

ONE-POT ALGAE CONVERSION INTO SUSTAINABLE BIOFUEL BY CATALYTIC HYDROPROCESSING

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Abstract Microalgae have emerged as a promising feedstock for third generation biofuels. This study aims to investigate the reaction conditions for biodiesel production from microalgae. Microalgae were liquefied and transformed into a mixture of diesel like hydrocarbons using commercial bifunctional NiMo/ γ -Al₂O₃ catalyst. GC-MS analysis revealed that the produced bio-oils are a complex mixtures of partially or completely deoxygenated compounds. The most promising experiment using 25 wt% of catalyst at 350 °C of reaction temperature and 50 bar of initial hydrogen pressure yielded 22.6 wt% of liquid alkanes with the high selectivity towards pentadecane, hexadecane, heptadecane and octadecane.

Keywords:
adipic acid,
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dehydroxylation,
heterogeneous
catalysis,
rhenium

1 Introduction

Environmental problems along with the increasing energy demand, instable fuel prices and limited fossil fuel have led to the growing interest in renewable fuels. Expensive raw materials and consequently higher biodiesel price compared to petroleum fuels represent the main obstacle for general use of biofuels.

Microalgae have recently emerged as an attractive and suitable feedstock for biofuel production, mostly because of its high biomass productivity and photosynthetic efficiency. Furthermore, microalgae exhibit high growth rate and high accumulation capacity of lipids and fatty acids. Moreover, it can grow on waste, it does not require arable land of fresh water, hence it's not a threat to traditional agricultural goods. Low carbon footprint and GHG emissions make biofuel technology even more interesting (Bwapwa et al., 2017; Delrue et al., 2013). The advantage of having high tolerance to CO₂ makes microalgae a promising organism for CO₂ mitigation. (Moreira & Pires, 2016).

The algal biofuel technology has been the subject of numerous studies throughout the previous decade. The three principal bio-fuel pathways used for the biofuel production are pyrolysis, the lipid extraction and conversion into bio-diesel through transesterification and the hydrothermal liquefaction (HTL). The latter was developed to be the most practical one due to the algal high water content (Yang et al., 2016). In comparison to HTL, which can convert biomass with high moisture content (above 50% mass fraction), pyrolysis can decompose only dry organic matter (Hognon et al., 2015). Additional drying cause high electricity and heat consumption (Delrue et al., 2012).

HTL is a thermochemical process, where the biomass is transformed directly into liquid biocrude while using high pressures (10-25 MPa) and temperatures (280-370 °C) for 5-120 minutes (Xu et al., 2018). Due to the high oxygen and nitrogen concentrations in bio-crude and consequently poor product quality, further catalytic hydrotreatment is required (Yang et al., 2016). Additional treatment leads to the energy, time and cost prohibitive processes, which limits the options for general use. Since high pressure and temperature are already some of the major HTL drawbacks (Delrue et al., 2013), the improvement is necessary. In this study the one-pot algae

conversion into sustainable biofuel was carried out by catalytic hydroprocessing. The main goal was to combine liquefaction and hydrotreatment processes.

This study is a part of a bilateral research project in collaboration with the French Alternative Energies and Atomic Energy Commission (CEA). Microalgae cultivation, harvesting and lipid extraction was done by CEA. Our department at the National Institute of Chemistry carried out the hydrotreatment of microalgae oils.

2 Methods

The catalytic hydrotreatment of *Chlorella* microalgae was performed in a 300 mL cylindrical stainless steel slurry reactor equipped with a Rushton turbine impeller (Fig. 1). The reactor was filled with 120 mL of reaction mixture that contained 5 wt% of algae, the rest being dodecane. Commercially available NiMo/Al₂O₃ catalyst was used in this study. The catalyst mass was set to 25 wt% with respect to the initial mass of microalgae. The system was purged with nitrogen twice to ensure inert gaseous headspace and then pressurized with hydrogen to the desired pressure (Table 1). The reaction mixture was heated-up by increasing the temperature from room temperature with the heating ramp of 5 °C/min to the desired reaction temperature. The reaction conditions were maintained constant for 4 hours before rapid cooling down. Decompressed gas phase from the reactor was analyzed by micro-GC. Before opening, the reactor was purged with nitrogen. The reaction mixture was filtered. The solid samples collected from the filtration were washed three times with dodecane and once with hexane, then analyzed by Fourier transform infrared (FTIR) spectroscopy. The liquid samples collected from the filtration were analyzed by Gas Chromatography – Mass spectroscopy (GC-MS, Shimadzu Ultra 2010) and by FTIR.



Figure 1: 300 mL high-temperature and high-pressure reactor.

Source: own.

Table 1: Reaction conditions for each run in batch slurry reactor.

Run	Catalyst form	T ^a (°C)	P ^b (bar)	W _{cat} (wt%)
1	Sulf NiMo/ γ -Al ₂ O ₃	200	50 ^c	25
2	Sulf NiMo/ γ -Al ₂ O ₃	300	50 ^c	25
3	Sulf NiMo/ γ -Al ₂ O ₃	312	50 ^c	25
4	Sulf NiMo/ γ -Al ₂ O ₃	325	50 ^c	25
5	Sulf NiMo/ γ -Al ₂ O ₃	350	50 ^c	25
6	Sulf NiMo/ γ -Al ₂ O ₃	325	30 ^c	25
7	Sulf NiMo/ γ -Al ₂ O ₃	325	20 ^c	25
8	Sulf NiMo/ γ -Al ₂ O ₃	325	50 ^d	25
9	Sulf NiMo/ γ -Al ₂ O ₃	350	30 ^c	25
10	Sulf NiMo/ γ -Al ₂ O ₃	350	20 ^c	25
11	Ox NiMo/ γ -Al ₂ O ₃	325	50 ^c	25
12	Red NiMo/ γ -Al ₂ O ₃	325	50 ^c	25
13	/	325	50 ^c	0 ^e
14	/	325	50 ^c	0 ^f

^a Set temperature of plateau.

^b Initial pressure in reactor.

^c Hydrogen atmosphere.

^d Nitrogen atmosphere.

^e Blank – no catalyst

^f Blank – no algae and catalyst

3 Results

3.1 Liquid phase analysis

GC-MS analysis revealed that the produced bio-oils are a complex mixtures of partially or completely deoxygenated compounds. The most promising experiment using 25 wt% of catalyst at 350 °C of reaction temperature and 50 bar of initial hydrogen pressure yielded 22.6 wt% of liquid alkanes with respect to the initial mass of microalgae. The results showed high reaction selectivity towards pentadecane, hexadecane, heptadecane and octadecane. The chromatogram shown in Fig. 2 confirmed low oxygen and nitrogen content, where the main oxygen compound was nonadecanol. The removal of unwanted heteroatom compounds was reached by hydrodeoxygenation (HDO). Hydrogenation and hydrogenolysis reactions transform oxygen composed molecules into o-free hydrocarbon chains, which are suitable for the use as biofuel (Valencia et al., 2018).

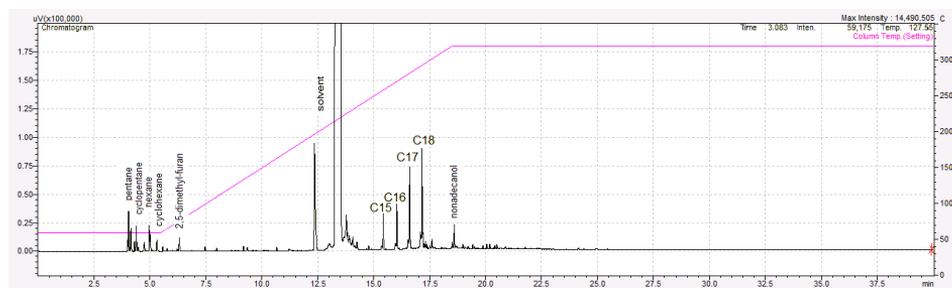


Figure 2: GC-MS chromatogram of produced biooil at optimal reaction conditions (350 °C and 50 bar of initial hydrogen pressure).

Source: own.

Higher temperature resulted in higher alkane concentration (up to 4,53 mg/ml) and higher yields (up to 22.6 wt%). The higher the hydrogen pressure, the more hydrogenation reactions of alkenes occurred. In addition, stricter reaction conditions (such as higher temperature and higher hydrogen pressure) resulted in lower mass residue, suggesting that the liquefaction was more intense.

$\text{NiMo}/\text{Al}_2\text{O}_3$ is being widely used as a commercial catalyst in petrochemical industry. Among the reduced, oxygenated and sulfided form, the latter was found to be the most promising, while the first two were much less active. GC-MS chromatogram of produced biooils using different catalyst form is presented in Fig. 3.

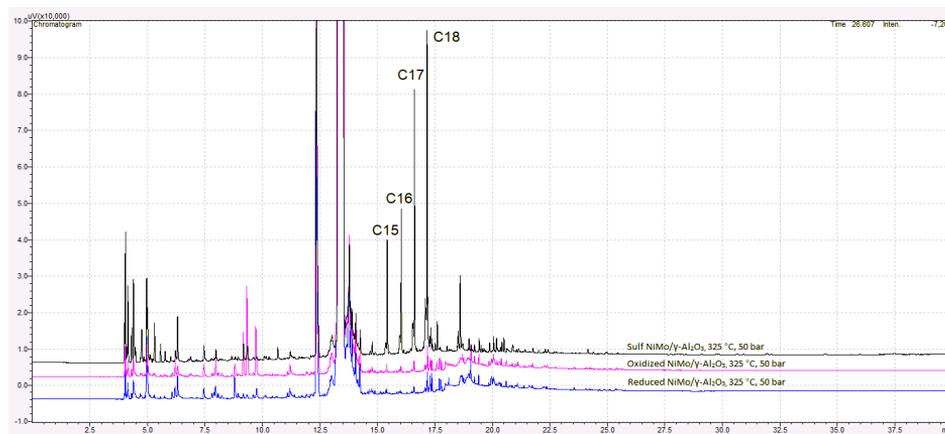


Figure 3: GC-MS chromatogram of produced biooils using reduced, oxygenated and sulfided catalyst form.

Source: own.

The FTIR spectra of liquid (Fig. 4) and solid samples were obtained in the range of $4500 - 400 \text{ cm}^{-1}$ for determining the functional groups present in the feedstock and the product. FTIR spectrum of liquid product match quite well with the spectrum of the dodecane, since the solvent represents a high proportion of the product. The major difference were two weak bands around 3700 cm^{-1} and 1070 cm^{-1} which are related to O—H stretching vibration.

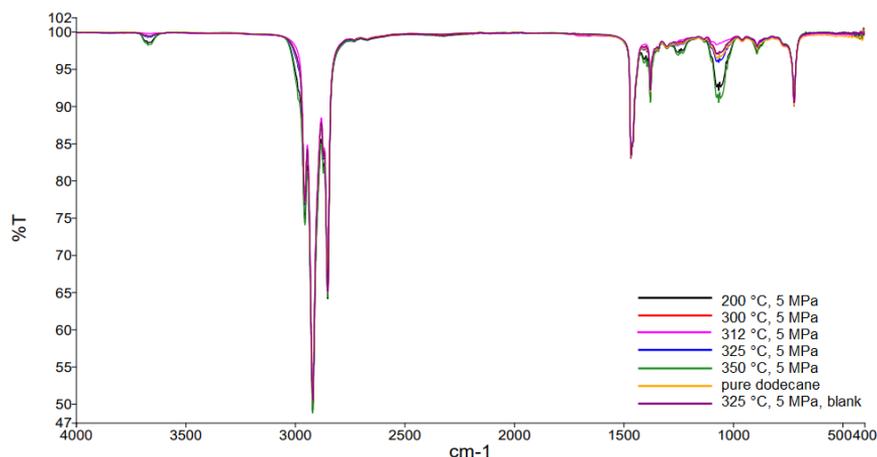


Figure 4: FTIR analysis results of produced biooils.

Source: own.

3.1 Gas phase analysis

Gas products were mostly composed of H₂O, CO, CO₂ and light hydrocarbons such as CH₄ and C₂H₆. Fatty acids under hydrogen pressure can undergo three main deoxygenation routes; hydrodeoxygenation, decarbonylation or decarboxylation. From the gas composition we can conclude that hydrodeoxygenation (removal of O atoms as H₂O) is more dominant deoxygenation pathway than decarbonylation and decarboxylation (DCO, removal of O atoms as CO and CO₂) (Arora et al., 2021; Soni et al., 2017; Yang et al., 2016).

4 Conclusion

Microalgae slurry was successfully processed in a cylindrical reactor at temperature of 300 – 350 °C, hydrogen pressure of 20 – 50 bar and reaction times of 4 hours. The catalytic hydroprocessing led to the conversion of microalgae into a complex mixture of diesel like hydrocarbons (C₁₄–C₁₈). The oil yields were higher (up to 22.6 wt%) at higher temperature and H₂ pressure.

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