Catalytic hydrotreating of bio-oil derived from *Chlorococcum* sp.

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**Abstract.** Hydrotreating of bio-oil derived from *Chlorococcum* sp. in the absence of NiMo/Al-SBA-15 catalysts has been investigated. The silica alumina supports decreased product yields (DCM solubles and hydrocarbon gases) due to severe coking. Incorporation of NiMo increased the product yields up to 65 wt.% and increased the proportion of products in the kerosene boiling point range (C₁₂-C₁₇). The superiority of the high acidity supports persisted after incorporation of NiMo.

**1. Introduction**

Issues related to limited availability of fossil fuels, an increase in oil price and emissions generated from fossil fuels have created an increased interest in renewable fuels. Bio-oil production from microalgae has therefore attracted an increasing proportion of the research in this area, particularly due to the many advantages of this biomass type, including high productivity and the ability to grow on marginal land [1]. It is essential to deploy a suitable upgrading method to improve the quality of the bio-crude derived from microalgae so that the upgraded oil will be environmentally and industrially safe and also useful as commercial fuel.

Mesoporous alumina-silicates, such as Al-SBA-15, have been widely used as catalysts [2,3] or supports [4-6] in many catalytic reactions. Compared to other mesoporous silicas, e.g. MCM-41 and HMS, SBA-15 has many potential advantages, such as higher surface area, larger pore volume, thicker pore walls and higher thermal stability [7]. Introduction of aluminium into the silica framework, especially by direct synthesis, increased the catalytic activity in the Fischer Tropsch synthesis due to the presence of acid sites [4]. While metals supported on Al-SBA-15 materials have been used in many catalytic reactions, there is a dearth of information on the use of this type of catalyst for hydrotreating of bio-oil derived from microalgae.

In this work, we report hydrotreating of bio-oil derived from single strain microalgae, *Chlorococcum* sp., catalysed by NiMo/Al-SBA-15 with different Si/Al ratios, investigating the effect of H₂ pressure and catalyst support acidity on product yields and product composition.
2. Materials and method

2.1. Materials
Biocrude oil was derived from Chlorella sp., a marine microalga provided by Biomax Australia. The preparation and the production of the bio-crude oil are described in our previous report[8]. The chemicals used in the study were the non-ionic block copolymer surfactant EO<sub>20</sub>-PO<sub>70</sub>-EO<sub>20</sub>, Pluronic P123, poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) and aluminium isopropoxide (Aldrich), hydrochloric acid (32%) (Ajax), tetraethyl orthosilicate (TEOS 98%) and ammonium fluoride (NH₄F 98%) (Sigma-Aldrich), NH₃·H₂O (Univar), nickel acetate (Sigma-Aldrich), ammonium heptamolybdate (Merck), N₂, H₂ and 10% NH₃/90% He (Air Liquide), liquid chromatography grade dichloromethane (DCM) and hexane (C₆H₁₄) (Merck). All chemicals were used without further purification.

2.2. Preparation of catalysts
Al-SBA-15 with different Si/Al molar ratios (10, 20) were synthesised using a modified hydrolysis-controlled approach as described in Li et al.[9]. Al-SBA-15 with different Si/Al ratios was doped with nickel (Ni) and molybdenum (Mo). The concentrations of Ni and Mo were chosen to be 2.4 and 10%, respectively. Ni and Mo were impregnated into Al-SBA-15 using the wet impregnation method. The resulting products were denoted NiMo/Al-SBA-15. The NiMo/Al-SBA-15 catalysts were characterised with Nitrogen adsorption/desorption analyser, ammonia-temperature programmed desorption, Raman spectroscopy, and inductively coupled plasma-atomic emission spectroscopy, and X-Ray diffraction.

2.3. Hydrotreating
Hydrotreating was carried out in 27 mL stainless steel autoclaves fitted with glass liners, to minimize any catalytic effect of the autoclave walls. For catalytic hydrotreating, ~1.0 g of bio-oil, 10 % catalyst (by weight of the bio-oil) and 3, 6, or 9 MPa (cold) H₂ were charged into the autoclave. The autoclaves were placed in a pre-heated fluidized sand bath, continuously agitated for 15 minutes at 425 °C, removed, allowed to cool and finally weighed.

The gas, solid and liquid products were worked up as described in Subagyono et al. [8]. During work up, a fraction of the DCM solubles was taken for further analyses. The lighter fraction (DCM soluble, hexane soluble) was defined to be oil and the heavier and more polar fraction (DCM soluble, hexane insoluble) was defined to be asphaltene. The product yield was defined as the total yield of oil, asphaltene, hydrocarbon (if any, and sulphide) gases, and CO₂. The reproducibility of the reactions is indicated by error bars given on figures; error bars were calculated from duplicate experiments. It is important to note that the large variation in the oil yields was due to the fact that the oil yield is obtained by difference, not by direct weighing. DCM soluble fractions were analyzed by gas chromatography–mass spectrometry (GC–MS) on a HP6890 instrument in splitless mode as described in Subagyono et al.[8].

3. Results and discussion

3.1. Characterisation of catalysts
The wide-angle XRD patterns of NiMo/Al-SBA-15 (Figure 1a) showed low intensity peaks due to orthorhombic MoO₃ at 2θ values of 23, 27 and 33°. The low intensity peaks observed indicated that Ni and Mo were mainly amorphous and hence, probably evenly dispersed[10]. The small-angle XRD patterns of Al-SBA-15 showed a high intensity peak and two well defined smaller peaks, corresponding to the (100), (110), and (200) planes, between 2θ values of 0.6–1.8° (Figure 1c). These three peaks similar to the SBA-15 structure with p6mm hexagonal symmetry [7]. After incorporation of Ni and Mo, the three peaks were still clearly resolved, indicating that the average structural order of the silica-alumina supports was retained (results not shown). The NH₃-TPD profiles of Al-SBA-15 (Si/Al=10) (Figure 1b) showed only one broad band peaking at 240-280 °C, indicating the presence of
weak to medium strength acid sites, probably due to the tetrahedrally coordinated aluminium. In the Raman spectrum of Al-SBA-15 (Si/Al=10) (Figure 1d), peaks observed at 289, 335, and 666 cm\(^{-1}\) were due to crystalline MoO\(_3\) [10]. A peak at 377 cm\(^{-1}\) was due to distorted surface polymolybdenum [11]. The presence of large clusters of MoO\(_3\) molecules was indicated by the appearance of the most prominent peak at 819 cm\(^{-1}\) [10, 11]. Furthermore, a medium intensity peak at 994 cm\(^{-1}\) was due to asymmetric vibrations of bridging Mo-O-Mo in polymolybdates [12].

![Raman spectrum of Al-SBA-15 (Si/Al=10) (Figure 1d)](image)

**Figure 1.** (a) Wide angle XRD spectrum of Al-SBA-15 (Si/Al=10) (* = trace of orthorhombic MoO\(_3\) (PDF card 00-005-0508); (b) NH\(_3\)-TPD profiles of Al-SBA-15 (Si/Al=10) obtained at different heating rates (c) low angle XRD spectrum of NiMo/Al-SBA-15 (Si/Al=20); d) average Raman spectrum of NiMo-Al/SBA-15, Si/Al =10

The BET surface area, pore volume and pore diameter (Table 1) (NiMo)/Al-SBA-15 were calculated from the N\(_2\) adsorption isotherms.

| Si/Al ratio | Measured Si/Al ratio\(^{a}\) | Measured %\(^{a, b}\) Ni | Measured %\(^{a, b}\) Mo | surface area\(^{c}\) (m\(^2\)/g) | Pore volume\(^{d}\) (cm\(^3\)/g) | Pore diameter\(^{d}\) (nm) |
|------------|----------------------------|-------------------------|-------------------------|-------------------------------|-----------------------------|-----------------------------|
| 10         | 10.6                       | -                       | -                       | 332                           | 1.34                        | 14.3                        |
| NiMo/10    | 2.5                        | 9.2                     | -                       | 230                           | 0.92                        | 14.3                        |
| 20         | 21.0                       | -                       | -                       | 449                           | 1.45                        | 11.3                        |
| NiMo/20    | 2.3                        | 8.9                     | -                       | 315                           | 1.04                        | 11.2                        |

\(^{a}\) determined by ICP-AES  
\(^{b}\) determined by EDS  
\(^{c}\) calculated by the BET method  
\(^{d}\) calculated by the BJH method from desorption branch of the nitrogen isotherm  
* the calculated/theoretical percentage of Ni= 2.5 and Mo=10.0

The BET surface area decreased with increasing aluminium content. The silica-alumina supports had a larger pore diameter (10-14 nm) and slightly higher pore volume (1.3-1.5 cm\(^3\) g\(^{-1}\)) than those
reported for Al-SBA-15 prepared by Li et al. and Shujie et al. [2, 9]. The larger pore diameter possibly resulted from the prolonged calcination (20 hours) necessary to completely remove the organic template and the high pore volume from formation of secondary mesoporous channels when aluminium was introduced into the silica framework by the direct-synthesis method [13]. The BET surface areas for the Al-SBA-15 materials were lower than those reported by other workers [2, 9]. This may be due to the larger pore volume of the Al-SBA-15 and not be due to the presence of non-framework aluminium in the pores [14]. After incorporation of Ni and Mo, the surface area and pore volume decreased, suggesting that Ni and Mo were incorporated inside the pore (and not just deposited on the particle surface). The ICP-AES results showed that Ni and Mo were successfully loaded into the Al-SBA-15 materials (Table 1).

3.2. Hydrotreating of bio-oil

Incorporation of NiMo into the supports decreased coking and product yields while generally increased oil, asphaltene and gas yields (Figure 2). The product yields and oil yields of reactions with NiMo/Al-SBA-15 with Si/Al=10 and 20 exceeded those of the non-catalysed reactions (results not shown). The results imply that Ni and especially Mo were catalytically active in hydrogenation reactions and therefore in reducing coke production. In the absence of catalyst, the major reactions were thermal cracking of high molecular weight components, but in the presence of catalyst, thermal and catalytic cracking both occurred.

In the presence of NiMo/Al-SBA-15, product yields and asphaltene yields increased with increasing pressure (Figure 3). The less acidic catalyst (Si/Al=20), however, reached its best performance at a H$_2$ pressure (cold) of 6 MPa; the yields fell when the H$_2$ pressure was increased to 9 MPa (cold) H$_2$.

The chromatograms of DCM solubles produced in the presence NiMo catalyst under different H$_2$ pressures were generally similar (Figure 4). The peaks due to heavy molecules, observed in the chromatogram of the bio-crude oil, disappeared when 9 MPa H$_2$ was introduced to the system. Peaks due to pentadecane, heptadecane and phytane were the most prominent in the chromatograms but peaks due to other hydrocarbons were also observed. The appearance of other hydrocarbon peaks and the higher product yields in the presence of NiMo catalyst than in the presence of only the supports suggested that NiMo helped to stabilise reaction products against repolymerisation, to increase decarboxylation of fatty acids or to hydrogenate high boiling point saturated compounds.
The degree of cracking, decarboxylation and thermal decomposition of the bio-oil was examined in the presence and in the absence of catalyst under different conditions. The total ion chromatograms were divided into three regions, 1. C_6-C_{11} (gasoline type, boiling point 70-200 °C); 2. C_{12}-C_{17} (kerosene type, boiling point 200-300 °C); and 3. C_{18} (heavy oil, boiling point 300-470 °C), and the total peak area of all compounds (not only hydrocarbons) in the three ranges were calculated. The estimated weight (EW) percent of each fraction in the DCM solubles (excluding hydrocarbon gas and CO_2) was then calculated (Figure 5).

![Figure 3. Product yields and oil, asphaltene and gas yields for hydrotreating of Chlorococcum sp. at 425 °C for 15 minutes as a function of H_2 pressure in the presence of NiMo-Al/SBA-15 catalysts](image)

![Figure 4. Chromatograms of bio-oil and DCM solubles produced by hydrotreating of Chlorococcum sp. for 15 minutes at 425 °C in the presence of NiMo-Al/SBA-15 (Si/Al=10)](image)
The EW values of C_{12-17} fractions for the supports were generally only slightly higher than or similar to, the EW values found in the absence of supports. Thus, the increase in proportion of the C_{12-17} in the bio-oil produced in the presence of supports may be due to repolymerisation and coking of the high boiling materials in the presence of supports, thus reducing the proportion of high boiling point material in the products, rather than to more cracking of the long chain hydrocarbons or decarboxylation of fatty acids. Recalling that incorporation of the supports alone tended to induce coking (Figure 2 and reduced product yield; the silica alumina supports themselves are perhaps responsible for coke formation due to polymerisation of dehydrogenated species including high boiling point materials. After incorporation of the NiMo catalyst, the EW of the kerosene range rose and those of the heavy oil fell. Furthermore, the increase in the percentage of the kerosene range was greatest when the hydrogen pressure was increased to 9 MPa, suggesting more effective hydrogenation.

![Graph showing weight percent (%) of DCM soluble fractions from hydrotreatings of the bio-oil derived from Chlorococcum sp. at 425 °C for 15 minutes under 3 MPa H₂ and 9 MPa H₂ (*) in the presence of NiMo-Al/SBA-15 catalysts.](image)

**Figure 5.** Estimated weight percent (%) of DCM soluble fractions from hydrotreatings of the bio-oil derived from Chlorococcum sp. at 425 °C for 15 minutes under 3 MPa H₂ and 9 MPa H₂ (*) in the presence of NiMo-Al/SBA-15 catalysts.

### 4. Conclusions

The Al-SBA-15 supports did not have any upgrading effect but higher acidity NiMo/Al-SBA-15 increased the overall yield of DCM solubles up to 65 wt.% db and greatly increased the proportion of product in the lower boiling point kerosene range, by stabilizing products against repolymerization and by promoting cracking and decarboxylation of fatty acids. Thus the catalyst synthesized as described is useful. However, the extent of coking of the upgraded oil remained too high, so that improvements in the upgrading approach would be required to obtain a practically useful fuel.

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