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# A parameter study for co-processing of petroleum vacuum residue and oil palm empty fruit bunch fiber using supercritical tetralin and decalin

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## HIGHLIGHTS

- Co-processing of heavy oil and biomass was conducted using supercritical solvents.
- Positive effects on co-processing led to a high conversion of both feed materials.
- Residue conversion reached 86.4 wt% with only 0.8 wt% of coke formation.
- $Fe_3O_4$ catalyst with $H_2$ contributed to a significant suppression of coke formation.

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## ABSTRACT

Co-processing of petroleum vacuum residue (VR) and oil palm empty fruit bunch (EFB) fiber was carried out through the use of supercritical solvents. The effects of solvent (tetralin and decalin), temperature (400 and 450 °C), a catalyst, and hydrogen on the co-processing were evaluated according to residue conversion and product distribution analysis. The results were compared with only the VR upgrading results as well as the co-processing of VR and microcrystalline cellulose. Supercritical tetralin exhibited high reaction performance in both VR upgrading and co-processing of VR/EFB without significant coke formation, compared with the results in decalin. In the presence of $H_2$, the $Fe_3O_4$ catalyst contributed toward suppressing coke formation. The co-processing of VR/EFB using tetralin could achieve a residue conversion of 86.4 wt% with only 0.8 wt% of coke formation, showing more favorable conversion than that of VR/microcrystalline cellulose. Therefore, it led to a positive effect which improved the residue conversions and yielded a great quantity of light product.

## 1. Introduction

As demand for transport fuel has increased, petroleum industries have been forced to refine low-quality heavier oils. Among the heavy feedstocks, petroleum vacuum residue (VR), which is the heaviest fraction of crude oil, has high boiling points over 520 °C and contains about 5 wt% of sulfur and 0.5 wt% of nitrogen in the form of heterorganic compounds [1,2]. As VR volumes make up approximately 25 wt% of the crude feedstock on average, these increasing volumes are critical issues for refiners and its use as a fraction of heavy furnace oil accounts for a considerable amount of environmental pollution.

Heavy feedstocks can be converted into light products by either carbon rejection process or hydroconversion process. Compared with the carbon rejection process, hydrocracking and hydrotreating processes require moderate temperatures for reactions and provide high conversion levels with less coke formation using various catalysts [3] with the optional use of solvents [4–6]. However, due to low hydrogen to carbon ratio and the high concentration of asphaltenes, sulfur, nitrogen, and metal-containing compounds in the heavy oil, hydrocracking or hydrotreating of VR could cause coke formation and catalyst poisoning.

To suppress coke formation and improve conversion, the supercritical fluids were applied for upgrading heavy residues or bitumen [1,2]. This method is promising because supercritical fluids provide unique physical and chemical properties (gas-like diffusivities and liquid-like densities), and exhibit complete miscibility of

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*Abbreviations:* ASTM, American Society for Testing and Materials; DVU-VR, distilled vacuum unit vacuum residue; EFB, oil palm empty fruit bunch fibers; IBP, initial boiling point; SIMDIS, simulated distillation gas chromatography; VGO, vacuum gas oil; VR, vacuum residue.

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liquid/vapor products, which can promote reactions and inhibit catalyst deactivation [7]. Recently, it was reported that supercritical organic solvents could upgrade VR efficiently, achieving a high level of conversion with suppressed formation of carbonaceous solids [8–10].

Utilization of biomass has received significant attention as a renewable energy source [11]. A promising feedstock for the commercial production of biofuels and related chemicals is lignocellulosic biomass [12]. The biomass can play a role as not only a substitute for fossil fuels but also a carbon sink. In addition, the use of biomass as energy resources can increase energy security and reduce the need to import fossil fuels because it is abundant in most countries [13].

Positive effects were reported for the co-pyrolysis of waste tires and wood biomass because it could inhibit the formation of polyaromatic hydrocarbons produced from the pyrolysis of the tires alone [14,15]. Moreover, the quantity of aldehydes and phenolic compounds decreased due to radical interactions between intermediate products. It was also reported that the addition of biomass to gasification of bituminous coal noticeably improved the gas yield and reduced char and tar yields due to the transfer of active hydroxyl and hydrogen radicals from the biomass to coal along with the catalytic role of alkali metals [16].

Similarly, the addition of biomass materials to heavy oil upgrading may have great potential toward improving the quality of oil products by decreasing the molecular weight of heavy compounds and coke formation due to the transfer of the active radicals. Additionally, the supercritical organic solvent in the co-processing of heavy oil with biomass can be a key factor toward minimizing coke formation and maximizing conversion because proper solvents contribute to reducing the self-assembly step of polyaromatic carbons through formation of small micelles. Therefore, positive effects with regard to the co-processing of heavy oil and biomass using supercritical solvents are expected. After co-processing, liquid product could be separated in the process for solvent recovery or be directly combined with other streamlines in residual treating or blending processes without separation. Co-processing of conventional petroleum feedstocks with biomass via pre-existing oil refinery seems to be a promising alternative with respect to the possibility of bulk treatment and low infrastructure investment [17–19].

In many studies on upgrading heavy oils using metal catalysts, one of the major problems is the rapid loss of the catalytic activity due to heteroatoms in the feedstocks or carbonaceous materials after the reaction. Therefore, an inexpensive and easily regenerated catalyst is recommended for such the upgrading processes. In accordance with the requirements, iron-based catalysts have been widely used in hydrocracking heavy oils such as vacuum gas oil, atmospheric residue, and vacuum residue, which show very high activity in the upgrading reaction [20–22]. Low cost eco-friendly material, iron oxide, also showed good catalytic activity in the decomposition reactions of biomass and significantly suppressed char formation in the presence of hydrogen [12,23]. Furthermore, strong magnetic properties of the catalyst contributed to easy separation from liquid products after the reaction even though a small amount of char was mixed with the catalyst.

In this study, we demonstrated the feasibility of the co-processing of vacuum residue and wood biomass through the use of supercritical organic solvents. Microcrystalline cellulose (Avicel), oil palm empty fruit bunch (EFB) fiber, and petroleum vacuum residue (VR) from an industrial stream were used as a feedstock for co-processing.

As an alternative to conventional hydroconversion processes which use large quantities of hydrogen, hydrogen donating solvents (tetralin and decalin) were used for co-processing because free radicals formed during the reaction could be more easily stabilized with hydrogen from hydrogen-donating solvents. In addition to solvent and temperature effects, the influence of dispersed $Fe_3O_4$ catalyst and pressures (3.45 MPa $H_2$ or vacuum) on co-processing was also investigated. Since the critical points of the solvents were lower than 450 °C and 4.0 MPa, the experimental study could be performed from subcritical to supercritical conditions, which were similar to the operating conditions of heavy oil upgrading (HOU) units.

Coke formation control is practically an important factor because it is strongly related to shut-down period and filtering cost in industrial processes. Therefore, co-processing results were evaluated in terms of residue conversion, coke formation, and product distribution (light product, vacuum gas oil, and residue), and compared with the results achievable through only VR upgrading. The results can offer a keen insight into the co-processing process for extra heavy oil and biomass.

## 2. Materials and methods

### 2.1. Materials and reagents

A 200 ml batch reactor constructed from a nickel-based alloy (Inconel 625) was used (Fig. 1), which is equipped with a magnetic-driven stirrer. To prevent some reactants from interacting with the surface of the reactor, a quartz liner was used inside the reactor. Temperature and pressure profiles were observed by a data acquisition unit as shown in Fig. 1.

Real vacuum residue from a distilled vacuum unit (DVU-VR) was supplied by a domestic petroleum refinery. The given VR could only be recovered up to 77.9 wt% at 750 °C. The VR also contained 22.23 wt% of Conradson carbon residue. Moreover, it contained more than 93 wt% of pitch in addition to a large quantity of sulfur compounds (5.29 wt%). Microcrystalline cellulose (Avicel) was purchased from Sigma–Aldrich. After the cellulose was dried at 70 °C for 2 h, it was used for experiments in the study without softening step (ball milling). Oil palm empty fruit bunch (EFB) fiber with lignin (28.3 wt%) was used without pretreatment. The average size of EFB fiber was 5–10 mm.

The characteristics of DVU-VR and EFB fiber are provided in Table 1. The composition of EFB was analyzed by the laboratory analytic procedure which is substantially similar to the standard method for the determination of carbohydrates by HPLC (ASTM E1758-01) [24,25]. XRD analysis of biomass materials is shown in Fig. 2. Microcrystalline cellulose has higher crystallinity than EFB fiber because it has intense peaks which correspond to the (110) crystallographic plane (14.8–18.4° $2\theta$) and the (200) crystallographic plane (21.9–22.2° $2\theta$). Regardless of the high crystallinity of cellulose, EFB with high lignin content produced more coke than cellulose during pyrolysis under nitrogen (Fig. 2).

In this study, tetralin and decalin (Sigma–Aldrich, HPLC-grade) were selected as representative hydrogen donating solvents. The critical conditions of tetralin and decalin are 447 °C/3.7 MPa and 430 °C/3.2 MPa, respectively. Hydrogen and nitrogen gases with high purity (99.999%) were used in all experiments.

Iron (II, III) oxide nanoparticles with 50–100 nm sphere sizes were purchased from Sigma–Aldrich and supplied to the reaction mixture as a catalyst. Due to the instability of $\alpha$-$Fe_2O_3$ at high temperature, the material was converted to magnetic $\gamma$-$Fe_2O_3$ and $Fe_3O_4$ (magnetite) [26,27].

### 2.2. Experimental methods

In general, 5 g of feedstock (5 g of VR or 3 g of VR + 2 g of biomass) and 0.75 g of catalyst were mixed with solvent (40 cc) in a quartz liner. The mixture was sonicated for 20 min and placed in