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Biofuel upgrading via catalytic deoxygenation in trickle bed reactor: Crucial issue in selection of pressure regulator type

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Abstract:

Trickle bed reactors (TBRs) are commonly used in various chemical and associated processes. The selection of a proper back pressure regulator (BPR) is crucial for maintaining the system's upstream pressure. In this study, we investigate the impact of BPR selection on deoxygenation reaction in a TBR with two typical types of BPR, including gas-phase type back pressure regulator (Gas-BPR) and multiphase type back pressure regulator (Multi-BPR). Notably, Gas-BPR introduces interruptions and pressure drops during the sampling step, impacting the hydrogen flow rate, while Multi-BPR ensures more consistent hydrogen flow. To examine the performance of BPR systems, hydrotreating experiments were conducted at 330 °C, 50 bar of hydrogen over Ni/γ-Al_2O_3 catalyst using crude *Pongamia pinnata* oil as a feedstock and refined palm olein as a benchmark. Insignificant difference in the reaction performance between Multi-BPR and Gas-BPR systems was observed when using refined palm olein. Interestingly, there was a significant difference between the two systems when feeding with crude *Pongamia pinnata* oil. The multi-BPR system demonstrated superior performance, achieving 100% conversion of the feedstock over a prolonged period compared to the interrupted hydrogen flow in the Gas-BPR system. Further characterization of fresh and spent catalysts using N_2 sorption, XRD, SEM-EDS and TGA-DTG-DSC techniques revealed that a gum and coke formation was a reason for the rapid catalyst deactivation. Furthermore, the interrupted flow in the Gas-BPR system led to substantial gum production, ultimately causing a blockage in the reactor bed. Consequently, for feedstocks with high impurities, a robust continuous flow of hydrogen is essential. Thus, the study strongly recommends selecting Multi-BPR for continuous operation in TBRs to enhance efficiency and avoid catalyst deactivation.

Keywords: Bio-hydrogenated diesel; nickel catalyst; catalyst deactivation; renewable energy; reactor configuration

1. Introduction

Currently, several technologies for biofuel production have been demonstrated and continuously developed, aiming at reducing fossil fuel dependence and environmental problems associated with using fossil-based energy. Hydroprocessing of lipids is one of the efficient methods for biofuel production as such fuels contain hydrocarbons similar to those found in conventional petroleum-derived fuels, making them usable as a drop-in transportation fuel [1]. The production of biofuels through the hydrotreating process entails the saturation of unsaturated hydrocarbons and the removal of heteroatom contained in bio-based feedstock such as sulfur (S), nitrogen (N), and oxygen (O). This process is achieved by subjecting the bio-based feedstock to a substantial amount of hydrogen at elevated temperatures and pressures in the presence of a catalyst. The process involves a variety of liquid and gas-phase reactions, which are influenced by the operating conditions and the type of feed. In the case of biomass-derived oil (bio-oil) and triglyceride-based or lipid-based feedstock, oxygenate compounds are the predominant constituents. Therefore, a crucial reaction of the process is the elimination of oxygen from these compounds, including decarboxylation (DCO_x), decarbonylation (DCO), and hydrodeoxygenation (HDO), during which oxygen is released by the formation of CO_2, CO, and H_2O, respectively [2,3]. For algae bio-crude oil, one of the promising bio-based feedstocks, the challenge of hydrotreating the bio-crude oil is the elimination of nitrogen. As the bio-crude oil produced via hydrothermal liquefaction (HTL) consists of a complex mixture of oxygenated compounds, also (hetero)cyclic nitrogenates and their derivative. Accordingly, further catalytic hydrotreating is necessary to eliminate both oxygen and nitrogen [4,5].

For several decades, the performance of catalytic hydrotreating of lipid-based feedstocks has been extensively evaluated using different catalyst types, including metal sulfides (Ni, Co, and Mo), noble metals (Pt, Pd, and Rh) [6–8], transition metals (Cu, Ni, and Fe) [9–11], and other phases in forms of nitride [12], carbide [13], and phosphide [14], which have been reported to have effective hydrotreating performance. The liquid product of the catalytic hydrotreating process resembles petroleum-based diesel in both physical and chemical properties.

However, catalyst deactivation is one of the challenges for hydrotreating bio-based feedstock. Coke formation is one of the most prevalent causes of catalyst deactivation, as reported by many studies [15–18], which principally involves with decomposition, cyclization, aromatization, condensation, and polymerization of oxygenated hydrocarbons in reactant, intermediates, and/or product to form polyaromatic and heavy hydrocarbon compounds. The heavy compounds can accumulate either on external surfaces or inside catalyst pores, leading to loss of active sites and pore blocking. This phenomenon results in the reduction of catalyst activity, conversion, hydrocarbon yield, product selectivity, and catalyst's lifetime [19–21]. Nevertheless, coke formation may not be the major reason for hydrotreating catalyst deactivation, particularly when unpurified or crude plant oil is used as feedstock. This statement could be confirmed based on our recent study [22]. We studied the hydrotreating activity of *Pongamia pinnata* oil over NiMoS catalyst supported on different support materials and found that the catalyst deactivation was dominated by phosphorus and alkali impurities contained in unpurified *Pongamia pinnata* oil, which effectively hasten catalyst deactivation through the poisoning, blocking the active site, and even accelerating coke formation. Among the supported catalysts, NiMoS catalysts supported on Al_2O_3 demonstrated superior performance and strong resistance to the presence of significant impurities for a prolonged period compared to those supported on TiO_2 and SiO_2. This result could be attributed to the synergistic effect of pore size, acidity, and metal-support interaction [22].

Recently, several alternative bio-based feedstocks (mostly inedible and biomass-based feedstock) have been extensively investigated for renewable energy production to meet energy consumption and avoid food-energy competitive problems. Raw or waste lipid feedstocks contain many mineral matters such as alkali metals (e.g., Ca, Mg, K, and Na) and phosphorus which have been reported for their harmful effects on the hydrotreating catalysts [23–26]. This is in good agreement with our recent study [22]. In addition, the effect of phosphorus also causes pressure drops because it accelerates the gum formation, resulting in reactor blockage and further severe system failures [27].

In the refining, chemical and associated industries, trickle bed reactors have been extensively used for chemical conversion operations. The hydrotreating process is commonly studied and operated in a trickle bed reactor. During the hydrotreating, pressure drops could be built up with time on stream by a bunch of factors—e.g., the fluid velocity and flow behavior [28], deposition of suspended solids in liquid feed, and deposition of solid or heavy compounds formed during chemical/thermal reactions of feedstocks [29,30], causing operational problems. Therefore, the utilization of unpurified feedstock causing the pressure drop and accelerating catalyst deactivation is a challenge for biofuel production.

A high-pressure continuous operating system necessitates using a back pressure regulator (BPR) to maintain upstream pressure and decrease outlet pressure. Nevertheless, the use of various types of BPR leads to different characteristics of the reactor system. The regular back pressure regulator enables only one phase (gas or liquid) to flow through its valve. BPR for the gas phase (Gas-BPR) has typically been utilized in the system, and consequently, the liquid product cylinder should be installed before the gas-BPR, and the liquid product be collected under a high-pressure atmosphere, creating a drop in pressure during the sampling step. Also, this system requires make-up pressure to retain the system pressure at the desired level, which may affect the steady-state of the operation. On the other hand, the make-up pressure step is not required when a multiphase back pressure regulator (Multi-BPR) is applied because the multi-BPR has a unique ability to pass mixed-phase of gas and liquid, simultaneously, allowing the liquid product be collected under atmospheric conditions. The multiphase back pressure regulator (Multi-BPR) would be preferable to the regular one since it can decrease pressure drops during the operation.

Several researchers have studied the catalytic deoxygenation of triglycerides and fatty acids by using continuous systems, i.e., trickle-bed reactor, to investigate the activity and stability of the catalyst [31–35]. To our knowledge, there is no information on the influence of different types of BPRs in the trickle-bed operation and the deoxygenation reaction. Therefore, we investigated the activity of deoxygenation reaction by comparing two different BPRs, including Gas-BPR and Multi-BPR, which provide interrupted and constant hydrogen flow systems, respectively. The monometallic Ni supported on alumina was employed for this work due to its strong deoxygenation activity and sulfur-free catalyst. Crude *Pongamia pinnata* oil was selected to use as a feedstock because it has potential as an alternative feedstock for biofuel production, e.g., high oil content (20-40% dry basis) and resistance to the drought-prone environment as well as poor quality soils [36–38]. Furthermore, the contaminants in crude *Pongamia pinnata* oil have been examined to see whether they impact the processes according to the aforementioned literature. The hydrodeoxygenation of refined palm olein was also performed as a reference experiment. In addition, the fresh and used catalysts were characterized to elucidate the potential difference in reaction performance by the change in H_2 feed scheme from the use of different types of BPR.

2. Materials and Methods

2.1 Materials

Ni/γ-Al_2O_3 catalyst used in this study was in-house prepared. γ-Al_2O_3 support was obtained from Sasol Company, Germany. The catalyst precursor $Ni(NO_3)_2 \cdot 6H_2O$ (purity, 99.99%) was purchased from Sigma-Aldrich Chemical Co. LLC., Germany. *Pongamia pinnata (P. pinnata)* oil was also in-house prepared. The seeds were obtained from mangrove forest in Khlung district, Chanthaburi, Thailand.

2.2 Feed preparation

Prior to the hydrotreating step, crude *Pongamia pinnata (P. pinnata)* oil was prepared via Soxhlet extraction method using hexane as solvent. Fatty acid distribution of extracted *Pongamia pinnata* (*P.pinnata*) oil was examined using Trace GC Ultra gas chromatography equipped with Polaris Q mass spectrometer (GC-MS) and TR-FAME column (30 m × 0.25 × 0.25 μm). The fatty acid mainly composed of palmitic acid (C16:0) 15.2%; stearic acid (C18:0) 4.6%; oleic acid (C18:1) 54.6%; linoleic acid (C18:2) 13.5%; linolenic acid (C18:3) 0.2%; arachidic acid (C20:0) 1.0%; eicosenoic acid (C20:1) 1.4%; and behenic acid (C22:0) 8.2%. In addition, metallic impurities in the oil were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, PerkinElmer, Cedar Rapids, IA, USA), as shown in Table 1.

2.3 Catalyst preparation and characterization

Ni/γ-Al_2O_3 was prepared by an incipient wetness impregnation. $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich, 99.99%) was employed as a corresponding metal salt precursor. The aqueous solution of precursors (Ni 10 mass%) was loaded into the γ-Al_2O_3 support (Sasol, Germany). After impregnation, the sample was dried at 110 °C overnight. Subsequently, the dried catalyst was calcined in flowing air (30 ml/min) at 500 °C for 5 h with a heating rate of 5 °C/min.

The textural properties (surface area, pore volume and pore size) of catalysts were characterized by nitrogen adsorption at -196 °C using BELSORP mini II (BEL Japan, Inc). The surface area was calculated by Brunauer-Emmett-Teller (BET) method, and total pore volume was evaluated using N_2 volume adsorbed at the relative pressure P/P_0 of 0.973. X-ray diffraction (XRD) patterns were measured with Bruker Advance D8 using Cu K_α radiation. The patterns were recorded over the ranges $10° < 2\theta < 80°$ in 0.02° step size with 0.5 s per step.

A scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM-EDS, Tescan Mira3) was employed to analyze the morphology and elemental composition of the synthesized catalyst. The sample was ground into a fine powder before being applied on conductive carbon double-sided adhesive tape attached to an aluminium pin stub.

The amount of carbon deposition on the spent catalyst was determined by thermogravimetric analysis (TGA) using DSC-TGA (TA instruments SDT Q600). The spent catalyst was placed in an alumina cup, and then the temperature was heated up from room temperature to 1000 °C, at a ramping rate of 10 °C/min under air atmosphere.

2.4 Experimental setups of a trickle bed reactor system with different back pressure regulators

The hydrotreating *of P. pinnata* oil over Ni/γ-Al_2O_3 catalysts was carried out in a down-flow stainless steel trickle bed reactor with an inner diameter of 10 mm, a length of 50 cm, as shown in Fig. 1. The catalyst was loaded into the reactor with glass beads with a diameter of 3 mm at the bottom and the top of the reactor for distributing gas and liquid phase feeds, whereas 3 g of the catalyst with a particle size of 250 – 500 µm was packed at the center with quartz wool to prevent catalyst displacement. Before the reaction test, the catalyst was reduced *in-situ* under 10 bar of H_2 with a flow rate of 60 ml/min at a temperature of 500 °C for 3 h. Then the gas was switched to nitrogen gas (10 bar of N_2) until the reactor temperature was reduced to 330 °C, then pressurized with H_2 of 50 bar controlled by a back pressure regulator (BPR). Subsequently, the oil and H_2 were introduced into the reactor at a H_2/oil ratio of 1000 Ncm^3/cm^3 with liquid hourly space velocity (LHSV) of 1 h^{-1}, which was controlled by a high-pressure piston pump (Shimadzu LC-20AD HPLC pump, Columbia, MD, USA) and a mass flow controller (Brookes instrument, Hatfield, PA, USA), respectively. The oil was preheated at 180 °C before feeding into the reactor.

In the case of Gas-BPR, which provided interrupted H_2 flow, as shown in Fig. 1 (dashed blue line), the spring-loaded BPR (Swagelok) was placed after the high-pressure product cylinder, enabling only gas-phase delivery through the BPR. As a result, the liquid product was at the bottom of the cylinder, while the gas phase was at the top and went through the BPR for analysis. The liquid product was sampled using a portable high-pressure cylinder (cylinder 2), resulting in a pressure drop of approximately 5-10 bar; the gas in the portable cylinder was then purged out in a fume hood. The solid red line (Fig. 1) shows the setup of Multi-BPR, which provided constant H_2 flow. The BPR (Equilibar, Fletcher, NC, USA) was positioned before the product cylinder, and then the liquid product was collected at atmospheric pressure. To compare these two systems, the excessively high H_2 flow rate was introduced into the reactor only for the Gas-BPR experiments to compensate for the dropped system pressure when collecting the liquid product (every 3 hours in this study). It took around 10 minutes of high H_2 flow rate to rebuild the pressure to 50 bar.

2.5 Liquid product characterization

The liquid reaction products were analyzed by off-line gas chromatography (GC) equipped with a capillary column DB-1HT (30 m× 0.32 mm × 0.1 μm) and a flame ionization detector (FID) (GC-2014 Shimadzu). Prior to injection, 50 mg of sample was diluted with 1 ml of chloroform, and 1 μL of diluted sample was injected into the GC with a split ratio of 100. Ultra-high purity helium was used as the carrier gas with a flow rate of 30 ml/min. The injector and detector temperature were maintained at 340 °C and 370 °C, respectively. The column temperature was controlled by a temperature program which increased from 40 to 270 °C with a ramping rate of 8 °C/min, and held for 11 min, followed by an increase of 15 °C/min to 370 °C, and held for 15 min.

The conversion, product selectivity, and yield are calculated using the chromatogram areas as given by Eqs. (1)-(5), respectively.

$$\text{Conversion (\%)} = \frac{\text{mass of TG and FFA in feed} - \text{mass of TG and FFA in product}}{\text{mass of TG and FFA in feed}} \times 100 \tag{1}$$

$$\text{Gasoline selectivity (\%)} = \frac{\text{mass of C6-C12 in product}}{\text{mass of TG and FFA in feed} - \text{mass of TG and FFA in product}} \times 100 \tag{2}$$

$$\text{Diesel selectivity (\%)} = \frac{\text{mass of C13-C22 in product}}{\text{mass of TG and FFA in feed} - \text{mass of TG and FFA in product}} \times 100 \tag{3}$$

$$\text{Product yield (\%)} = \frac{\text{mass of liquid product}}{\text{mass of feed}} \times \text{conversion} \times \text{product selectivity} \tag{4}$$

$$\text{Yield of liquid fuel} = \text{diesel yield} + \text{gasoline yield} \quad (5)$$

All experiments were carried out twice to confirm the reproducibility. The average deviation of the conversion, gasoline selectivity, diesel selectivity and product yield were ± 0.38, ±0.27, ±0.55 and ±1.41, respectively.

3. Results and discussion

3.1 Hydrotreating of Pongamia pinnata oil

The hydrotreating reaction consists of a three-phase reaction in which gas-liquid-solid interaction influences the reaction performance. In the reaction, hydrogen gas must first diffuse through the gas-liquid interface, then dissolve in the bulk of the liquid feedstock, and consequently diffuse through the pores of the catalyst alongside the liquid reactant reacting on the catalyst's active sites. As a result, the procedure necessitates a high gas-liquid distribution toward excellent mass and heat transportation over the catalyst surface as well as a long liquid residence time to accomplish the required degree of reactant conversion.

3.1.1 Trickle-bed reactor – flow pattern

In a trickle-bed reactor, fluid-phase distribution is a critical parameter influencing reactor performance. A poor phase distribution can result in inefficient catalyst and deactivation and induce local hot spots toward low reactor efficiency. Depending on the gas-liquid flow rate and their individual properties and packing properties, the fluid flow regime in the trickle bed reactor is broadly categorized into two regimes: low interaction (i.e., trickle flow) and high interaction (i.e., pulsing, bubble, and spray flow) [39–42].

Table 2 depicts the flow regime in terms of gas and liquid flow rates [42,43]. Most trickle bed reactors are operated in either the trickle flow or pulse flow regime. The trickle flow has advantages for high wetting of the exterior catalyst particle due to the liquid film moving, enabling high residence time and a stable operation; however, it has poor mass and heat transfer [44]. While, increasing in mass and heat transfer rate is obtained for the pulse flow regime, resulting in high fluid distribution, complete catalyst wetting, and reduced hot spots formation that significantly affect the catalyst efficiency and reactor performance. However, the pulsing flow causes a higher pressure drop over the bed catalyst and decreases in a liquid holdup, owing to the instability reactor operation [45]. Although the stable operation and high residence time could be favorable for the process, the high phase distribution and excellent heat-mass transfer are significantly required for the catalytic reaction process. Therefore, the pulse flow regime is more attractive for industrial operation.

Based on our laboratory reactor and research conditions, hydrogen gas and *Pongamia pinnata* oil were introduced into the reactor with moderate and relatively low flow rates, the fluid flow pattern in our system was the trickle flow regime [46,47]. The mass and heat transfer could be accomplished by using small-sized catalyst particles (250 – 500 μm). Since the small particle size of the catalyst can provide an effective contacting surface area and void distribution, resulting in an improvement of the gas-liquid mass transfer rate to enhance the catalyst efficiency [48,49]. Meanwhile, the relatively low conversion of 87% was observed during interrupted hydrogen flow when using Gas-BPR and decreased to 82% at 9 h on stream (Fig. 2). It was observed that the liquid fuel yield initially decreased at 6 h and the lowest liquid yield of 54% was obtained at 9 h on stream.

3.1.2 Liquid product distribution

Considering product distribution (Table 3), in both cases, the liquid products mostly composed of *n*-C_{15} to *n*-C_{18} hydrocarbons which are in diesel range hydrocarbons (Fig. 2). In addition, *n*-C_{17} is a predominant hydrocarbon composition, supposed to be derived from oleic acid (C18:1), the main feed component. This result could indicate that the liquid product was produced mainly through decarboxylation/decarbonylation (DCO_x/DCO) reaction rather than hydrodeoxygenation (HDO) reaction [50,51], as confirmed by the percent of the contribution of HDO and DCO_x/DCO (Table 3) which were calculated using the ratio of mass percentage of *n*-alkanes with even number (*n*-C_{18}) or odd number (*n*-C_{17}) to total mass percentage of *n*-C_{18} and *n*-C_{17} in product.

Obviously, there is no significant change in the selective reaction pathway between these two types of back pressure regulator (BPR) which provide different hydrogen flow characteristics, except the yield and product appearance (Figure S1). The visual colour of liquid products obtained by the constant hydrogen flow (Multi-BPR) is clear and colourless during the entire experiment, as shown in Fig. S1 whereas the interrupted system (Gas-BPR) experiment produced liquid products with light yellow at the early stage, and turn into the dark yellow, then a part of the liquid product eventually became soft wax (at room temperature) at 9 h time-on-stream. This might be due to the unsteady flow of supplied hydrogen gas during the reaction, resulting in an interrupted hydrotreating process and a decrease in catalytic activity as the intermediates were discovered in the liquid product. As a result, undesirable side reactions such as oligomerization of alkenes or intermediate compounds, which might be enhanced in the presence of phosphoric acid [52], were encouraged. In addition, the change of product colour may be related to the existence of remaining oxygen-containing compounds such as TGs, FFAs and other intermediates in the product. This indicates the reduction in the degree of deoxygenation resulting from the losing catalytic activity during the reaction under interrupted hydrogen flow. Intermediate oxygen-containing compounds, for example, as evidenced by the detection of 1-octadecanal (selectivity of 1.28%) at the early stage, while 1-octadecanol of 0.13% and stearic acid (1-octadecanal precursors) of 0.62% were observed after time-on-stream of 3 h and 6 h, respectively. The selectivity of the oxygen-containing compounds at 9 h time-on-stream is presented in Table 3.

3.1.3 Effect of back pressure regulator type in flow reactor setup on catalytic activity

Figs. 3a, 3b, and 3c depict the monitoring of the change in pressure and flow rate during the reaction when using Gas-BPR and Multi-BPR. The extremely high hydrogen feed for the Gas-BPR system, as shown in Fig. 3a, influences pressure changes in both the reactor and the liquid feed stream.

After a reaction time of 5 h-on-stream, the operating pressure began to oscillate, whereas the pressure in the liquid stream gradually increased from 3 h time-on-stream, and the pressure of the HPLC pump reached 100 bar after product collection at 9 h time-on-stream. The HPLC pump then malfunctioned, eventually failing to supply liquid feed. Consequently, the reactor unexpectedly stopped running, and the experiment could no longer be carried out for the Gas-BPR system. This could be attributed to system blockage, which was only detected in the case of interrupted hydrogen flow of unpurified *Pongamia pinnata* oil. Also, it was evidenced by the observation of gum deposition on glass beads placed upper the reactor in the interrupted hydrogen system, which could be caused by phosphorus and alkali impurities contained in the feed (Table 1), resulting in accumulation and plugging of the reactor. While no significant gum was detected in the constant hydrogen case, as shown in Fig. S2.

At prolonged reaction time, alkali metals and phosphorus impurities in feedstock eventually accumulate on the catalyst surface and reactor bed and cause plugging, resulting in pressure drop, limiting flow, and potentially impacting catalyst activity [53,54]. Surprisingly, the plugging problem occurred rapidly in the interrupted hydrogen flow experiment for the same feedstock containing the same amounts of contaminants, which is probably due to the fluid's behavior inside the reactor. It should be noted that no noticeable influence on the hydrotreating reaction was observed when purified oil was used as feedstock. We also repeated the experiment in the same reactor with Gas-BPR (dashed blue line arrangement in Fig.1) but using refined palm olein (RPO) as a feedstock. The result showed that constant RPO conversion of 100% can be remained over 150 h of time on stream (results are not shown here). Furthermore, the primary hydrocarbon liquid products were heptadecane and pentadecane, corresponding to palmitic acid and oleic acid present in the RPO.

Considering the interrupted hydrogen flow experiment (Gas-BPR), a very high hydrogen flow rate was introduced into the reactor to restore reactor pressure at a given liquid flow rate. The liquid in such a system would be discrete and flow in the form of thin layers or droplets, resulting in lower liquid film thickness and increased liquid spreading, which leads to improved interaction between the gas and liquid phases. This transition regime may favorably influence the catalytic process; nevertheless, the liquid holdup reduces simultaneously due to greater drag force during high gas flow rate operation, as observed by Guo et al. [55]. The liquid holdup consists of a dynamic and a static holdup, both of which are deeply related to residence time and hence reactant conversion. Lower liquid holdup might result in partial catalyst wetting and further limiting catalyst utilization. The relationship between liquid holdup and catalyst performance has been well established in the literature [56–60].

According to the literature, the decrease in liquid holdup during the excessive hydrogen feed could severely impact the hydrotreating process by shortening residence time and possibly restricting liquid-solid diffusion, which could explain the poor catalytic efficiency and reactor performance of the interrupted hydrogen system. Because the catalyst was not fully exploited, undesired reactions such as oligomerization and gum formation may occur during the hydrotreating operation, notably if unpurified feedstock was employed. This occurrence reduces reactor void and may hasten catalyst deactivation. This suggests that the combination of contaminants and an unstable operating system might rapidly harm the catalyst and reactor system

3.2 Catalyst characterization

Table 4 presents the textural properties of fresh and spent Ni supported on γ-Al_2O_3 catalysts, including surface area, total pore volume, and pore diameter. The post-run (spent) catalyst was characterized via nitrogen-sorption, XRD, and TGA-DSC to examine the reason for loss of catalytic activity and the effect of hydrogen flow on the catalysts. After the hydrotreating reaction, all experiments were fed with hexane at room temperature to clean the reactor system and facilitate catalyst unloading.

3.2.1 Brunauer-Emmett-Teller (BET) nitrogen adsorption/desorption

The surface area of commercial γ-Al_2O_3 support was measured as 202 m^2/g. After loading Ni metal into the support, the surface area and pore volume of fresh catalysts decreased, which could be due to coverage of surface and partial pores blockage by Ni incorporated. A significant decrease in BET surface area by 47.2% and 33.4% were observed for the spent Ni/γ-Al_2O_3 catalyst used in the interrupted and constant hydrogen flow, respectively, which could be due to the deposition of hydrocarbon molecules on the surface and pores of catalyst (confirmed by TGA). These occurrences cause catalyst deactivation by decreasing active sites [35]. The pore size distributions of fresh and spent Ni/γ-Al_2O_3 are shown in Fig. 4. The rather large pore diameter with an average of 9.2 nm and pore volume were observed in the case of fresh catalyst. After the reaction, the pore diameter and pore volume of spent catalysts significantly decreased. The lowest pore diameter with an average value of 6.1 nm was obtained from interrupted hydrogen flow, while for the constant hydrogen flowrate experiment, the higher average pore diameter of 7.1 nm was noticed. This indicates that the pores of the catalysts were highly blocked by the molecules of reactants and products. Thus, interrupted hydrogen flow has more influence on the rate of carbonaceous deposition compared to the constant hydrogen case. Coke deposition is an obstacle to diffusion through the pores by either reactants or products, affecting the catalytic activity.

3.2.2 X-ray diffraction (XRD)

The XRD patterns of support and reduced catalysts at 500 °C are shown in Fig. 5a. The characteristic peaks at 2θ of 37.2°, 39.1°, 45.6°, 60.61°, and 66.3° are exhibited as dominant peaks of all catalysts, corresponding to (311), (222), (400), (511), and (440) crystal planes of γ-Al_2O_3 (JCPDS 29-0063), respectively. The diffraction of metallic Ni at 2θ of 44.4°, 51.8° and 76.3° (JSPDS 04-0850) are barely observed, implying the small amount and well dispersion of Ni on the surface catalyst. For the spent catalysts, the intensity of diffraction peaks of metallic Ni becomes gradually higher (at 44.5°, 51.7°, and 76.2°), enlarged the XRD part presented in Fig. 5b, which indicate that the size of Ni particle increases due to agglomeration. However, crystallite size measurement via the Scherrer equation could not be determined because the intensity of the peaks is relatively low and no significant change is observed between interrupted and constant hydrogen flow, indicating that Ni metal agglomeration may not be the main cause for catalyst deactivation.

3.2.3 Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS)

The morphology of fresh and spent catalysts used in both configuration systems was characterized via SEM technique and the elemental deposition on the surface of catalysts was also examined by EDS analysis, as shown in Fig. 6. A thick film coating on the surface of the catalyst (red dash-line circles) has been observed in the interrupted hydrogen flow experiment. The EDS analysis reveals a greater amount of carbon on the catalyst in the interrupted experiment. This is also confirmed by analysis of the TGA as discussed below. The catalyst employed in the interrupted experiment contains not only carbon, but also phosphorus (P) and a trace of calcium (Ca). This might imply that the thick film covering the surface was formed by C and P, resulting in the loss of active sites and blocking pores. The phosphorus deposition on the catalyst might result from the deposition/decomposition of phospholipid in the reactant during the reaction, as the high P content of *Pongamia pinnata* oil was considered (see Table 1).

3.2.4 Thermogravimetric (TGA) - derivative thermogravimetric analysis (DTG) - differential scanning calorimetry (DSC)

Thermogravimetric analysis (TGA) was performed in atmospheric air to quantify the coke formation on the catalysts by monitoring the mass loss of the catalyst as a function of temperature during its combustion. Figs. 7a and 7b show thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the Ni catalyst used in constant and interrupted hydrogen flows, respectively. The initial mass loss approx. 1.3% at a temperature of 100 °C can be attributed to the vaporization of physically adsorbed water [61,62]. The maximum mass loss of both samples exhibits in the temperature range of 250-550 °C: at approximately 18% and 13% in the interrupted and constant hydrogen flow systems, respectively. The DTG curves of the two systems (Figs. 7a-7b) revealed two distinct peaks in the temperature ranges of 320 to 340°C and 370 to 385°C. These peaks can be attributed to the desorption or combustion of residual hydrocarbon molecules adsorbed on the external surface of catalyst. In addition, the higher temperature at 400-600 °C may correspond to the decomposition of heavy hydrocarbons deposited within the catalyst pores and/or the oxidation of more stable amorphous coke [63–67]. The DTG curve of the interrupted hydrogen flow experiment has shifted to a relatively high temperature, which could be attributed to the disintegration of organophosphorus compounds accumulated on the surface catalysts. This result is consistent with the EDS results as aforementioned. Alosmanov et al. [68] studied the influence of phosphorus/nitrogen functional groups during thermal degradation of polymer compounds. The phosphorus-containing compounds disintegrated at temperatures ranging from 170 to 440 °C, which depends on the structure and molecular mass of the associated polymer.

The DTG profiles of both constant (Fig. 7a) and interrupted hydrogen (Fig. 7b) experiments are well correlated with DSC curves presented in Fig. 7c, indicating that the reactions corresponding to the exothermic (DSC peak) influence the change of mass loss. The exothermic peak revealed in temperature of 300 – 400 °C is assigned to the decomposition of the different reactive carbonaceous species, which could be generated from the heavy hydrocarbons and/or fatty acids with corresponding boiling temperature range [69]. Furthermore, DSC peaks were observed at higher temperatures, ranging from 450 °C to 550 °C, which could be attributed to the oxidation of slow reactive carbon species or the combustion of coke located within the pores of the catalyst and amorphous coke, resulting in a higher energy requirement [70]. Compared to the interrupted hydrogen experiment, it is evident that the DTG and DSC curves of the constant hydrogen experiment show a slight shift toward lower temperatures, suggesting that its accumulated carbon species are more effortless to be removed.

Considering the relative effect between the amount of coke formation and the pore size distribution and pore volume, the decrease in pore size and volume may relate to coke deposition within the catalyst pores. In addition, the pore blockage may occur by a significant amount of carbon deposition on an external surface at the beginning and plugging the pores' mouths. The deposited materials may expand and narrow the voids between catalyst particles in the bed, resulting in feedstock unevenly flowing through the reactor or channeling through the bed, leading to an increase in the pressure drop throughout the reactor. This induces a necessary increase of liquid feed pressure to the reaction system, as shown in Fig. 3a. The rate of coke formation of Ni/γ-Al_2O_3 in the interrupted hydrogen experiment is 5.53 x 10^{-3} mg C g cat^{-1} s^{-1} which is higher than that of a constant hydrogen experiment of 2.48 x 10^{-3} mg C g cat^{-1} s^{-1}, as shown in Table 3. These results can be explained through a few existing experiments on inert gas which were reported elsewhere by the fact that hydrogen gas has a crucial role not only in enhancing the deoxygenation activity but also in preventing catalyst deactivation by coke formation [71–73]. The role of hydrogen gas can describe these results during deoxygenation reactions.

With the interrupted H_2, the hydrotreating reaction was interrupted by an extremely high inlet hydrogen flow rate for restoring the system pressure of 50 bar. This circumstance may shorten the contact time between the reactants and the catalyst, reducing conversion and hydrotreating activity (Fig. 2), as also confirmed by increasing oxygen-containing molecules (see Table 3). Besides, the polymerization could be catalyzed by phosphoric acid contained in the oil [74], which may be enhanced due to the reduction of hydrotreating activity. These possibilities are evidenced by the relatively high selectivity of high-molecular-weight hydrocarbons (>C23) contained in the liquid product of the interrupted hydrogen experiment compared to the constant hydrogen flow (Table 3), which finally accumulate on the catalyst surface and further inside the pores [75,76], causing the catalyst deactivation.

By this point, it is rather apparent that the Ni/γ-Al_2O_3 used in the Multi-BPR system with constant hydrogen flow and the steady operating condition is relatively more stable than that in the Gas-BPR that interrupted the hydrogen flow during the sampling and making pressure up steps. This implies that the contaminants in *Pongamia pinnata* oil have a considerable influence on catalytic activity by accumulating on the surface and reducing the active site. The impurities, particularly phosphorus, could cause coke formation by accelerating oligomerization and cause a reactor to be damaged by gum formation. It is worth noting that the catalyst deactivation was accelerated and the reaction became poor while the reactor system was operated in an unstable condition as the interrupted hydrogen flow.

4. Conclusion

The use of different BPRs could influence the characteristics of the hydrogen flow, and consequently affect catalytic activity and deactivation during the hydrotreating process, particularly when utilizing unpurified or crude plant oil as feedstock, such as *Pongamia pinnata* oil. Conversion and product yield were lower in the interrupted hydrogen flow system that resulted from the use of a single gas phase back pressure regulator (Gas-BPR) than in the constant hydrogen flow system that resulted from the use of a multiphase back pressure regulator (Multi-BPR). A decrease of liquid fuel yield was observed with prolonged reaction time, whereas complete conversion can be achieved in a constant hydrogen flow without deterioration at a certain period.

The carbonaceous deposited on the catalyst from the constant hydrogen flow system is mainly reactive coke, which is easily removed. Besides, in the interrupted hydrogen flow, the contaminants in *Pongamia pinnata* oil enhanced the catalyst deactivation. Phosphoric acid, in particular, decomposed from phospholipid, can function as a catalyst for an oligomerization, resulting in heavy hydrocarbon production and, eventually, gum formation, leading to reactor bed blockage. These could be attributed to the extremely high velocity of hydrogen supply, which shortens contact time and hence poorer hydrotreating efficiency. This event can further accelerate catalyst deactivation, resulting in a faster rate of catalyst deterioration.

As a result of our observations, we consider that using unpurified feedstock (*Pongamia pinnata* oil) necessitates a more stable operating system. In order to retain desired pressure and steady conditions, a flow reactor setup with multiphase BPR is recommended. However, both typical reactor configurations could effectively be performed when using purified plant oil as feedstock.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version,

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