents, such as vanadium, nickel, and iron [4,5]. A considerable amount of VR (about 25–40% of the total crude processed) is obtained by vacuum distillation [6–8]. In addition, the quantity of VR is expected to increase because crude oil reserves are becoming heavier.

VR can be upgraded by hydrogen addition processes, which may be classified as destructive and nondestructive. Hydrocracking is a destructive hydrogenation in which thermal decomposition is performed, and hydrogen contributes to mitigating coke formation under a relatively high pressure (10–20 MPa) [8]. Despite the high capability to reduce coke formation, the hydrocracking process must reach a compromise between the yields of light products and the catalyst lifespan. The deactivation of metal catalysts by coke and impurities (sulfur, nitrogen, and metals in VR) is a major problem. In addition, it is difficult to maintain normal operations because of the rapidly increased pressure drop in the reactor. The operational difficulties tend to become

more serious when a feedstock with larger amounts of carbon residue and metals is used [9]. Therefore, hydrocracking is characterized by high operating costs because the catalysts display a short lifespan and shut-down is more frequent [10].

Various studies have reported that hydrogen-donor solvents could decrease the coke yield in heavy oil upgrading [11–13]. The hydrogen-donor solvents assist in accelerating the radical capping reaction [14]. Thus, elimination of radicals reduces the condensation reactions related to coke formation [15]. Tetralin is a well-known hydrogen-donor solvent, and its use originated from the coal liquefaction process [16,17]. Tetralin possesses hydrogens in the saturated ring, which are highly activated by the adjacent aromatic ring and are sufficiently reactive to minimize undesired reactions that lead to coke formation during pyrolysis [18]. In other words, the active hydrogens in tetralin participate in the reaction with free radicals produced from pyrolysis of heavy oils, and help to prevent radical condensation and coking [19]. Therefore, heavy feedstocks may be converted into lighter products with suppressed coke formation using a hydrogen-donor solvent.

The hydrocarbon/carbon system can be used for hydrogenation instead of metal catalysts and molecular hydrogen [20–22]. In addition, the use of a hydrocarbon solvent as a diluent can help to prevent aggregation of large molecules and improve the hydroprocessing of heavy

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oils in catalyst pores. Activated carbon is an attractive catalyst or catalyst support for hydroprocessing because of its excellent textural properties, reasonable price, and high resistance to deactivation by coke deposition [23,24]. It was also reported that activated carbon can inhibit coupling and polycondensation of hydrocarbon radicals [25]. Therefore, the hydrocarbon/carbon system might be a powerful hydrogen donor media in upgrading heavy feedstocks.

Reaction mechanisms are dependent on the physical properties of supercritical fluids, which are intermediate to those of gases and liquids [23,26,27]. The unique properties of supercritical solvents have been utilized in heterogeneous catalysis to extract coke precursors from the catalyst, thereby prolonging the catalyst lifespan. Moreover, complete miscibility of reactants and improved transport properties can promote the hydrogen transfer reaction [28]. Other studies have shown that supercritical solvents can enhance VR upgrading and suppress coke formation [21,29,30].

In upgrading of heavy oil with diluent solvents, the product distribution (gas, light oil, vacuum gas oil, and coke) could be sensitively dependent on the operating conditions due to significant property changes of solvents near the critical region. Therefore, it is required to understand the change in heavy oil fractions (saturates, aromatics, resins and asphaltenes) at reaction conditions. In addition, an effective way to maximize conversion and minimize coke formation is needed for VR upgrading using supercritical solvents.

The objective of this study is to investigate the feasibility and effectiveness of the hydrogen-donor solvent/carbon system in VR upgrading. Some refinery streams (e.g. light cycle oil (LCO) and fluid catalytic cracking slurry) contain a relatively abundant amount of condensed aromatic compounds, such as alkylated naphthalenes, anthracenes, and phenanthrenes [31,32]. After partial hydrogenation of these streams, the streams can provide hydrogen to free radicals in a similar manner as tetralin and, as a result, prevent coke formation during VR upgrading [32,33]. Therefore, in the study, tetralin was used as a representative hydrogen-donor solvent for partially hydrogenated streams. In addition, the physical and transport properties of the solvent could change significantly with the operating conditions in the near-critical region. Thus, the effects of operating conditions (reaction time and temperature) on VR upgrading were also evaluated based on the residue conversion, coke formation, and product distribution. Considering the applicability of this upgrading system to conventional oil refineries, all experiments were conducted below 450 °C and 6.0 MPa.

2. Experimental section

2.1. Materials

Real vacuum residue (VR), supplied by a domestic oil refinery, was used as a heavy feedstock. The VR contains Conradson carbon residue (23.0 wt%), sulfur (5.3 wt%), nitrogen (0.3 wt%), and metal impurities (about 165 wppm). The VR is composed of vacuum gas oil (16.2 wt%) and residue (83.8 wt%), which has more residue fraction than Athabasca bitumen (approximately 48–55 wt%) [21,34,35]. The properties of VR, including boiling point range and group analysis, are shown in Table 1.

We selected the bituminous coal-derived activated carbon (Calgon Filtrasorb 300) as a carbon catalyst. This catalyst was modified using sulfuric acid (96 wt%) to increase the surface area, porosity, and surface acidity. After the modification at 250 °C for 3 h, the catalyst was washed with distilled water until the filtrate was free of sulfate; then, it was dried overnight at 120 °C. Modified activated carbon (Mod AC) showed the specific surface area (BET method) of 1216 m²/g, specific mesopore volume of 0.29 cm³/g and average mesopore diameter of 3.4 nm (BJH method). In addition, its surface acidity increased by approximately a factor of 15 (from 0.124 meq/g to 1.834 meq/g).

Tetralin (Sigma-Aldrich, HPLC-grade) was selected as a hydrogen-donor solvent; its critical properties are $T_c = 447$ °C and $P_c = 3.7$ MPa.

Table 1
Properties of the VR.

Conradson carbon residue (CCR), wt%	23.0 ^a
S, wt%	5.3 ^a
N, wt%	0.3 ^a
Ni, wppm	38.4 ^a
V, wppm	104.2 ^a
Fe, wppm	23.2 ^a
Viscosity, cSt (at 100 °C)	3580 ^a
SIMDIS analysis (wt%)	
– Light oil (IBP – 343 °C)	0.0
– Vacuum gas oil (343–525 °C)	16.2
– Residue (> 525 °C)	83.8
SARA analysis (area%)	
– Saturates	4.6
– Aromatics	53.7
– Resins	23.3
– Asphaltenes	18.4

^a Data from an oil refining company.

All the experiments were conducted in the pressure range of 1.6–5.3 MPa, which is lower than that employed in conventional hydrocracking because hydrogen gas was not used as a reducing agent in the study. The reaction conditions were described as the subcritical or supercritical condition on the basis of the critical point of tetralin.

2.2. Procedures

All experiments were carried out in a stirred batch reactor (200 mL), which was made of a nickel-based alloy (Inconel 625). The reactor was equipped with a spinning catalyst basket (Carberry-type reactor) to improve the contact efficiency between the catalyst and reactants. A schematic diagram of the reactor is presented in Fig. 1.

In a typical experiment, 5 g of VR was mixed with 40 mL of tetralin by sonication for 20 min. The mixture was loaded into the reactor, followed by the addition of 8 g of the catalyst (acid-treated activated carbon) to the spinning catalyst basket. The reactor was sealed and then purged several times with nitrogen (99.999%) to remove air inside the reactor. An agitation speed of 500 rpm was used for all experiments. The reactor was heated to the desired temperature at an average rate of 15 °C/min by an electric furnace, and then the reaction time was counted.

After the experiment was carried out for the specified time, the stirred reactor was quenched in a water bath and cooled to room temperature. The gas product was collected in Tedlar® sampling bags (1 L) for compositional analysis until the pressure in the reactor was dropped to an atmospheric level. The amount of gas product was obtained from the change in mass after removing the gas product from the reactor. The liquid and solid products were recovered from the reactor. The liquid product was separated from the mixture by vacuum filtration, and stored at 4 °C in a refrigerator. All solids (catalyst and coke) were washed with toluene using the Soxhlet method to extract residual oils. The extracted solutions were dried at 100 °C under vacuum to remove toluene, and then the residual oils were mixed with the liquid product stored in the refrigerator. The collected solids were dried at 120 °C for 5 days and weighed to calculate the amount of coke. In addition, the blank experiment without the VR was also conducted under the same conditions to calculate the net amount of gaseous product derived from the VR. Each experiment was repeated at least twice, and the error of the method was less than 3%.

2.3. Product analysis and characterization

Instead of true distillation, simulated distillation by gas chromatography (SIMDIS) was introduced according to the American Society for Testing and Materials (ASTM D 7500). This analysis method determines

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