

## Co-processing of heavy oil with wood biomass using supercritical *m*-xylene and *n*-dodecane solvents

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**Abstract**—Heavy oil was co-processed with wood biomass by using supercritical *m*-xylene and *n*-dodecane. The effects of the solvent, temperature, hydrogen, and catalyst on vacuum residue (VR) upgrading were evaluated using residue conversion, coke formation, and product distribution as performance parameters. VR was subjected to co-processing with microcrystalline cellulose (cellulose) or oil palm empty fruit bunch fiber (EFB), and the parameters were compared with those obtained from VR upgrading. Co-processing of VR/cellulose using a catalyst and hydrogen led to higher conversion (72.6 wt%) than co-processing of VR/EFB at 400 °C and the highest yield of light product (65.7 wt%). Using the Fe<sub>3</sub>O<sub>4</sub> catalyst with H<sub>2</sub> for co-processing positively influenced generation of the light product fraction. VR upgrading and co-processing using supercritical solvents could eliminate a certain amount of sulfur compounds from heavy oil. Co-processing of wood biomass with petroleum feedstocks in existing oil refineries can reduce the capital costs of bulk treatment.

Keywords: Co-processing, Supercritical Solvent, Vacuum Residue, Cellulose, EFB

### INTRODUCTION

Due to the strong motivation to convert heavy oil feedstocks into value-added products, the upgrading of bitumen, oil sands, and residues from conventional refinery processes is an attractive prospect for refineries. Vacuum residue (VR) is the heaviest fraction derived from the distillation of atmospheric residue (AR) under reduced pressure. VR contains the majority of the heteroatoms found in the petroleum and high proportions of asphaltenes and resins, even in amounts up to 40% (or higher) of the residue [1].

Heavy oil upgrading can be achieved by either carbon rejection or the hydroconversion process. In comparison with carbon rejection, hydroconversion (including hydrocracking and hydrotreating processes) requires relatively mild reaction temperatures and provides high liquid yield; moreover, coke formation can be suppressed by using alumina-supported Ni, Mo, or Co [2-4] with the optional use of solvents [5,6]. However, the distinguishing features of VR, such as the high concentrations of sulfur, nitrogen, and asphaltenes and ash-forming metallic constituents (V, Ni, etc.), lead to rapid deactivation of the catalysts due to the deposition of coke and metals.

An emerging trend in the field of renewable energy is the utilization of energy from biomass sources, because exploiting biomass energy can mitigate the reliance on fossil fuels and the issues

surrounding greenhouse gas emissions [7,8]. An attractive source of biomass energy is lignocellulosic biomass, which is abundant and cheap in most countries. However, a significant challenge in biomass treatment is the depolymerization of lignin and crystalline cellulose, both of which possess rigid structures that often cause serious coking issues.

To cope with the issues related to coke formation, supercritical fluids were applied to hydroconversion or liquefaction. Supercritical fluids have excellent miscibility with liquid/vapor products and unique properties such as gas-like diffusivities and liquid-like densities, which can increase the reaction efficiency [9]. Recent studies reported that supercritical organic solvents can efficiently facilitate VR upgrading [10-12]. Moreover, coke formation could be suppressed below a certain level, and the product quality could be controlled by judicious selection of supercritical solvents and operating conditions [13]. The liquefaction of biomass in sub- or supercritical solvents has also gained prominence in research because this process consumes less energy and is much simpler than indirect methods [14-16]. In a study of cellulose hydrolysis, the reaction rate in sub- and supercritical water was found to increase drastically at temperatures above 350 °C, and the yield of the hydrolysis products reached 76.5% at 400 °C [17].

The current thrust in the petrochemical industries is toward the development of processes with higher conversion under mild reaction conditions. One potential process to meet such demands is the co-processing of heavy oils with biomass feedstock. It has been reported that the co-pyrolysis of waste tires and wood biomass could prevent the formation of polycyclic aromatic hydrocarbons to a greater extent than the pyrolysis of tires only [18,19]. Moreover, the addition of biomass also improved the gas yield and reduced the

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\*This article is dedicated to Prof. Ki-Pung Yoo on the occasion of his retirement from Sogang University.

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char yields during coal gasification because of the catalytic role of the metals in the biomass [20]. Therefore, positive effects are expected to be derived from the co-processing of VR and biomass using supercritical solvents. The use of supercritical solvents in the co-processing may lead to a decline in coke formation and cause enhanced conversion because the use of suitable solvents contributes to reducing the aggregation of polyaromatic hydrocarbons.

Catalyst deactivation is a major challenge that occurs due to the deposition of heteroatoms or carbonaceous materials on the catalyst during the process. Therefore, iron-based catalysts have been widely used in the hydrocracking of heavy oils because they are inexpensive and easily regenerated, and have high activity in the upgrading reaction [21,22]. In addition, these catalysts could be easily separated from the liquid products due to their strong magnetic properties, even if a small amount of coke was mixed with the catalysts.

In this study, VR was co-processed with wood biomass using supercritical solvents. Oil palm empty fruit bunch fiber (EFB) and microcrystalline cellulose (Avicel) were used as biomass feedstocks for co-processing. The effects of the supercritical solvents,  $\text{Fe}_3\text{O}_4$  catalyst, and pressure (3.45 MPa hydrogen or nitrogen) on VR upgrading and co-processing were evaluated and compared on the basis of residue conversion, coke formation, and product distribution (light product, vacuum gas oil, and residue). The results provided herein demonstrate the feasibility of co-processing for the treatment of extra heavy oil and biomass in existing oil refineries.

## EXPERIMENTAL SECTION

### 1. Materials

The heavy feedstock used in all experiments was vacuum residue (VR), supplied by a domestic oil refinery. The recovery of VR was

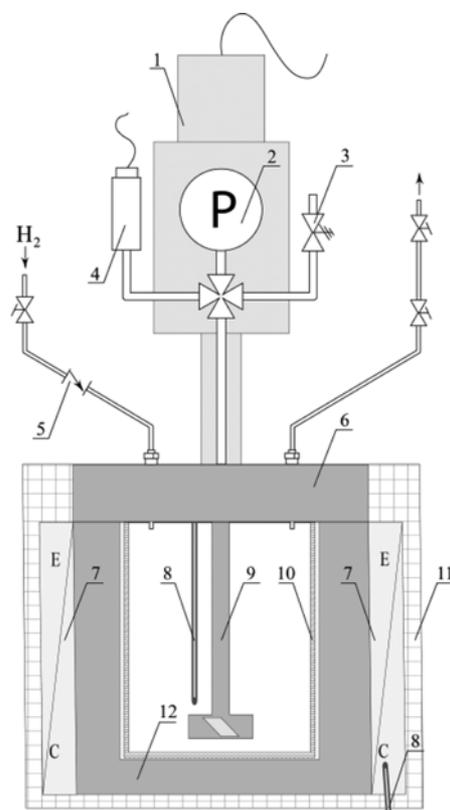
**Table 1. Properties of feedstocks**

Characteristics of DVU-VR	
Conradson carbon residue (CCR, wt%)	22.2
S (wt%)	5.29
N (wt%)	0.29
Ni (wppm)	55.2
V (wppm)	154.3
Fe (wppm)	102.9
Viscosity (cSt) (at 100 °C)	3,425
Recovered (wt%) (at 750 °C)	77.9
Cut point (wt%)	
- Naphtha (initial boiling point - 177 °C) (wt%)	0.0
- Middle distillate (177-343 °C) (wt%)	0.0
- Vacuum gas oil (343-525 °C) (wt%)	7.0
- Residue (525-750 °C) (wt%)	70.9
Composition of EFB fiber	
- Glucan (wt%)	36.3
- Xylan (wt%)	21.4
- Lignin (wt%)	28.3
- Ash (wt%)	6.0
- Moisture (wt%)	8.0

only 77.9 wt% at 750 °C and the VR contained a small amount of vacuum gas oil fraction (7.0 wt%). Furthermore, as shown in Table 1, the VR contained 22.2 wt% of Conradson carbon residue, 5.29 wt% of sulfur compounds, and certain amounts of metal impurities.

Microcrystalline cellulose (Avicel, Sigma-Aldrich) and oil palm empty fruit bunch fiber (EFB) with lignin (28.3 wt%) were used without pretreatment after drying at 70 °C for 2 h. The composition of EFB (Table 1) was analyzed according to the laboratory analytical procedure, which is largely similar to the standard used for the determination of carbohydrates (ASTM E1758-01) [23,24]. X-ray diffraction (XRD) and thermogravimetric analysis (TGA) of the biomass materials showed that EFB with a high lignin content produced more coke than cellulose during pyrolysis under nitrogen in spite of the high crystallinity of cellulose [25]. Therefore, the role of lignin in the supercritical process could be evaluated by comparison with the results from the co-processing of cellulose.

The two hydrocarbon solvents (*m*-xylene and *n*-dodecane) used in this study were HPLC-grade solvents supplied by Sigma-Aldrich. The supercritical conditions for *m*-xylene and *n*-dodecane are 344 °C/3.5 MPa and 385 °C/1.8 MPa, respectively. Iron(II, III) oxide nanoparticles (Sigma-Aldrich) with sizes of 50-100 nm were employed as a catalyst. It was reported that due to the low stability of  $\alpha\text{-Fe}_2\text{O}_3$  at high temperatures, the material could be converted to



**Fig. 1. Schematic of experimental apparatus.**

- |                           |                     |
|---------------------------|---------------------|
| 1. Magnetic stirrer motor | 7. Electric heater  |
| 2. Pressure gauge         | 8. Thermocouple     |
| 3. Safety valve           | 9. Stirrer          |
| 4. Pressure transducer    | 10. Quartz liner    |
| 5. Check valve            | 11. Insulator       |
| 6. Reactor cover          | 12. Reactor, 200 ml |

magnetic  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  (magnetite) [26-28].

## 2. Apparatus and Methods

All experiments were carried out in a 200 mL batch reactor, as shown in Fig. 1. The reactor, made of a nickel-based alloy (Inconel 625), was equipped with a magnetic-driven stirrer. To inhibit undesirable reactions with the surface of the reactor, a quartz liner was employed inside the reactor.

In a typical run, 5 g of feedstock (5 g of VR or 3 g of VR+2 g of biomass) was weighed into the quartz liner, followed by the addition of 0.75 g of catalyst and 40 mL of the specified solvent. After the mixture was sonicated in the liner for 20 min, the liner was placed into the reactor. The reactor was purged with nitrogen to remove air inside the reactor and then pressurized to 3.5 MPa at 25 °C with hydrogen or nitrogen (99.999%). Subsequently, the reactor was heated at a rate of 20 °C/min in a furnace and agitation speed was fixed at 500 rpm. After a reaction time of 30 min under the desired conditions, the reactor was quenched in a water bath to rapidly stop the reactions. The liquid product was filtered under vacuum to separate the solid residue and then stored in a refrigerator. Prior to weighing, the solid residue was washed several times with toluene and acetone and dried at 100 °C overnight. All extracted solutions were collected and evaporated at 100 °C in a vacuum oven to completely remove the toluene. Subsequently, the oily residue was mixed with the liquid product.

Instead of true distillation, a temperature-programmed gas chromatographic analysis was introduced to simulate the boiling point distribution of the hydrocarbons by matching their retention times with the distillation temperatures. Simulated distillation by gas chromatography (SIMDIS) is frequently used for oil analysis in the refinery industry because it can effectively save time and reduce costs [1]. Therefore, SIMDIS was employed to obtain the boiling points of the liquid products according to the American Society for Testing and Materials protocol (ASTM 7213A-7890) [11,12]. The liquid products were subjected to SIMDIS analysis and were categorized into three fractions: light product (initial boiling point (IBP)-343 °C), vacuum gas oil (VGO, 343-525 °C), and residue (525-750 °C). The solvent amount was subtracted from the products on the basis of the feedstock to solvent ratio [25]. The error of the method was confirmed to be within a margin of 5% by repeated experiments.

The coke, ash, and oil products are presented as wt% based on the weight of the feedstock. Eqs. (1)-(5) were used to calculate the yield (wt%) of the light product, vacuum gas oil, residue, coke, and ash (if EFB was used), respectively. The residue conversion was calculated from the difference in the weight of the residue before and after the reaction (Eq. (6)). Cellulose or EFB was excluded from the residue fraction in the SIMDIS analysis because the high boiling points of these species cannot be handled by the analyzer. It was assumed that liquid products (light product and VGO) were generated from both biomass and VR, and a negligible amount of the residue fraction was generated by decomposition of the biomass during the co-processing reaction.

$$\begin{aligned} & \text{- Light product (wt\%)} \\ & = \frac{\text{mass (light product)}}{\text{mass (feed)} - \text{mass (moisture in EFB)}} \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} & \text{- Vacuum gas oil (VGO; wt\%)} \\ & = \frac{\text{mass (VGO)}}{\text{mass (feed)} - \text{mass (moisture in EFB)}} \times 100 \end{aligned} \quad (2)$$

$$\begin{aligned} & \text{- Residue (wt\%)} \\ & = \frac{\text{mass (residue)}}{\text{mass (feed)} - \text{mass (moisture in EFB)}} \times 100 \end{aligned} \quad (3)$$

$$\begin{aligned} & \text{- Coke (wt\%)} \\ & = \frac{\frac{\text{mass (solids)}}{0.90} - \text{mass (catalyst)} - \text{mass (ash)}}{\text{mass (feed)} - \text{mass (moisture in EFB)}} \times 100 \end{aligned} \quad (4)$$

$$\text{- Ash (wt\%)} = \frac{\text{mass (ash)}}{\text{mass (feed)} - \text{mass (moisture in EFB)}} \times 100 \quad (5)$$

$$\begin{aligned} & \text{- Residue conversion (wt\%)} \\ & = \left( 1 - \frac{\text{mass (residue in product)}}{\text{mass (residue in feed)}} \right) \times 100 \end{aligned} \quad (6)$$

Blank experiments without the feedstock were performed to confirm the recovery ratio of the catalyst. The catalyst recovery ratio was set to 90% and this ratio was applied to calculation of the amount of coke.

## RESULTS AND DISCUSSION

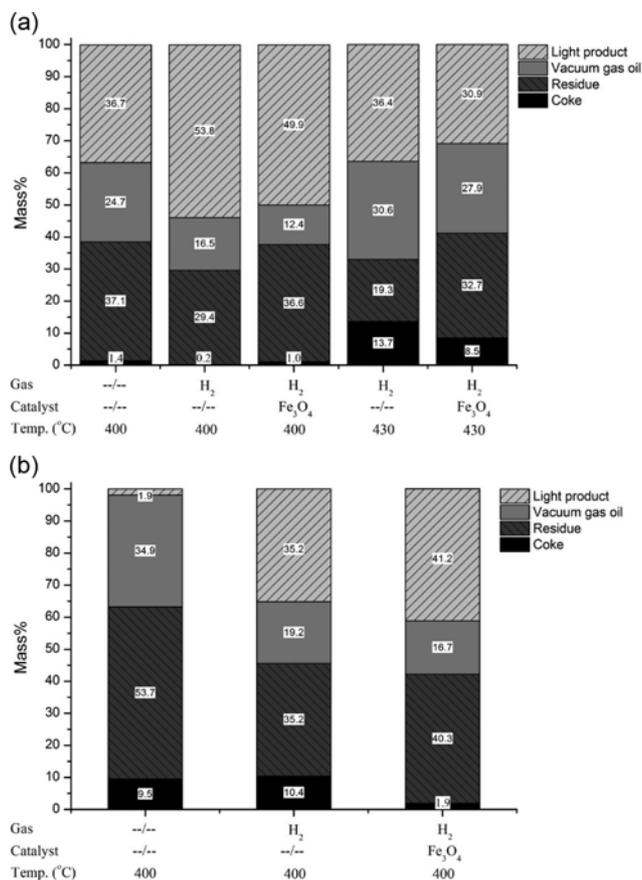
### 1. VR Upgrading in *m*-Xylene and *n*-Dodecane: Influence of Temperature, Catalyst, and Hydrogen

The reaction mechanisms are strongly influenced by the physical and chemical properties of the solvents at near-critical conditions. Therefore, it is necessary to evaluate the effect of the solvent and operating conditions on the VR upgrading process.

The criteria for selecting a proper solvent for the supercritical process are as follows: (1) high solubility of heavy fractions and ability to reduce viscosity of heavy oils; (2) relatively mild critical temperature and pressure applicable to the real field; and (3) economical solvent available in petrochemical industry. A previous study showed that supercritical *m*-xylene and *n*-dodecane were more effective in VR upgrading than the other solvents [11]. Therefore, *m*-xylene and *n*-dodecane were selected as solvents for the VR upgrading and co-processing.

Fig. 2(a) and Table 2 show the product distribution and residue conversion for VR upgrading using *m*-xylene. The physical and transport properties of supercritical fluids can change sensitively from gas-like to liquid-like values with changes in the reaction pressure. As the reaction pressure increases, the more liquid-like behavior contributes to increasing the solubility of the coke precursors, whereas reduction of the pressure improves both the transport properties and the catalyst effectiveness factor [29].

In this study, the reaction pressure could be significantly changed by the addition of hydrogen. As shown in Table 2, when hydrogen only was introduced without the  $\text{Fe}_3\text{O}_4$  catalyst, the residue conversion in the VR upgrading process using *m*-xylene at 400 °C increased by about 11 wt% with a large quantity of the light product fraction. This implies that gaseous hydrogen not only acted in its primary role as a hydrogen source in the hydroconversion, but also contributed to the conversion by changing the phase proper-



**Fig. 2. Product distribution (yields of light product, vacuum gas oil, residue, and coke) of VR upgrading in supercritical solvents: (a) *m*-xylene and (b) *n*-dodecane.**

ties. Simultaneous addition of the Fe<sub>3</sub>O<sub>4</sub> catalyst and H<sub>2</sub> to the reaction resulted in a similar level of residue conversion and coke formation. In other words, the Fe<sub>3</sub>O<sub>4</sub> catalyst was not effective for VR upgrading in *m*-xylene due to catalyst deactivation by coking.

Increasing the reaction temperature to 430 °C in the absence of the catalyst caused the residue conversion to improve considerably to 73.2 wt%, but a large quantity of coke was also formed (13.7 wt%), as shown in Table 2. It was expected that fragmentation of the heavy components and condensation reactions of the coke precursors would occur more rapidly at higher temperature. Even in the reaction with the catalyst and H<sub>2</sub> at 430 °C, the effect of the hydrogen on suppressing the condensation reactions was also confirmed to be insignificant, showing higher residue conversion and more coke formation than obtained at 400 °C.

The dominant product of VR upgrading using *m*-xylene at 400 °C was the light product, the generation of which could be increased by the addition of hydrogen and the catalyst, as shown in Fig. 2(a). As the temperature increased from 400 to 430 °C, the yield of light product decreased, but the fraction of vacuum gas oil and coke increased. The rate of transport of gaseous hydrogen into the intermediate products was too slow to satisfy the high demand for hydrogen created by thermal cracking at high reaction temperature. Although increasing the temperature from 400 to 430 °C could significantly improve the conversion, coke formation was not effectively suppressed, regardless of the operating conditions. Therefore, supercritical *m*-xylene was considered as a more appropriate medium for stabilizing the reactants in VR upgrading at 400 °C than at 430 °C.

As shown in Fig. 2(b) and Table 3, the residue conversion and coke formation in VR upgrading using *n*-dodecane followed a trend similar to that obtained with *m*-xylene. However, under all conditions, the conversion in the *n*-dodecane system was consistently lower than the corresponding result obtained in *m*-xylene. Because coke formation is highly dependent on the precipitation and accumulation of asphaltenes, the large degree of coke deposition in the *n*-dodecane system could be attributed to the low solubility of the asphaltenes in the *n*-alkane versus that in the aromatic solvent (*m*-xylene). When the catalyst and H<sub>2</sub> were simulta-

**Table 2. Experimental conditions and results for VR upgrading and co-processing of VR/cellulose or VR/EFB in supercritical *m*-xylene**

Experimental condition					Results	
Feed	Temperature (°C)	Gas	Initial pressure (MPa)	Catalyst	Coke formation (wt%)	Residue conversion (wt%)
VR	400	-	-	-	1.4	48.3
VR	400	Hydrogen	3.45	-	0.2	59.2
VR	400	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	1.0	49.0
VR	430	Hydrogen	3.45	-	13.7	73.2
VR	430	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	8.5	54.5
VR/cellulose	400	Hydrogen	3.45	-	24.7	74.9
VR/cellulose	400	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	18.2	72.6
VR/cellulose	400	-	-	Fe <sub>3</sub> O <sub>4</sub>	29.3	75.3
VR/cellulose	400	Nitrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	19.3	69.2
VR/EFB	400	Hydrogen	3.45	-	19.6	76.8
VR/EFB	400	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	1.9	53.5
VR/EFB	430	Hydrogen	3.45	-	23.1	64.9
VR/EFB	430	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	16.1	59.4

**Table 3. Experimental conditions and results for VR upgrading and co-processing of VR/cellulose or VR/EFB in supercritical *n*-dodecane**

Experimental condition					Results	
Feed	Temperature (°C)	Gas	Initial pressure (MPa)	Catalyst	Coke formation (wt%)	Residue conversion (wt%)
VR	400	-	-	-	9.5	27.3
VR	400	Hydrogen	3.45	-	10.4	51.2
VR	400	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	1.9	44.1
VR	430	Hydrogen	3.45	-	24.8	-
VR	430	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	19.2	-
VR/Cellulose	400	Hydrogen	3.45	-	23.2	59.9
VR/Cellulose	400	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	8.1	47.0
VR/Cellulose	400	-	-	Fe <sub>3</sub> O <sub>4</sub>	29.0	75.1
VR/Cellulose	400	Nitrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	21.9	58.9
VR/EFB	400	Hydrogen	3.45	-	18.7	39.6
VR/EFB	400	Hydrogen	3.45	Fe <sub>3</sub> O <sub>4</sub>	5.6	53.4

neously added to the reaction in the *n*-dodecane system at 400 °C, the coke formation was successfully suppressed and generation of the light product fraction increased considerably, as shown in Fig. 2(b) and Table 3. In other words, the contribution of hydrogen toward suppression of coke formation was more effective in the reaction with Fe<sub>3</sub>O<sub>4</sub> than without the catalyst in the *n*-dodecane system at 400 °C.

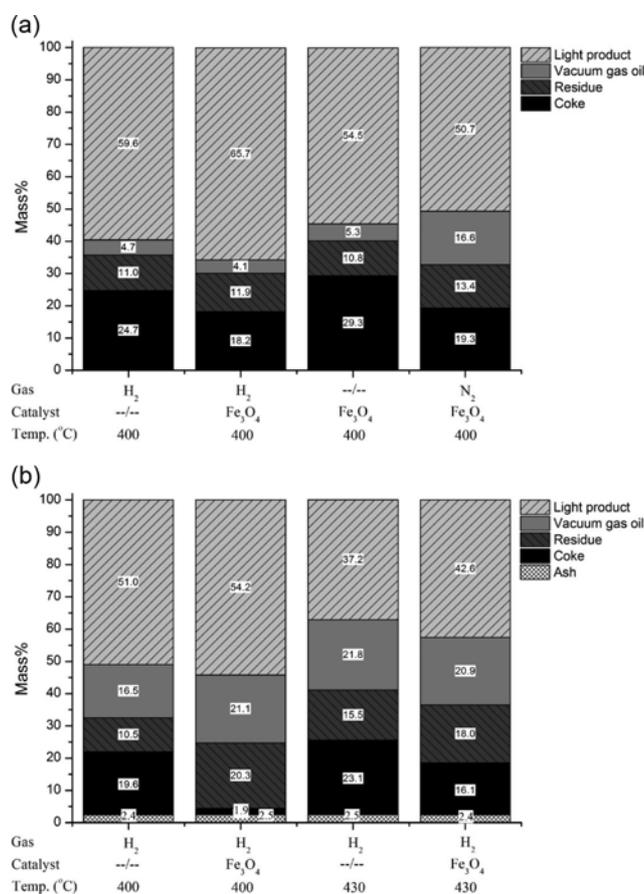
VR upgrading using *n*-dodecane was performed at 430 °C, where a large amount of coke was observed (Table 3). An increase in the chain length of the *n*-paraffin leads to a rise in the rate of hydro-conversion and a decline in the reaction temperature required for both hydroisomerization and hydrocracking [30]. In the system using *n*-dodecane, the solvent became unstable at 430 °C. Therefore, it is highly possible that the change in the VR-to-solvent ratio resulted in wrong information in terms of the residue conversion and product distribution obtained from the SIMDIS analysis. Therefore, the conversion and product distribution are not presented in Table 3 and Fig. 2(b), but the amount of coke generated is specified.

Precipitation and aggregation of the high-molecular-weight materials can result from a change in the molecular equilibria in the solution, which is related to a change in the balance of the oil composition. When the extent of conversion in the upgrading process increases at high temperatures, the ability of *n*-dodecane to solubilize the heavy and polar molecules (asphaltenes) decreases due to shortening of chain length of the paraffin. In addition, removal of the alkyl side chains from the asphaltenes during thermal cracking could make the materials more polar. Because of the reduced solvency and increased polarity of the solutes, the radicals produced by thermal cracking of the asphaltenes can be readily separated and react with one another to form larger molecules [31]. Consequently, coke formation increased significantly in the *n*-dodecane system at 430 °C. Compared to the corresponding results obtained in *m*-xylene (Table 2), coke formation was twice as high in *n*-dodecane as in *m*-xylene. The importance of the solvency in heavy oil upgrading using supercritical solvents is thus noted.

## 2. Co-processing in *m*-Xylene and *n*-Dodecane: Influence of Temperature, Catalyst, and Hydrogen

Various studies have reported that the co-processing of fossil

fuel with biomass could have positive effects, which might lead to improved reactivity [32], exponential enhancement of the efficiency [33], and low tar formation [34]. Therefore, co-processing of VR with cellulose or EFB was conducted and the performance of this system was compared with that of VR upgrading under corre-



**Fig. 3. Product distribution (yields of light product, vacuum gas oil, residue, coke, and ash) of co-processing in supercritical *m*-xylene: (a) VR with cellulose and (b) VR with EFB.**

sponding conditions.

Fig. 3 and Table 2 show the influence of hydrogen, the catalyst, and the reaction temperature on the conversion and product distribution in co-processing of VR/cellulose or VR/EFB using *m*-xylene. The co-processing of VR/cellulose was preliminarily conducted to find the optimal operating condition for maximizing light product fraction and suppressing coke formation before applying VR/EFB as a feedstock. The residue conversion in the co-processing at 400 °C was much higher than that in VR upgrading only (Table 2). However, the enhanced conversion resulted mainly from high coke formation in the VR/cellulose system. Notably, when either hydrogen or Fe<sub>3</sub>O<sub>4</sub> catalyst was added to the co-processing system, a large amount of cellulose-derived coke was formed (24.7–29.3 wt%). Co-processing also generated a higher fraction of light product than the VR upgrading reaction. Simultaneous addition of hydrogen and the catalyst resulted in enhanced production of the light product fraction. In contrast, when the reactor was initially pressurized with N<sub>2</sub> instead of H<sub>2</sub>, the conversion was similar to that obtained with hydrogen and the catalyst (Table 2), but the fraction of vacuum gas oil became richer with a similar degree of coke formation (Fig. 3(a)).

According to the co-processing results of VR/cellulose using various gases, it was expected that the fraction of light product would decrease with increasing coke yield in the co-processing of VR/EFB using N<sub>2</sub>, whereas the addition of H<sub>2</sub> would improve the performance of co-processing. Therefore, in the study, hydrogen was applied to the co-processing of VR/EFB to obtain a high fraction of light product with suppressed coke formation. In the co-processing of VR/EFB with hydrogen only in *m*-xylene, the coke formation and residue conversion were similar to the corresponding results for VR/cellulose at 400 °C. On the other hand, co-processing of VR/EFB with both Fe<sub>3</sub>O<sub>4</sub> and hydrogen produced similar results to that obtained with VR upgrading only. This implies that the mechanism of reaction with the catalyst may differ, based on the type of biomass feedstock. In addition, the use of EFB generated a lower fraction of light product and a higher fraction of vacuum gas oil than achieved with cellulose. This may be because EFB has less light components than cellulose, in accordance with the TGA analysis [25].

Based on the results of VR upgrading and co-processing of VR/EFB at 430 °C, a higher reaction temperature is not recommended for the *m*-xylene system, as it is related to coke formation and residue conversion (Table 2). Furthermore, a lower fraction of light product was generated at 430 °C than at 400 °C (Fig. 3(b)). As observed for VR upgrading using *m*-xylene, the supply of hydrogen to the radicals appears to be insufficient and the condensation reaction tends to be accelerated at a higher temperature.

Co-processing experiments using *n*-dodecane were not carried out at 430 °C due to the instability of *n*-dodecane, as mentioned above. Fig. 4 and Table 3 present the results of co-processing in *n*-dodecane at 400 °C under the same conditions employed for the *m*-xylene system. The co-processing of VR/cellulose in *n*-dodecane led to higher residue conversion than VR upgrading only, but the coke formation was much higher (Table 3). In the co-processing of VR/cellulose with the Fe<sub>3</sub>O<sub>4</sub> catalyst only, the coke formation and residue conversion in the *n*-dodecane system were almost

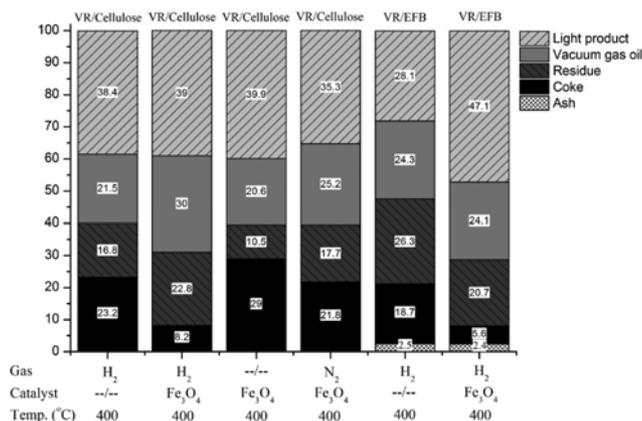


Fig. 4. Product distribution (yields of light product, vacuum gas oil, residue, coke, and ash) of co-processing of VR/cellulose or VR/EFB in supercritical *n*-dodecane.

equivalent to each result obtained using *m*-xylene (Table 2). However, co-processing in *n*-dodecane usually gave worse results in terms of residue conversion and coke formation than achieved with *m*-xylene. Furthermore, the fraction of light product obtained with *n*-dodecane was smaller than that obtained with *m*-xylene in all cases (Figs. 3 and 4).

Since complex reactants such as asphaltenes, cellulose, and lignin simultaneously participate in various reactions, it was difficult to understand the exact mechanism depending on the solvent, hydrogen, and catalyst. However, several points of insight for co-processing of VR and biomass were found from the results in this study. First, when *m*-xylene and *n*-dodecane are applied to the co-processing, reaction temperatures of over 400 °C are not desirable because a higher temperature is not advantageous for residue conversion, coke suppression, and product quality. If coke suppression is considered to be an important factor in co-processing, the system employing the Fe<sub>3</sub>O<sub>4</sub> catalyst and hydrogen is effective because the catalyst facilitates hydrogen transport to intermediate products. In contrast, when conversion is regarded as a first priority regardless of the extent of coke formation, the addition of H<sub>2</sub> or Fe<sub>3</sub>O<sub>4</sub> is desirable. However, the most important factor is the selection of the solvent in co-processing because the conversion, product quality, and coke suppression are significantly affected by the solvent. From the present results, the solvency appears to play a key role in the co-processing reaction, and aromatic solvents are preferred to paraffinic solvents in the reaction.

### 3. Solid Product Analysis

As representative cases, some of the recovered catalysts were characterized via XRD analysis (Fig. 5). The crystalline structure (magnetite) of the iron oxide catalyst was largely preserved after VR upgrading and the co-processing reaction at 400 °C. Fine catalyst particles dispersed in the feedstock could be sulfided in situ due to the high concentration of sulfur contained in the VR (Table 1), forming a pyrrhotite layer (Fe<sub>1-x</sub>S) on the surface of magnetite [35,36]. Due to overlap of the peaks of the iron minerals, it was hard to distinguish the exact components of the peaks, although several forms of iron sulfide may coexist. However, after VR upgrading, XRD analysis of the catalysts (Fig. 5) revealed new peaks corre-

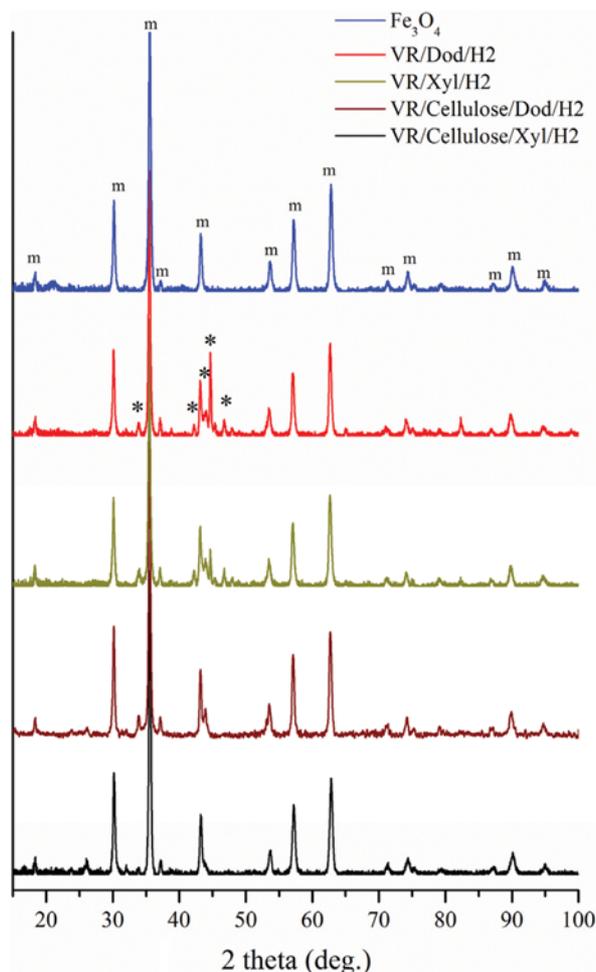


Fig. 5. XRD peak patterns of solids obtained from VR upgrading and co-processing of biomass and VR in various solvents under  $H_2$  with  $Fe_3O_4$  at  $400^\circ C$ .

sponding to iron sulfide ( $2\theta=33.74^\circ$ ,  $42.23^\circ$ ,  $43.89^\circ$ , and  $46.68^\circ$ ).

It was reported that the degree of sulfidation was dependent on the sulfur concentration, pressure, and temperature [35]. After co-processing of VR with biomass, the new peaks had much lower intensities and were almost indistinguishable from the background. These results could be attributed to the reduced concentration of

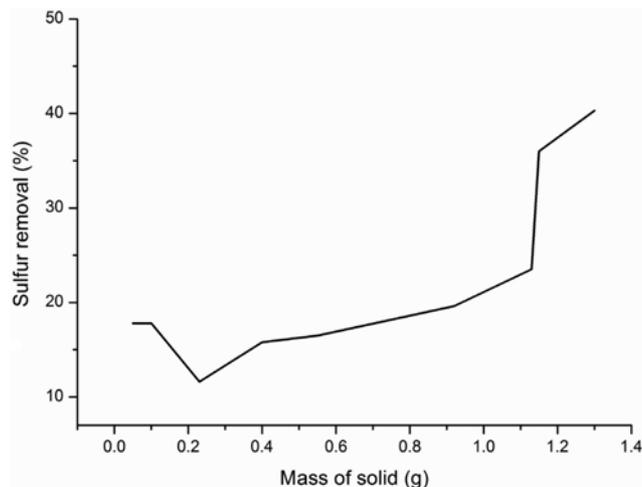


Fig. 6. Correlation between sulfur removal and mass of solids.

sulfur compounds in the feedstock (reduced quantity of VR in the feedstock). Therefore, a reduction in the quantity of iron sulfide may have led to the formation of amorphous regions on the surface of magnetite.

Most of the nitrogen (>90%), oxygen (>50%), and sulfur (>60%) in the asphaltenes remain in the generated coke, according to the literature [1]. In this study, sulfur removal during VR upgrading and co-processing was also confirmed via elemental analysis of the solid products (Table 4). The sulfur components may be adsorbed onto the coke surface or be converted to metal sulfides [37]. In general, the quantity of sulfur in the solid products was proportional to the mass of deposited solids (coke+ash), as shown in Fig. 6. However, even when the coke generated in the reaction with the  $Fe_3O_4$  catalyst was as low as 0.05 g, the sulfur removal was still higher than 17%. These results suggest that some amount of sulfur compounds in the feedstock is adsorbed or reacts with iron oxide [38,39]. Therefore, VR upgrading and co-processing using supercritical solvents may offer the added advantage of reducing the sulfur concentration in the liquid products.

## CONCLUSIONS

VR upgrading and co-processing of VR with biomass were per-

Table 4. Elemental analysis of solids obtained from VR upgrading and co-processing

Experimental condition			Elemental analysis (%)				Results	
Feed	Solvent	Catalyst	C	H	N	S	Solid mass (g)	S removal (%)
VR	<i>n</i> -Dodecane	--/--	83.4	5.3	1.4	8.4	0.55	16.5
VR	<i>n</i> -Dodecane	$Fe_3O_4$	10.3	0.7	0.1	5.4	0.10	17.8
VR/cellulose	<i>n</i> -Dodecane	--/--	82.7	5.1	0.7	4.9	1.15	36.0
VR/cellulose	<i>n</i> -Dodecane	$Fe_3O_4$	32.3	2.4	0.2	2.5	0.92	19.6
VR/EFB	<i>n</i> -Dodecane	$Fe_3O_4$	48.0	3.1	0.5	2.3	0.40	15.8
VR	<i>m</i> -Xylene	$Fe_3O_4$	4.7	0.3	0.1	5.9	0.05	17.8
VR/cellulose	<i>m</i> -Xylene	--/--	89.5	4.3	0.9	5.3	1.30	40.3
VR/EFB	<i>m</i> -Xylene	--/--	75.1	3.9	1.1	3.6	1.13	23.5
VR/EFB	<i>m</i> -Xylene	$Fe_3O_4$	13.8	0.9	0.1	2.2	0.23	11.6

formed in a batch-type reactor by using supercritical solvents. The effects of the solvent type and operating conditions on the reaction were evaluated by using the residue conversion, coke formation, and product distribution as performance parameters. The light product fraction and residue conversion in the co-processing of VR/cellulose were much higher than those in VR upgrading alone, although some portion of residue shifted towards coke formation in the VR/cellulose system. Generally, the co-processing of VR/cellulose produced better results than co-processing of VR/EFB because EFB contains more refractory components.

When *m*-xylene and *n*-dodecane were applied to VR upgrading or co-processing, reaction temperatures of over 400 °C were not desirable because coke formation was not effectively suppressed at the high temperature. In addition, a large amount of coke was formed in the *n*-dodecane system because of the low solubility of asphaltenes and the low stability of the *n*-alkane solvent compared to the aromatic solvent (*m*-xylene). *m*-Xylene gave rise to better conversion and less coke formation than *n*-dodecane, making the former a better solvent. The product distribution could also be controlled by selection of the solvent.

Hydrogen improved the residue conversion and generation of the light product fraction. This indicated that gaseous hydrogen not only acted as a hydrogen source in hydroconversion, but also improved the conversion by changing the phase properties. When coke suppression is considered as a top priority for the reaction, addition of Fe<sub>3</sub>O<sub>4</sub> catalyst with H<sub>2</sub> is recommended, although the conversion is lower than that achieved without the catalyst. During the supercritical process, the iron catalyst could be sulfided in situ due to the high concentration of sulfur in the VR. The quantity of sulfur in the solid products was proportional to the mass of the deposited solids (coke and ash). Therefore, the supercritical process could eliminate sulfur compounds in the liquid products.

With respect to practical feasibility, the stream available in oil refineries, which is rich in aromatic hydrocarbons including *m*-xylene or normal paraffins including *n*-dodecane, can be applied to the developed technology. After the reaction using the stream as a solvent, the product goes to an atmospheric distillation unit for recovering the solvent, or is directly supplied to the upgrading units such as residual fluid catalytic cracking (RFCC) as a partial feed. Therefore, for practical application of the developed technology, the first case needs to be evaluated by the energy cost of the distillation unit, and the second case is required to set the feeding ratio and operating conditions for existing RFCC process. To sum up, the results demonstrated the plausibility of co-processing process for extra heavy oil and biomass. If co-processing of biomass with conventional petroleum feedstocks can be performed in existing oil refineries, co-processing may offer the advantage of reducing the high capital costs of the bulk treatment.

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#### REFERENCES

1. J. G. Speight, *The chemistry and technology of petroleum*, CRC Press (2014).
2. C. Leyva, M. S. Rana, F. Trejo and J. Ancheyta, *Catal. Today*, **141**, 168 (2009).
3. J. Marques, D. Guillaume, I. Merdrignac, D. Espinat and S. Brunet, *Appl. Catal. B-Environ.*, **101**, 727 (2011).
4. M. S. Rana, V. Sámano, J. Ancheyta and J. A. I. Diaz, *Fuel*, **86**, 1216 (2007).
5. M. Watanabe, S.-n. Kato, S. Ishizeki, H. Inomata and R. L. Smith Jr., *J. Supercrit. Fluids*, **53**, 48 (2010).
6. J. Park and S. Son, *Korean J. Chem. Eng.*, **28**, 455 (2011).
7. Y. H. Oh, I. Y. Eom, J. C. Joo, J. H. Yu, B. K. Song, S. H. Lee, S. H. Hong and S. J. Park, *Korean J. Chem. Eng.*, **32**, 1945 (2015).
8. H. Lee, Y.-M. Kim, I.-G. Lee, J.-K. Jeon, S.-C. Jung, J. D. Chung, W. G. Choi and Y.-K. Park, *Korean J. Chem. Eng.*, **33**, 3299 (2016).
9. C. Xu, S. Hamilton, A. Mallik and M. Ghosh, *Energy Fuels*, **21**, 3490 (2007).
10. D. S. Scott, D. Radlein, J. Piskorz, P. Majerski and T. J. W. deBruijn, *Fuel*, **80**, 1087 (2001).
11. T. T. Viet, J.-H. Lee, J. W. Ryu, I.-S. Ahn and C.-H. Lee, *Fuel*, **94**, 556 (2012).
12. T. T. Viet, J. H. Lee, F. Ma, G. R. Kim, I. S. Ahn and C. H. Lee, *Fuel*, **103**, 553 (2013).
13. D.-W. Kim, F. Ma, A. Koriakin, S.-Y. Jeong and C.-H. Lee, *Energy Fuels*, **29**, 2319 (2015).
14. X. Huang, T. I. Korányi, M. D. Boot and E. J. M. Hensen, *ChemSusChem*, **7**, 2276 (2014).
15. D. A. Cantero, M. D. Bermejo and M. J. Cocero, *ChemSusChem*, **8**, 1026 (2015).
16. A. Koriakin, H. Van Nguyen, D. W. Kim and C.-H. Lee, *J. Supercrit. Fluids*, **95**, 175 (2014).
17. M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res.*, **39**, 2883 (2000).
18. Q. Cao, L. e. Jin, W. Bao and Y. Lv, *Fuel Process. Technol.*, **90**, 337 (2009).
19. J. D. Martínez, A. Veses, A. M. Mastral, R. Murillo, M. V. Navarro, N. Puy, A. Artigues, J. Bartrolí and T. García, *Fuel Process. Technol.*, **119**, 263 (2014).
20. Z. Zhu, S. S. Toor, L. Rosendahl, D. Yu and G. Chen, *Energy*, **80**, 284 (2015).
21. N. N. Nassar and M. M. Husein, *Fuel Process. Technol.*, **91**, 164 (2010).
22. E. Fumoto, T. Tago and T. Masuda, *Energy Fuels*, **20**, 1 (2006).
23. W.-I. Choi, J.-Y. Park, J.-P. Lee, Y.-K. Oh, Y. C. Park, J. S. Kim, J. M. Park, C. H. Kim and J.-S. Lee, *Biotechnol. Biofuels*, **6**, 1 (2013).
24. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, *Laboratory Analytical Procedure*, **1617** (2008).
25. D.-W. Kim, A. Koriakin and C.-H. Lee, *Fuel*, **181**, 895 (2016).
26. M. Azhar Uddin, H. Tsuda, S. Wu and E. Sasaoka, *Fuel*, **87**, 451 (2008).
27. E. Karimi, I. F. Teixeira, A. Gomez, E. de Resende, C. Gissane, J. Leitch, V. Jollet, I. Aigner, F. Berruti, C. Briens, P. Fransham, B. Hoff, N. Schrier, R. M. Lago, S. W. Kycia, R. Heck and M. Schlaf, *Appl. Catal. B-Environ.*, **145**, 187 (2014).
28. S. Funai, E. Fumoto, T. Tago and T. Masuda, *Chem. Eng. Sci.*, **65**, 60

- (2010).
29. V. Arunajatesan, K. A. Wilson and B. Subramaniam, *Ind. Eng. Chem. Res.*, **42**, 2639 (2003).
30. J. Scherzer and A. J. Gruia, *Hydrocracking science and technology*, CRC Press (1996).
31. P. M. Rahimi and T. Gentzis, *Fuel Process. Technol.*, **80**, 69 (2003).
32. K. Sjöström, G. Chen, Q. Yu, C. Brage and C. Rosén, *Fuel*, **78**, 1189 (1999).
33. M. Lapuerta, J. J. Hernández, A. Pazo and J. López, *Fuel Process. Technol.*, **89**, 828 (2008).
34. C. Brage, Q. Yu, G. Chen and K. Sjöström, *Biomass Bioenerg.*, **18**, 87 (2000).
35. T. Kaneko, K. Tazawa, T. Koyama, K. Satou, K. Shimasaki and Y. Kageyama, *Energy Fuels*, **12**, 897 (1998).
36. W. L. T. M. Ramselaar, M. W. J. Crajé, R. H. Hadders, E. Gerkema, V. H. J. de Beer and A. M. van der Kraan, *Appl. Catal.*, **65**, 69 (1990).
37. N. N. Nassar, M. M. Husein and P. Pereira-Almao, *Fuel Process. Technol.*, **91**, 169 (2010).
38. S. W. Poulton, M. D. Krom and R. Raiswell, *Geochim. Cosmochim. Acta*, **68**, 3703 (2004).
39. O. Lahav, G. Ritvo, I. Slijper, G. Hearne and M. Cochva, *Aquaculture*, **238**, 263 (2004).