

**Citation:** Yang, C., Li, R., Cui, C., Liu, S., Qiu, Q., Ding, Y., Wu, Y., and Zhang, B. (2016). Catalytic hydroprocessing of microalgae-derived biofuels: a review. *Green Chemistry*, 18(13), 3684-3699. DOI: 10.1039/c6gc01239f  
**Web:** [http://pubs.rsc.org/en/content/articlelanding/2016/gc/c6gc01239f/](http://pubs.rsc.org/en/content/articlelanding/2016/gc/c6gc01239f)

# Catalytic Hydroprocessing of Microalgae-Derived Biofuels: A Review

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## Abstract

The algal biofuel technology has been accelerated greatly during last decade. Microalgae can be processed into a broad spectrum of biofuel precursors, which mainly include crude algal oil recovered by extraction and bio-crude oils produced from hydrothermal liquefaction and pyrolysis processes. Due to the high protein content in algal species and the limitations of conversion technologies, these biofuel precursors require further catalytic removal of heteroatoms such as oxygen, nitrogen, and sulfur, being upgraded to biofuels like green diesel and aviation fuel.

This article reviews the state-of-the-art in hydroprocessing of microalgae-based biofuels, as well as the catalyst development and the effect of process parameters on hydrotreated algal fuels. Hydroprocessing of algal fuels is a new and challenging task, and still underdeveloped. For the long term, an ideal catalyst for this process should possess following characteristics: high activities towards deoxygenation and denitrogenation, strong resistance to poisons, minimized leaching problems and coke formation, and an economically sound preparation process.

**Keywords:** Microalgae-derived Biofuels; Hydroprocessing; Hydrodenitrogenation (HDN); Hydrodeoxygenation (HDO); Catalyst Development; Process Parameters

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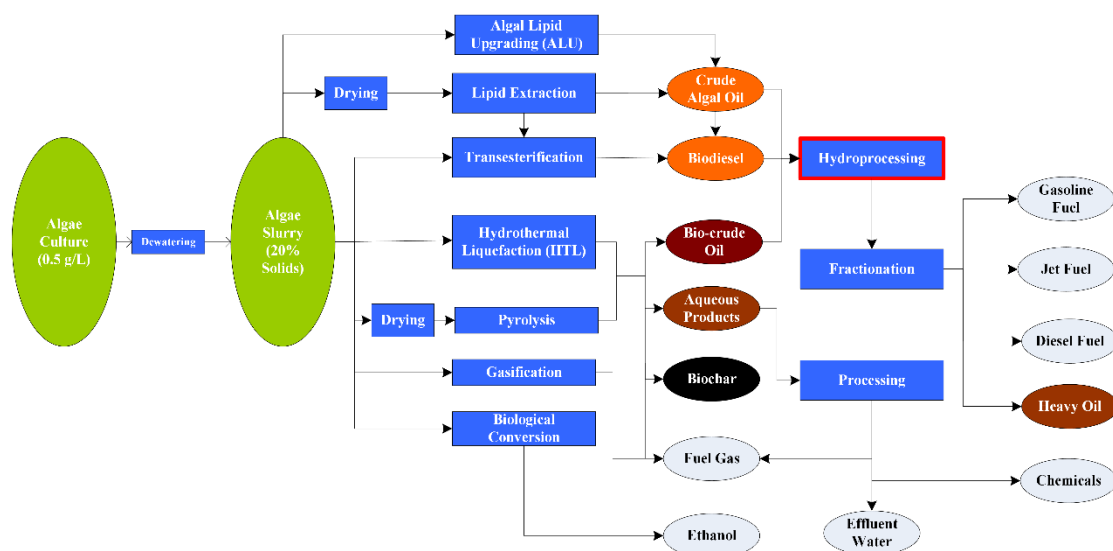
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## 1. Introduction

With growing concerns about declining fossil fuel supplies, environmental issues, and increasing demand of fossil fuels, renewable biofuels have received a large amount of research attention. While the first generation sugar or oil based biofuels (*i.e.* ethanol and biodiesel) cannot meet the requirement for fuel supply and caused a conflict between food and fuel production, the second generation advanced biofuels (such as cellulosic ethanol and cellulosic butanol) are still under-development and gradually entering market <sup>1</sup>. Recently, algae were considered as a promising third-generation biofuel feedstock due to their superior productivity, high oil content, and environmentally friendly nature <sup>2</sup>. Algae perform oxygenic photosynthesis like higher plants, representing a big variety of species living in a wide range of environmental conditions <sup>3</sup>. Algae are not traditional foods or feeds, and they can be cultivated in large open ponds or in closed photobioreactors located on non-arable land. Some algal species hold higher potential as the oil-producer than oil crops. Algae can sequester carbon (CO<sub>2</sub>) from many sources and may be processed into a broad spectrum of products including biodiesel, green diesel, gasoline replacements, bioethanol, methane, heat, bio-oil, fertilizer, high protein animal feed, etc. <sup>4</sup>

The algal technology for biofuels production has been greatly advanced over the past decade <sup>5</sup>. Experts from industry, academia, and national laboratories made invaluable contributions to its development from the biology to fuel conversion, reducing the cost of algae-based bio-crude from \$240 to \$7.50 per gallon <sup>6</sup>. However, in order to meet the long term goal of \$3/gasoline gallon equivalent, it still requires a combination of improvements in all key technologies including productivity, conversion, and processing <sup>7</sup>.

As shown in Figure 1, currently, there are three approaches that are used mainly for producing algae-based biofuels. The first technique involves extracting lipids from algal cells, which is followed by transesterification of triglycerides and alcohol into fatty acid alkyl esters (*i.e.* biodiesel) <sup>8</sup> or upgrading (*i.e.* algal lipid upgrading, also called ALU pathway) <sup>9</sup>. The second technique employs the hydrothermal liquefaction (HTL) process that produces water-insoluble bio-crude oil (simply called bio-oil) by using treatments at high pressure (5-20 MPa) and at the temperature range of 250-450°C <sup>10</sup>. Bio-oil produced after the water separation has lower water content and thus higher energy content than that produced directly by biomass pyrolysis. The third technique relies on the pyrolysis technology, which thermally degrades biomass at 300-700°C in the absence of oxygen, resulting in the production of bio-oils, solid residues, and gaseous products. The advantages of this technique include short process time, increased process yield, and environmental compatibility <sup>11, 12</sup>. Both pyrolysis and traditional lipid extraction might not be practical for algal biomass due to its high water content. The dehydration is energy prohibitive, which limits the options for algae as feedstock and overall process economy <sup>13, 14</sup>. Thus, the ALU process and the HTL process are chosen by U.S. Department of Energy (US DOE) as the two most promising approaches <sup>15-17</sup>.



**Figure 1.** Strategies for fuel production from algae

Other techniques for converting algae to biofuels include gasification (supercritical

water or steam) <sup>18, 19</sup> and biological conversion of sugar-rich algae <sup>20</sup>. The products from these two processes are hydrogen and ethanol, respectively. It will require extensive efforts prior to bringing up more research interests on these two processes. Usually, the choice of the conversion technology is dependent on the composition of available feedstock. For example, biological conversion is preferred for marine macroalgae with the high carbohydrate content <sup>20</sup>, while HTL uses the whole algae <sup>21</sup>, although their biochemical makeup has important effects on the yields and the product distribution <sup>22</sup>.

**Table 1.** Composition of microalgal biomass used for biofuel production

	Chlorella pyrenoidosa	Chlorella sorokiniana (DOE 1412)	Chlorella sp.	Microcystis sp.	Nannoch loropsis sp.	Nannoch loropsis sp.	Scene desmus	Spirulina platensis
Ultimate/Reference	23	24	25	26	24	25	27	28
C, %	49.6	50.2	44.93	42.26	51.9	49.07	50	46.16
H, %	7	6.8	6.42	6.27	7.5	7.59	7.11	7.14
N, %	8.2	9.8	6.41	7.88	4.8	6.29	7.25	10.56
S, %	0.5	0.68	1.57	0.52	0.61	1.42	0.54	0.74
O, %	25.4	24.3	40.67	43.07	22.4	35.63	30.7	35.44
Proximate								
moisture, %	10.4	74	4.13	9.59	79.6	5	4.59	4.54
volatile matter, %	81.2	n.r.	69.45	70.13	n.r.	79.69	75.33	79.14
fixed carbon, %	16.4	n.r.	16.22	14.14	n.r.	10.64	12.78	15.24
ash, %	9.3	2.5	10.2	6.14	7	5.03	7.3	6.56
Component								
protein, %	n.r.	44.6	42.7	59.93	14.3	44	36.4	48.36
polysaccharide, %	n.r.	10-16	9.42	20.19	n.r.	21	29.3	30.21
lipid, %	n.r.	10.7	2.5	5.22	21.7	30	19.5	13.3
HHV, MJ/kg	n.r.	n.r.	n.r.	16.2	n.r.	n.r.	21.1	20.52

n.r.: not reported by authors

The compositions of some representative algal species are listed in Table 1. According to ultimate analyses, the carbon contents of these algal species are approximately 50% of total dry weigh (TDW), and the hydrogen contents are around 7% of TDW. The nitrogen content, which is an indicator of the protein content, are between 4.8% and 10.6% of TDW. The sulfur content is relatively low, representing 0.5-1.5% of TDW. The volatile matter is products given off as gas or vapor by heating a material at a temperature of  $950 \pm 20^\circ\text{C}$ , while the fixed carbon is the solid combustible residue after heating. The analyses of these two characteristics are often applied to estimate the quality of solid fuel materials such as coal <sup>29</sup>. The volatile matter of algae listed is 69-81% of TDW, and the fixed carbon content is 10-16% of TDW. The protein, polysaccharide, and lipid contents highly depend on many factors, such as species, growth conditions, and growth phase. As shown in Table 1, the protein, polysaccharide, and lipid contents of these algal species are 14.3-60%, 9.4-30.2%, and 2.5-30% of TDW,

respectively.

Due to the limitations of aforementioned conversion technologies and the high protein content in algal species, the algal oil generated from the ALU process requires further catalytic processing to remove oxygen and other heteroatoms<sup>30</sup>, while the bio-oils produced via HTL and pyrolysis need to be upgraded to remove both nitrogen and oxygen. This article reviews hydroprocessing of algae-derived fuels including algal oil (lipids), algae-based biodiesel, and bio-oils produced from HTL and pyrolysis processes.

Obviously, large quantities of hydrogen are needed for hydroprocessing, which limits the application of this biofuel upgrading technology, unless economically viable hydrogen production processes are developed<sup>31</sup>. Currently, a significant number of technologies, including biogas reforming, biomass gasification, and bio-hydrogen from algae, have been explored to make hydrogen a less costly chemical<sup>32</sup>. These hydrogen production technologies use renewable feedstock, indirectly enhancing the economics of the hydroprocessing process.

The rest of this paper is structured as: In Section 2, an overview of algal biofuels produced via extraction, esterification, HTL, and pyrolysis is presented. Attention is given on the needs of hydrodenitrogenation and hydrodeoxygenation. Section 3 provides a thorough presentation of the current development of hydroprocessing of algal biofuels. In Section 4, the catalyst development for hydrodenitrogenation of algal fuels is analyzed. Section 5 summarizes the effect of process parameters on the hydroprocessing process. Section 6 concludes this paper.

## 2. Overview of Microalgae-Derived Fuels

### 2.1 Algal Oil Recovered by Extraction and Algae-Based Biodiesel

Algal lipid extraction has been investigated extensively for over two decades<sup>33</sup>, and techniques applied included the use of solvents (such as hexane and chloroform), mechanical approaches (like ultrasound and microwave), and/or chemical rupture. Advantages and disadvantages of these techniques have been reviewed by Ehimen *et al.*<sup>34</sup>. Alternatively, the algal lipid upgrading (ALU pathway) was developed by US nation laboratories<sup>15</sup>. This process selectively converts algal carbohydrates to ethanol and lipids to a renewable diesel blendstock, being considered as a promising conversion pathway.

However, because the low selectivity of extraction approaches, crude algal oil (*i.e.* algal lipids) often contains neutral lipids, polar lipids, chlorophyll a, and undetermined chemicals. For instance, the O, N, S, and P contents in a crude algal oil from *Nannochloropsis salina* were 12.06%, 0.43%, 2033 ppm, and 246 ppm, respectively<sup>35</sup>. Even after purification, heteroatoms (like N and S) carried in the polar heads of lipids might still exist, deactivating catalysts or shortening their life<sup>36</sup>.

In terms of algae-based biodiesel (*i.e.* fatty acid alkyl esters), transesterification of the algal oil extracted from dry biomass has been demonstrated<sup>37</sup>. Meanwhile, studies showed that traditional solvent-based lipid extraction and direct transesterification

techniques are inhibited when performed in the presence of a water phase<sup>34,38</sup>. In order to avoid drying algae and improve the transesterification efficiency, several methods including acid and base hydrolysis<sup>39</sup>, employing alternative solvents<sup>40</sup>, and super critical fluids<sup>41,42</sup>, have been developed to process wet algal biomass for oil extraction and/or in situ transesterification. Even though, most of these processes are still not considered economically feasible<sup>43</sup>.

Furthermore, biodiesel has a relatively high oxygen content, which makes it less stable, poorer flow property, less efficient than fossil fuels, and not suitable as high-grade fuels<sup>44</sup>. In order to improve the quality, biodiesel has been processed via catalytic hydrodeoxygenation or deoxygenation, and converted to “Green diesel” that is a mixture of hydrocarbons meeting the American (ASTM) or European (EN) diesel standard<sup>45</sup>.

## 2.2 Bio-Crude Oil via Hydrothermal Liquefaction

Algae are natural wet biomass. Algae harvest requires concentrating the algal cells from below 0.01-0.1 wt% to 20 wt% solid content in the slurry. Further drying algae will need more energy and make the process costlier. Hydrothermal liquefaction (HTL), which could directly process wet feedstock with no lipid-content restriction<sup>46</sup>, has received increasing attention and been considered as the favorable technology for producing algae-derived biofuels.

The HTL of biomass can be done by using the continuous plug flow reactor or the batch reactor. Typically, algal biomass were loaded into a reactor with or without additional water and catalysts, then pressurized with inert gases (*e.g.*, N<sub>2</sub> or He) or reducing gases (*e.g.*, H<sub>2</sub> or CO), and the reactor was heated to a certain temperature (250-374°C) and pressure (4-22 MPa) for 5-90 min to convert biomass to the bio-crude oil<sup>47</sup>. Bio-crude oils from algae consist of hydrocarbons and nitrogenated compounds, which might be co-refined in an existing fossil refinery to produce energy and chemicals. In 2012, the US DOE added HTL as one of the five major pathways for biomass conversion technologies<sup>48</sup>. The development of algal HTL technology has been extensively reviewed by Tian *et al.*<sup>46</sup>, López Barreiro *et al.*<sup>49</sup>, Amin<sup>50</sup>, and Guo *et al.*<sup>51</sup>.

The use of homogeneous and heterogeneous catalysts in HTL has been investigated, and showed positive effects on algal bio-oils. Direct utilization of catalysts in HTL did promote production of hydrocarbons and H<sub>2</sub>/CH<sub>4</sub> from algae<sup>52</sup>. After the HTL reaction, low molecular weight and more polar compounds stay mainly in the aqueous phase, and larger less-polar compounds locate to the oil<sup>53</sup>. However, algae are complex biomass containing high amount of protein (N) and other heteroatoms (S, P, K, Na, etc.), which makes it impossible for one-step catalytic HTL to generate desired products. Bio-crude oils of algae often have high molecular weight species and high viscosity, containing 5-18% O, 4-8% N, 0.2-1% S, and 3-30 ppm P<sup>17,47,54</sup>. Major compounds in the algal bio-oil that are identifiable via gas chromatography-mass spectrometry (GC-MS) are heterocyclic nitrogenates (pyrroles, indole, pyridines, pyrazines, imidazoles, and their derivatives)<sup>7</sup>, cyclic oxygenates (phenols and phenol derivatives with aliphatic side-chains), and cyclic nitrogen and oxygenated compounds

(pyrrolidinedione, piperidinedione, and pyrrolizinedione compounds) <sup>55</sup>. In addition, current heterogeneous catalysts for HTL are subject to low efficiency due to the absence of H<sub>2</sub> <sup>56</sup>, the presence of supercritical or hot compressed water, and deactivations due to other atoms. It seems that further hydroprocessing bio-crude oils and developing effective catalysts are urgently needed.

### 2.3 Bio-Oil via Pyrolysis

Pyrolysis requires the feedstock dried to a moisture content around 10 wt%, and is often not considered as a preferred conversion technology for algae. However, as one of the hottest biomass conversion technologies during last two decades, numerous pyrolysis studies were conducted on algae including *Botryococcus braunii* <sup>57</sup>, *Chlorella protothecoides* <sup>58</sup>, *Dunaliella tertiolecta* <sup>59</sup>, *Spirulina sp.*, *Chlorella vulgaris* <sup>60</sup>, *Nannochloropsis sp.* <sup>61</sup>, residues after lipid extraction <sup>59,62</sup>, and oleaginous algal species <sup>63</sup>. Recent developments of algal pyrolysis research have been reviewed by Marcilla *et al.* <sup>64</sup>, and Brennan and Owende <sup>65</sup>.

Pyrolysis of algae yields three streams of products (*i.e.* condensed liquid, gaseous products, and biochar). In most publications, this liquid is called bio-oil. Because a pyrolytic bio-oil normally contains 30-50% water, it will simultaneously form two layers of products: water phase and oily phase, which were called aqueous products (or water solubles) and bio-oil, respectively <sup>28</sup>. The product yields for bio-oil, water solubles, and gases are in ranges of 18-57.9%, 15-30%, and 10-60%, respectively <sup>64</sup>. The problems of algal pyrolytic bio-oils are similar to those of HTL oils and lignocellulosic biomass-based pyrolytic bio-oils. A comparison of properties of HTL and pyrolysis bio-oils is shown in Table 2. The high oxygen content in the pyrolytic bio-oil caused low vapor pressure, low heating value, and low thermal stability. In addition, because the high protein content in almost all algal species, the nitrogen content in pyrolytic bio-oil is somewhere between 5-13%. Thus, in order to apply algal bio-oils as the transportation fuel, it'll require reduction of both nitrogen and oxygen contents.

**Table 2.** Ultimate Analysis of HTL and Pyrolytic Bio-Crude Oils

Bio-oil source Ultimate	HTL			Pyrolysis			High Sulfur Diesel <sup>27</sup>	US DOE 2022 Objective* <sup>17</sup>
	Chlorella sp. <sup>66</sup>	Nannochloropsis sp. <sup>15</sup>	Spirulina <sup>67</sup>	Chlorella sp. <sup>25</sup>	Nannochloropsis sp. <sup>25</sup>	Spirulina platensis <sup>28</sup>		
C, %	68-72	77.32	68.3	73.2	80.2	67.52	85.9	86
H, %	8.9-9.4	10.52	8.3	9.61	6.2	9.82	12.98	14
N, %	6	4.89	6.9	9.25	6.2	10.71	0.57	<0.05
S, %	0.8	0.68	1.1	0.721	1.59	0.45	0.46	0
O, %	11.1-16.2	6.52	15.4	7.19	5.81	11.34	0.1	<1
H/C	1.55-1.57	1.63	1.46	1.57	0.928	1.73	1.813	1.95
O/C	0.11-0.18	0.06	0.17	0.07	0.05	0.13	<0.005	<0.009
HHV** (MJ/kg)	32.9-36.1	40.1	32	31.5	37.2	29.3	39.1	

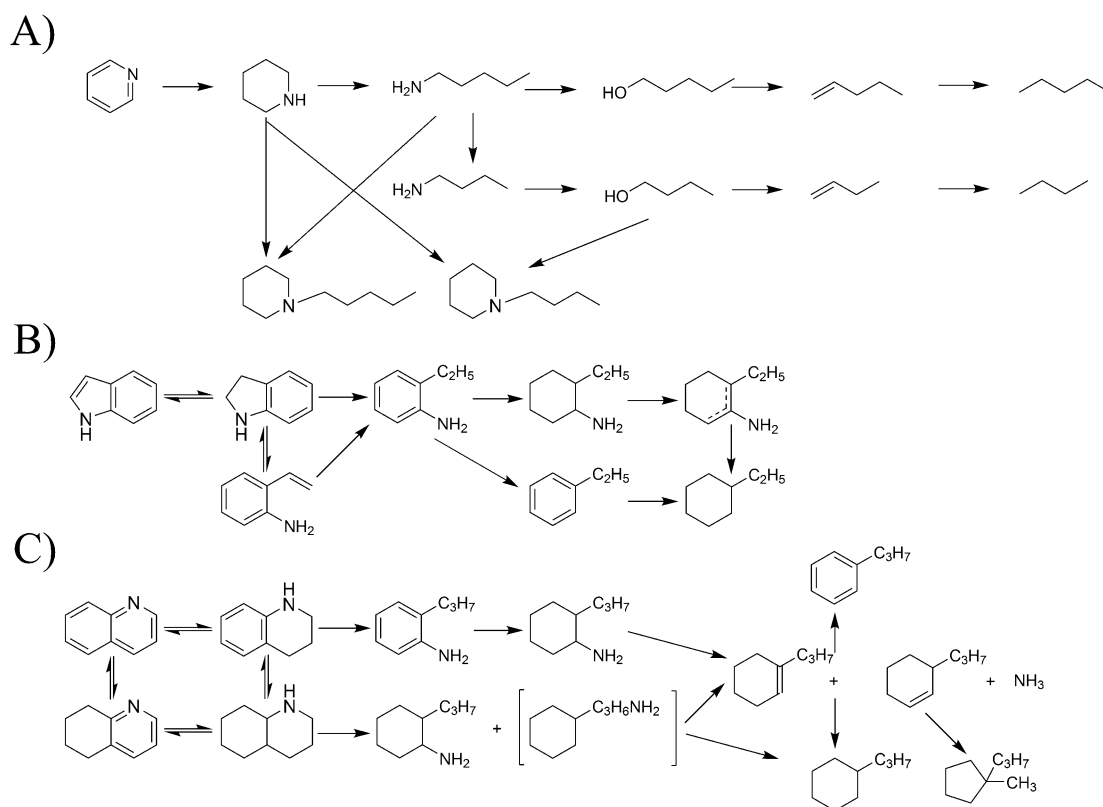
\* US DOE 2022 objective is the projected data, which was generated based on the experimental data and used as the input to the

modeled projection for 2022.

\*\* HHV: higher heating value

### 3. Algal Biofuel Production via Hydroprocessing

Algae-derived fuels require further catalytic processing to remove oxygen and/or nitrogen. Because of the low extent of sulfur present in algal biofuels, sulfur removal is often not an issue. During a hydrotreating process, sulfur is converted to hydrogen sulfide, and nitrogen is converted to ammonia<sup>68</sup>. These two processes are called hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), respectively. Due to the thermodynamics limitation of the aliphatic C-N bond hydrogenolysis reaction, HDN from heterocyclic compounds is a more difficult process than sulfur removal<sup>69</sup>. Mechanisms for HDN involve saturating intermediates, elimination, and nucleophilic substitution. An illustration of HDN processes of model nitrogenated chemicals including pyridine/piperidine, quinoline/tetrahydroquinoline, and indole/indoline is shown in Figure 2, which is re-illustrated according to<sup>70</sup> and<sup>71</sup>. Comprehensive reviews in HDN processes can be found at Ho<sup>71</sup> and Sánchez-Delgado<sup>72</sup>.



**Figure 2.** Possible reaction mechanisms of hydrodenitrogenation (HDN) for model chemicals: A) pyridine/piperidine, B) quinoline/tetrahydroquinoline, and C) indole/indoline (re-illustrated according to [70, 71])

Mechanisms for reducing the oxygen content in algae-based fuels include catalytic



cracking, hydrodeoxygenation (HDO), and decarboxylation/decarbonylation. Catalytic cracking does not require hydrogen, but the selectivity for certain hydrocarbons is low. Hydrodeoxygenation eliminates oxygen as water, while decarboxylation and decarbonylation remove oxygen to form CO<sub>2</sub> and CO, respectively. Three mechanisms might happen simultaneously in a single hydroprocessing reaction. The catalytic cracking process and catalysts including acids (Al<sub>2</sub>O<sub>3</sub>, AlCl<sub>3</sub>), alkalines (NaOH, MgO, CaO), zeolites (HZSM-5, HBEA, USY, SAPO5, SAPO11, MCM-41), etc., have been comprehensively reviewed by Zhao *et al.* <sup>73</sup>. Similar to HDN studies, there is a significant amount of HDO research that has been done with model compounds (such as guaiacol, phenol, sorbitol, vanillin, acetic acid, methyl heptonate, cresol, and eugenol) and vegetable oils. The work related to hydrotreating of model compounds has been systematically reviewed by Zhao *et al.* <sup>73</sup> and Arun *et al.* <sup>74</sup>.

### 3.1 Catalytic Hydrodeoxygenation of Extracted Algal Oil and Algae-Based Biodiesel

Many hydrotreating studies were conducted to upgrade crude algal oil, while few cases hydrotreated algae-based biodiesel. Because both algal oil and biodiesel normally don't contain too much sulfur and nitrogen, catalytic deoxygenation is an efficient method to upgrade them to green diesel that is also called renewable diesel.

Recent studies on hydrodeoxygenation of crude algal oils are summarized in the Table 3. When conducting deoxygenation of algal triglycerides with a noble metal catalyst of Pd/C, the Pd/C showed primarily decarbonylation activities, and exhibited stability within 200-h of continuous operation <sup>75</sup>. But noble metal catalysts were often considered costly and low selectivity <sup>76</sup>.

**Table 3** Studies on catalytic hydrodeoxygenation of crude algal oil

Microalgae provider or species	Catalysts	Experimental details	Key results	Ref
Phycal Inc.	Pd/C	Hydroprocessing was performed at 350°C and 5.5 MPa (800 psi) H <sub>2</sub> in a fixed bed reactor.	The Pd/C showed primarily decarbonylation activities, and exhibited stability within 200-h of continuous operation. Products were mainly C15-C18 alkanes.	75
Verfahrenstechnik Schwedt GmbH	Ni/ZrO <sub>2</sub> , Ni/TiO <sub>2</sub> , Ni/CeO <sub>2</sub> , Ni/Al <sub>2</sub> O <sub>3</sub> , and Ni/SiO <sub>2</sub>	The reaction was carried out at 260°C, 4 MPa H <sub>2</sub> , and 600 rpm for 8 h in an autoclave.	When applying Ni/ZrO <sub>2</sub> , a 76% yield of total liquid alkanes was attained, which is close to the theoretical yield. The major product was n-heptadecane (C17) with other minor hydrocarbons of C13–C21.	77
Verfahrenstechnik Schwedt GmbH	Ni/HBeta (Si/Al=180) and Ni/HZSM-5	Hydroprocessing was performed at 260°C and 4 MPa (580 psi) H <sub>2</sub> .	The hydrotreatment resulted in a 78 wt% yield of liquid alkanes with the high selectivity towards heptadecane (C17) and octadecane (C16).	78
Scenedesmus sp.	[Ni <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> ], Ni/Al <sub>2</sub> O <sub>3</sub> ,	The hydrotreating of the algal lipids (1.33% in dodecane)	The Ni-Al layered double hydroxide converted ~50% of algal lipids to	79

	Ni/ZrO <sub>2</sub> , and Ni/La-CeO <sub>2</sub>	was performed at 260°C or 300°C under a H <sub>2</sub> pressure of 4 MPa (580 psi).	hydrocarbons, showing better performance than rest catalysts.	
<i>Botryococcus braunii</i>	sulfided CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Hydrocracking was performed in a 6.5 m coiled stainless-steel tube reactor of 6.35 mm diameter at 400°C and 20 MPa (3000 psi) H <sub>2</sub> .	The upgraded algal oils can be fractionated into 67% gasoline, 15% jet fuels, 15% diesel, and 3% heavy oil.	80
<i>Nannochloropsis salina</i>	sulfided NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	The reaction was conducted in a continuous flow micro-reactor at 360°C and 3.45 MPa (500 psi) H <sub>2</sub>	Hydrodeoxygenation resulted in a nearly complete conversion (98.7%) of microalgal oil and a 56.2% yield of hydrocarbons with a range of C13-C20. After 7-h processing, the catalyst was deactivated due to accumulating oxygenated intermediates	35
<i>Nannochloropsis salina</i>	Pt/Al <sub>2</sub> O <sub>3</sub> , Rh/Al <sub>2</sub> O <sub>3</sub> , and presulfided NiMo/Al <sub>2</sub> O <sub>3</sub>	The hydrodeoxygenation was conducted in a continuous flow microreactor under various H <sub>2</sub> pressures (2-3.44 MPa) and temperatures (310-360°C).	The hydrocarbon yields were between 62.7-76.5%. The activity and selectivity of three catalysts were positively affected by increased reaction pressure, temperature, H <sub>2</sub> /Oil ratio and residence time.	81
Solix Biofuel, Inc.	Fe-MSN (mesoporous silica nanomaterials)	Hydrotreatment was conducted at 290°C and 3 MPa H <sub>2</sub> for 6 h.	Hydrotreatment gave 67% conversion, and the products were comprised of 16% alcohols, 33% unsaturated hydrocarbons, and 18% saturated hydrocarbons. The products were mainly C16 alcohol, c18:1 alkane, C20 alkanes, and other minor products with a range of C13-C20.	82

Most studies on non-noble metal-nickel (Ni) based catalysts were done by Dr. J.A. Lercher's group (Germany). A series of supports: ZrO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, were screened for deoxygenation of algal oil that mainly consists of neutral lipids. Among all catalysts studied, the Ni/ZrO<sub>2</sub> gave the highest alkane yield of 76%<sup>77</sup>, and it selectively cleaved C-C and C-O bonds in algal lipids. In another study by them, the crude algal oil was hydrotreated over Ni/HBeta with a Si/Al ratio of 180, resulting in a 78 wt% yield of liquid alkanes with the high selectivity towards heptadecane and octadecane<sup>78</sup>. The mechanism of this process was summarized as following: firstly double bonds in the alkyl chain were hydrogenated, and then fatty acids and propane were produced through the hydrogenolysis of saturated triglycerides, which was followed by hydrodeoxygenation of fatty acids to alkanes. When the particle size of Ni supported on HBEA zeolite was reduced from 5-18 nm to 3 nm, both initial reaction rates and the catalyst stability were enhanced<sup>83</sup>.

Another attempt on deoxygenating algal lipids over Ni catalysts was via decarboxylation/ decarbonylation mechanisms<sup>79</sup>. Four catalysts of

[Ni<sub>0.67</sub>Al<sub>0.33</sub>(OH)<sub>2</sub>][CO<sub>3</sub>]<sub>0.17</sub>·mH<sub>2</sub>O (layered double hydroxide - LDH), Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/ZrO<sub>2</sub>, and Ni/La-CeO<sub>2</sub> were applied to this hydrotreating process. The LDH catalyst was prepared via co-precipitation of Ni(NO<sub>3</sub>)<sub>2</sub>, Al<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>, NaOH, and Na<sub>2</sub>CO<sub>3</sub><sup>84</sup>; while others were prepared via excess wetness impregnation with Ni(NO<sub>3</sub>)<sub>2</sub>, followed by calcination and reduction. However, the hydrotreating conditions were not severe enough, the Ni-Al layered double hydroxide showed the best performance, converting only ~50% of algal lipids to hydrocarbons.

Molybdenum catalysts have been widely used for hydrodesulfurization of petroleum products for decades, and first application of the cobalt molybdate catalyst (HT 400E, Harshaw Chemical Co., US) on hydrocracking of algal lipids from *Botryococcus braunii* was reported in 1982<sup>80</sup>. The hydroprocessing was conducted under severe conditions (400°C and 20 MPa H<sub>2</sub>) and upgraded oils contained mostly gasoline (67%). But only until recent, the sulfided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was evaluated for hydrotreating algal oil extracted from *Nannochloropsis salina*<sup>35</sup>. This crude algal oil contained neutral lipids (>30 wt%), polar lipids, and undetermined natural substances. The hydrotreating experiments resulted in a nearly complete conversion of microalgal oil and a 56.2% yield of hydrocarbons with a range of C13-C20. But the activity of the sulfided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> only lasted for 7-h before deactivation due to coke formation. Compared with noble metal catalysts (Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub>), the NiMo bimetallic catalyst formed less coke and required less H<sub>2</sub> than noble metals<sup>81</sup>.

Iron is also an attractive candidate for this kind of conversion due to low cost, rich redox-chemistry, and high natural reserves. One study explored the possibility of using iron nanoparticles supported on mesoporous silica nanomaterials (Fe-MSN) in hydrotreating reactions<sup>82</sup>. The merit of the Fe-silica catalyst is the high selectivity for hydrodeoxygenation over cracking and decarbonylation. But the hydrotreatment over this Fe-silica catalyst only gave a 67% conversion, and the products contained a significant amount of alcohols (16%).

With regard to hydrogenation of biodiesel, most previous researches were conducted using vegetable oil or other feedstock based biodiesel<sup>85-87</sup>. Since the nature of different biodiesels is similar, their conclusions might be applicable to algae-based biodiesel. Recently, a report studied hydrogenation of algae-based biodiesel in dodecane over 5 wt% Pd/C and 5 wt% Ni/HY-80 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=80). Hydrotreating algal biodiesel was done at 300°C and 3 MPa H<sub>2</sub>. The performance of Ni/HY-80 was superior to Pd/C catalyst, giving a ~95% yield of hydrocarbons that mainly comprised octadecane, hexadecane, and heptadecane<sup>88</sup>.

### 3.2 Catalytic Hydroprocessing of Algal HTL Bio-Crude Oil

Developments in the field of catalytic hydroprocessing of cellulosic biomass-derived liquefaction bio-oil between 1980-2007 have been documented by Elliott<sup>89</sup>. Recent studies on hydroprocessing of algal HTL bio-oils are summarized in Table 4. Hydroprocessing of algae-derived fuels differs from upgrading lignocellulosic biomass-derived oils because of the importance of both deoxygenation and denitrogenation. Thus, an algal bio-oil upgrading process needs to fulfill following

purposes: oxygen and nitrogen removal, molecular weight reduction, minimizing hydrogen consumption, and avoiding saturation of the aromatic rings.

### 3.2.1 Hydroprocessing Bio-Oil with Molybdenum based and Noble Metal Catalysts

The work of hydroprocessing of the HTL bio-crude oil, led by Pacific Northwest National Laboratory (PNNL), examined allover material balances and upgraded fuel quality. Their hydroprocessing experiments were performed in a two-stage continuous system <sup>90</sup> by using sulfided CoMo/F-Al<sub>2</sub>O<sub>3</sub> (KF-1001, Akzo Chemicals Inc. <sup>91</sup>). A relatively high upgraded oil yield of 80-85% was obtained, and they concluded that this hydroprocessing process was effective for deoxygenation, denitrogenation, and desulfurization of the bio-oil from *Nannochloropsis* alga <sup>92</sup>. The oxygen, nitrogen, and sulfur contents in algal bio-oils were reduced to 1-2%, <0.5%, and <50 ppm, respectively. The products in the upgraded bio-oil fell primarily in the diesel range. The similar results were also confirmed for *Chlorella* alga, as the oxygen, nitrogen, and sulfur contents in algal bio-oils were reduced to 2.2%, <0.05%, and <50 ppm, respectively <sup>7</sup>. Further, the same process was applied to *Chlorella* grown heterotrophically, which had a lipid content of 57–64% and low nitrogen content of 0.5% <sup>93</sup>. After a hydrotreatment, the oxygen, nitrogen, and sulfur contents of this algal biofuel were reduced to 1.7%, <0.05%, and 18 ppm, respectively.

Concerning both the yield of treated HTL oil and the effects of HDO, HDN, and HDS, the results obtained by researchers at the PNNL are remarkably better than those of rest studies that are reviewed in following sections. The possible reasons are twofold: high availability of H<sub>2</sub>; and the reaction by-products (such as NH<sub>3</sub>, H<sub>2</sub>O, H<sub>2</sub>S, and cokes) were removed immediately from the continuous process, minimalizing their windows for reacting with hydrocarbons to form undesired products.

A similar work was done by scientists at the University of Leeds and the University of Illinois <sup>66</sup>, who hydroprocessed bio-crude oil from hydrothermal liquefaction of *Chlorella*. Both non-catalytic and catalytic hydroprocessing reduced nitrogen and oxygen contents in the upgraded oil, giving an oil yield between 41-94.8%. The treated oil can be fractionated into 25% gasoline, 50% diesel, and 25% heavy fuel oil. However, the lowest N content reached in this study was 2.4% by using NiMo/Al<sub>2</sub>O<sub>3</sub> at 405°C, so the catalytic function of catalysts towards hydrodenitrogenation needs to be further improved. Authors also pointed out the differences between their work and the PNNL study: 1) the higher O and N contents in the bio-crude (11-16% O and 6% N) compared to PNNL bio-oil (5-8% O and 4-5% N); and 2) hydroprocessing was conducted at the batch mode.

Some recent studies compared the catalytic effects of noble metals (like Pt and Ru) with transition metals (Ni, Mo, etc.) using various species of algae <sup>94, 95</sup>. Noble metals showed higher HDO activities than transition metals. But even the amount of Ru/C was increased to 30% of the total loading, the N content in upgraded oils was still higher than 2.4% of total oil <sup>95</sup>. In addition, the noble metals were often deactivated within a short period of time. The selection of the active metal for hydroprocessing bio-crude oil is discussed in the section 4.

**Table 4** Studies on catalytic hydroprocessing of algal HTL bio-crude oil

Microalgae provider or species	Catalysts	Experimental details	Key results	Ref
<i>Nannochloropsis</i>	sulfided CoMo/F-Al <sub>2</sub> O <sub>3</sub> (4% Co and 15% Mo)	Hydroprocessing was conducted in a bench-scale (412 mL), two-stage continuous system. The operation conditions for first and second stages were (125-170°C and 13.6 MPa) and (405°C and 13.6 MPa), respectively.	They obtained an upgraded oil yield of 80-85%. The products in the upgraded bio-oil that had a carbon number range of C6-C32 fell primarily in the diesel range (C14-C18).	92
<i>Chlorella</i>	sulfided CoMo/F-Al <sub>2</sub> O <sub>3</sub>	Same as the above	The oxygen, nitrogen, and sulfur contents in algal bio-oils were reduced to 2.2%, <0.05%, and <50 ppm, respectively.	7
<i>Chlorella</i> grown heterotrophically	sulfided CoMo/F-Al <sub>2</sub> O <sub>3</sub>	The bio-oil was upgraded at 400°C and 10.3 MPa (1500 psi) H <sub>2</sub> in a continuous system	Compared with the phototrophic culture, this alga produced twice amount of bio-oil and upgraded oil.	93
<i>Chlorella</i>	sulfided NiMo/Al <sub>2</sub> O <sub>3</sub> or CoMo/Al <sub>2</sub> O <sub>3</sub>	The hydroprocessing was operated at 350°C or 405°C under 6-6.6 MPa of initial H <sub>2</sub> pressure in a 500 ml Parr reactor.	The upgraded oil yield was between 41-94.8%. The treated oil contained alkane hydrocarbons ranging from C9 to C26, and can be fractionated into 25% gasoline, 50% diesel, and 25% heavy fuel oil.	66
<i>Scenedesmus sp.</i>	Pt/C, Ru/C, Ni/C, and Co/C	The experiments were carried out at 350°C under 6.9 MPa of initial H <sub>2</sub> pressure for 4 h in a 450 mL Parr reactor	Ru/C and Pt/C had the best efficiency in hydrogenation, and enhanced the production of octadecane and hexadecane.	94
<i>Spirulina platensis</i> , <i>Nannochloropsis sp.</i> , and a mixture of <i>Chlorella sorokiniana</i> , <i>Chlorella minutissima</i> , and <i>Scenedesmus bijuga</i> ,	Ru/C and sulfided CoMo/Al <sub>2</sub> O <sub>3</sub>	Hydrodeoxygenation was performed at 350°C under 5.17 MPa of H <sub>2</sub> pressure for 4 h in a batch reactor.	HDO reduced nitrogen heteroatoms in bio crude oil to 2.4.-3.1%.	95
<i>Nannochloropsis sp.</i>	Pt/C in the presence of water	The hydrotreating experiments were performed by adding certain amount of water in HTL bio-oils of <i>Nannochloropsis sp.</i> , which were followed by treatments in a 4 mL mini-	Pt/C resulted in an oil yield of 77% and 82% carbon recovery. However, the N and O contents in treated oils were still in ranges of 1.99-3.98% and 3.08-6.97%, respectively.	96

		reactor at 400°C and 3.4 MPa H <sub>2</sub> for 1-4 h.		
<i>Nannochloropsis sp.</i>	Pd/C	Same as the above	The use of Pd/C produced oils with 44 MJ/kg HHV and a yield of 79%. The most abundant alkane in the treated oil was pentadecane (C15) coexisting with others ranging from C8 to C32.	97
<i>Nannochloropsis sp.</i>	Pt/C, Mo <sub>2</sub> C, and HZSM-5	HTL oil upgrading was carried out in a stainless-steel mini batch reactor with 0.5 g of crude bio-oil, the desired amount of catalyst, and 0.4 ml water. Factors of temperature (330-530°C), time (2-6 h), catalyst types, and catalyst loading (5-20 wt%) were varied.	The reaction temperature was the most influential factor. The most abundant alkane in the treated oils was pentadecane (C15), and others alkanes ranging from C10 to C31 are also present.	98
<i>Chlorella pyrenoidosa</i>	Pt/γ-Al <sub>2</sub> O <sub>3</sub>	HTL oil upgrading was done in supercritical water (400°C) for 1 h, and H <sub>2</sub> or formic acid was used as the source of electrons.	Under supercritical water conditions, reactions caused an oil yield 60-70%. GC-MS showed the treated oil contained a series of n-alkanes starting at C11.	99
<i>Chlorella pyrenoidosa</i>	Pt/C, Pd/C, Ru/C, sulfided Pt/C, Pt/C(CO), Pt/C(n-C <sub>6</sub> H <sub>14</sub> ), Mo <sub>2</sub> C, MoS <sub>2</sub> , Al, sulfided CoMo/γ-Al <sub>2</sub> O <sub>3</sub> , Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> , HZSM-5, activated carbon, and Al/Ni	The hydrotreatment was done at 400°C and 6 MPa H <sub>2</sub> in a 58 mL reactor filled with 3 g bio-oil, 0.3 g catalyst, and 1.5 mL water.	The process showed upgraded oil yields of 53.1-77.2%. When using Ru/C with Raney Ni as the catalysts, the upgraded oil flows freely, and has 97 wt% of the material boiling below 400°C and a heating value of 45 MJ/kg.	100
<i>Chlorella pyrenoidosa</i>	A mixture of Ru/C with one of above mentioned catalysts	The hydrotreatment was performed at 400°C for 4 h in a batch reactor. For each run, 3 g bio-oil, 0.3 g catalyst (0.15 Ru/C and 0.15 g other catalyst), 1.5 mL water, and 6 MPa H <sub>2</sub> were loaded into the reactor.	Ru/C & Mo <sub>2</sub> C produced the highest oil yield of 77.2% and energy recovery. The treated bio-oil contained straight-chain alkanes ranged from C10 to C25, with pentadecane (C15), hexadecane (C16), and heptadecane (C17) as the three most abundant hydrocarbons.	23

### 3.2.2 Hydrotreating Bio-Oil in the Presence of Water

A series of studies on hydrotreating of bio-oil in supercritical water were conducted by Dr. P.E. Savage and his collaborators at the Henan Polytechnic University. The

motivation of their research is from a process engineering perspective, to take advantages of hydroprocessing HTL bio-oil in the same environment as HTL<sup>97</sup>. Their initial hydrotreating experiments were performed by adding certain amount of water in HTL bio-oils of *Nannochloropsis sp.*, which were followed by hydrotreatments with Pt/C<sup>96</sup> and Pd/C<sup>97</sup> catalysts. The use of Pd/C produced oil with 44 MJ/kg HHV and a yield of 79%, while Pt/C resulted in an oil yield of 77% and 82% carbon recovery. However, the N and O contents in treated oils were still in ranges of 1.99-3.98% and 3.08-6.97%, respectively. Further, they compared the functions of three catalysts: Pt/C, Mo<sub>2</sub>C, and HZSM-5, and concluded that reaction temperature was the most influential factor<sup>98</sup>. Among the catalysts studied, applying Mo<sub>2</sub>C at 530°C for 2 h showed the best deoxygenation performance, and using Pt/C at 530°C for 6 h resulted in the lowest N content of 1.5% in the treated oil.

Their recent research subject changed to HTL oils of *Chlorella pyrenoidosa*, which has a lower O content of 2.1-7.8% but higher N content of 7.8-8.0%. Treatment of this bio-oil was done with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, varying the source of electrons: H<sub>2</sub> or formic acid<sup>99</sup>. Although this research indicated that 0.025 g/cm<sup>3</sup> water density is the optimal condition for hydrotreating bio-oils, both deoxygenation and denitrogenation functions of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were not effective under supercritical water conditions.

Later on, fifteen hydrogenation catalysts including Pt/C, Pd/C, Ru/C, sulfided Pt/C, Pt/C(CO), Pt/C(n-C<sub>6</sub>H<sub>14</sub>), Mo<sub>2</sub>C, MoS<sub>2</sub>, Al, sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, HZSM-5, activated carbon, and Al/Ni were tested for upgrading HTL oils of *C. pyrenoidosa*<sup>100</sup>. The yields of upgraded oil fell in the range of 53.1-77.2%. Ru/C gave the best result for deoxygenation, and Al/Ni (Raney nickel) was shown to be a suitable catalyst for denitrogenation. Catalysts of Co-Mo/Al<sub>2</sub>O<sub>3</sub>, Mo<sub>2</sub>C, and MoS<sub>2</sub> performed poorly for deoxygenation in the presence of water, but remained high denitrogenation activity that is comparable to that of the noble metal catalysts.

In their recent work, a mixture of Ru/C with one of above mentioned catalysts was used. In respect of deoxygenation, denitrogenation, and desulfurization, Ru/C & Mo<sub>2</sub>C, Ru/C & Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, or Ru/C & Pt/C showed the best results, giving the O, N, and S contents of 0.1, 1.8, and 0.065 wt%, respectively<sup>23</sup>. Ru/C & Mo<sub>2</sub>C produced the highest oil yield of 77.2% and energy recovery. Although these experiments were performed in an engineering way, the results revealed some insights in hydrotreating reactions, indicating that catalytic synergy in bimetallic catalysts is worth further research. However, the N content of upgraded oils could not be reduced to less than 1.5% under supercritical water conditions according to their reports. Therefore, both the hydrotreating process and the catalyst will require further improvements.

### 3.3 Catalytic Hydrotreating of Algal Pyrolytic Bio-oil

As a separate unit operation, the study of hydrotreating always followed the waves of developments of algal research or conversion technologies. Even though there are an increased number of algal pyrolysis studies since 2009, up-to-date, only few articles reported hydrotreating of algal pyrolytic bio-oil. Zhong *et al.* studied hydrotreating of fast pyrolysis oil from *Chlorella* over a Ni-Co-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst<sup>101</sup>. Hydroprocessing

at 300°C and 2 MPa H<sub>2</sub> resulted in a refined oil yield of 89.6% and an 80.4% reduction of the oxygen content. The nitrogen content was reduced from 6.48% to 2.45%.

In another study, bimetallic Ni-Cu/ZrO<sub>2</sub> catalysts with various Cu/Ni ratios (0.14 to 1.00 w/w) were used for HDO of pyrolytic bio-oils of *Chlorella sp.* and *Nannochloropsis sp.* at 350°C and 2 MPa H<sub>2</sub><sup>25</sup>. Compared with Ni/ZrO<sub>2</sub> and sulfided NiMo/Al<sub>2</sub>O<sub>3</sub>, the addition of copper could facilitate the reduction of nickel oxide and limit sintering and coking, showing a higher HDO efficiency of 82%. But the denitrogenation activities of catalysts were not even considered.

## 4. Catalyst Development for Hydrodenitrogenation of Algal Bio-Oil

The crude algal oil produced from the ALU pathway has low S and N contents, so the traditional HDS catalysts might be effective enough to remove oxygen and improve its quality. A detailed review of the catalyst design strategies for hydrodeoxygenation can be found at Arun *et al.*<sup>74</sup>. For upgrading algal HTL and pyrolytic bio-oils, the catalysts have to be bifunctional, possessing both HDO and HDN activities. Until now, a limited number of catalysts have been investigated, and the results showed both promising possibilities and significant problems.

Most hydrogenation catalysts could denitrogenate the algal fuels to some extent, but the nitrogen content left in the hydrotreated oil was often between 1% and 4%. The residual nitrogen-containing compounds are in forms of pyrrole<sup>101</sup>, amides (like N,N-dimethylhexanamide, palmitamide, benzenamine), nitriles, quinolone<sup>96</sup>, and indole<sup>98</sup>. Although ASTM and EN standards do not regulate the minimal nitrogen content of current transportation fuels, US DOE's goal for the nitrogen content in upgraded algal fuels is less than 0.05% (500 ppm)<sup>17</sup>. In order to meet this goal, further development of highly selective catalysts for the C-N bond breakage is needed.

A significant number of HDN studies have been done with model chemicals. However, because the algal fuels are complex mixtures, the most active catalyst for HDN of model compounds might not show the highest catalytic activity for upgrading algal bio-oils<sup>100</sup>. Conversely, the use of model compounds is a logical way to investigate the possible mechanism of a catalyst that showed a high performance in hydroprocessing of algal fuels. In this section, the HDN studies on algal bio-oils and model chemicals were discussed together, which would give us new insights into the catalyst development strategy.

### 4.1 Molybdenum based Catalysts

The most active catalyst of sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> was identified for the HDN and HDO of algal bio-oils by researchers at the PNNL<sup>47</sup>. The hydroprocessing was conducted under relatively severe conditions in a continuous reactor. As the traditional HDS catalysts for petroleum, CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>, specifically sulfided form, have been widely studied for HDS and HDN of model chemicals. These catalysts exhibited higher HDS activity than HDN activity in competitive reactions between thiophene and pyridine<sup>102</sup>, and the presence of Co or Ni accelerated mainly the HDS reaction<sup>103</sup>. Because algal biofuels have low sulfur contents, the use of sulfided



catalysts will require the addition of external sulfur sources, *e.g.* hydrogen sulfide that was able to enhance denitrogenation and inhibit hydrogenation<sup>104</sup>. When applying the sulfided catalyst in the batch reactor, sulfur is removed through the sulfiding process as metal sulfides, poisoning catalysts<sup>105</sup>. In addition, sulfided catalysts have a poor hydrostability in the presence of water.

Instead of using sulfided CoMo or NiMo, unpromoted Mo<sup>103</sup>, Mo sulfides<sup>106</sup>, nitrides<sup>107</sup>, carbides, and phosphides<sup>108</sup> were proved to be more active in the HDN reactions of model compounds than sulfided CoMo and NiMo.

The Mo nitrides (Mo<sub>2</sub>N) showed as much as 5-10 times more activities for pyridine HDN than the sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> and MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>109</sup>, and the selectivity for C-N bond hydrogenolysis over C-C bond was higher for the nitride catalysts<sup>110</sup>. The bulk phase was predominantly  $\gamma$ -Mo<sub>2</sub>N with the surface consisting of either  $\beta$ -Mo<sub>16</sub>N<sub>7</sub> or mixtures of Mo and  $\beta$ -Mo<sub>16</sub>N<sub>7</sub>. The most active sites were located at the perimeters of raft-like domains, while lower activity sites were associated with the  $\gamma$ -Mo<sub>2</sub>N crystallite<sup>111</sup>.

The Mo carbides (Mo<sub>2</sub>C) were proven to have the similar catalytic properties for pyridine HDN to Mo nitrides<sup>112</sup>. HDN of pyridine over Mo carbides and Mo nitrides produced mostly cyclopentane and pentane, respectively. The selectivity difference between Mo carbides and Mo nitrides might be due to differing bonding geometries for pyridine on the Mo carbides and nitrides.

When MoP was tested for the catalytic activity in the HDN reaction of *o*-propylaniline, the intrinsic HDN activity of the surface Mo atoms was about 6 times higher than that of Mo edge atoms in MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub><sup>113</sup>, since the turnover numbers of them were  $13.6 \times 10^{-4}$  molecules (Mo center)<sup>-1</sup>s<sup>-1</sup> v.s.  $2.2 \times 10^{-4}$  molecules (Mo center)<sup>-1</sup>s<sup>-1</sup>, respectively.

Further modification of Mo<sub>2</sub>C, Mo<sub>2</sub>N, and MoP could improve their activities. Doping Mo<sub>2</sub>C with platinum (Mo<sub>2</sub>C-Pt) resulted in a higher HDN efficiency than Mo<sub>2</sub>C<sup>114</sup>; nickel promoted Mo nitrides (NiMoN<sub>x</sub> with Ni 5 wt% & MoN<sub>x</sub> 15 wt%, supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) were more active than Mo<sub>2</sub>N<sup>115</sup>; while addition of TiO<sub>2</sub> to MoP/MCM-41 enhanced the C-N bond cleavage, but inhibited the dehydrogenation function<sup>116</sup>.

Generally, the HDN activity of sulfided catalysts or Mo sulfides in the presence of sulfur sources is always superior to other Mo compounds. However, due to the high N content nature of algal fuels, Mo nitrides and carbides are more of interest to hydroprocessing of algae-derived biofuels. Since the catalytic performance of Mo nitrides and carbides relies on the surface and crystal structure<sup>117</sup>, future research attentions should be given to controlling crystal structure, surface modification, and selecting suitable promoters and supports.

## 4.2 Nobel Metal Catalysts

Noble metal catalysts (Ru, Pd, Rh, Ir, and Pt supported on carbon), specifically Ir and Pt sulfides, exhibited higher pyridine HDN activity than the sulfided molybdenum-based catalysts and can be used under milder conditions with high activity<sup>118</sup>. When hydrotreating algal HTL bio-crude, Pt/C and a mixture of Ru/C & Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed good HDN activities, reducing the N content in hydrotreated oil to 1.5-1.8 wt%<sup>23,97</sup>.

But the activities of noble metal catalysts were reduced fast during hydroprocessing algal bio-oils<sup>95</sup>, the use of noble metals as the only active metal may not be suitable.

Pt and Ru were often used to modify other metal catalysts, such as tungsten carbides<sup>119</sup>, Mo carbides<sup>114</sup>, Fe<sup>120</sup>, and CoMo<sup>121</sup>. The HDN activity over Pt or Ru modified catalysts was highly dependent on the amount of metallic sites introduced by them<sup>119</sup>.

Although, noble metal catalysts are the most reactive metals for the C-N bond cleavage, the cost and ease of deactivation are barriers for the process development. The use of these metals for doping might improve the HDN activity of bimetallic catalysts, as well as undergoing minimal hydrogenation reactions<sup>122</sup>

### 4.3 Other Transitional Metal Catalysts

Nickel is an attractive metal in hydrotreating because of its high activity and low cost<sup>123</sup>. Ni has been used to modify many other metallic catalysts (like Mo and Mo<sub>2</sub>N), and test results suggested that Ni-Mo species enhanced the hydrogenation of model chemicals like pyridine<sup>124</sup>. Catalytic hydroprocessing of algal bio-oil with Raney® Ni led to the lowest N content of 1.6 wt% in upgraded oil<sup>100</sup>. In addition, Ni phosphides exhibited supreme efficiencies in HDS and HDN of model compounds, which were 99% and 100%, respectively<sup>125</sup>.

As a relatively new hydrogenation catalyst, iron (Fe) is considered as a low cost, environmentally friendly, and sustainable material. However, the use of Fe as the only active metal for HDN of algal oil resulted in a low conversion ratio and produced a significant amount of alcohols<sup>82</sup>. Instead, Fe doped Mo, tungsten (W)<sup>126</sup>, and vanadium (V)<sup>127</sup> sulfides were reported to give an unusual high HDN effect.

Tungsten carbides and phosphides were often used as HDN catalysts. One study compared HDN of carbazole over W<sub>2</sub>C with Mo<sub>2</sub>C. The results indicated that W<sub>2</sub>C possessed higher hydrogenation activity but lower total activity<sup>128</sup>. Tungsten phosphides were more extensively studied for their HDN behaviors<sup>129</sup>. Bulk WP and WP/SiO<sub>2</sub> were found to be more active in HDN than W<sub>2</sub>C, W<sub>2</sub>N, WS<sub>2</sub>, and Ni-Mo-S/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>130</sup>.

Transition metal phosphides, such as WP, Ni<sub>2</sub>P, CoP, MoP, and Fe<sub>2</sub>P, emerged recently as an attractive group of hydroprocessing catalysts, which have excellent activity for HDS and HDN<sup>131, 132</sup>. Study showed that their catalytic activities for dibenzothiophene HDS and quinoline HDN followed the order: Ni<sub>2</sub>P > WP > MoP > CoP > Fe<sub>2</sub>P. The crystal structure of metal phosphides is built with blocks of trigonal prisms, which can well accommodate the large phosphorus atoms, leading to a more isotropic crystal morphology and potentially better exposure of surface metal atoms to fluid phase reactants<sup>133</sup>. Furthermore, they show good heat and electricity conductivities, and high thermal and chemical stability<sup>134</sup>. However, the deactivation of metal phosphides in the presence of water<sup>135</sup> and deficiency of P<sup>125</sup> was observed. Because HTL and pyrolytic bio-oils might contain a higher amount of water and low phosphorus, metal phosphides have less advantages in this application than metal carbides and metal nitrates.

#### 4.4 Effects of Supports

The catalyst support is the vehicle of active constituents, and affects the chemical and physical properties of the catalyst, the degree of dispersion of active components, and the stability. Catalyst supports also need to provide the certain reactants with high surface area and suitable pore size. Currently,  $\text{Al}_2\text{O}_3$  was most widely used as the support in traditional hydroprocessing catalysts, and studied for its effects on HDN reactions. For instance, the alumina-supported molybdenum nitride ( $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ ) catalyst was extremely active in the hydrodenitrogenation of carbazole, compared to the sulfided and reduced catalysts<sup>136</sup>. The result indicated that the C-N hydrogenolysis occurred on partially hydrogenated carbazole, suggesting the possibility of reducing hydrogen consumption. A modification of the alumina support with borate ions could increase the amount of acidity centers (or the acidity) of NiMo catalyst, leading to an increased resistance to coking<sup>137</sup>. However, it's generally accepted that the  $\text{Al}_2\text{O}_3$  was not stable in the presence of large amount of water due to the formation of hydrated boehmite<sup>138, 139</sup>, and its acid sites could result in carbon deposition<sup>140</sup>.

Compared with the  $\text{Al}_2\text{O}_3$  support, carbon supports showed better ability in water-resistance and anti-coking. Hydroprocessing of pyridine over carbon-supported NiMo sulfide formed less undesired products than Al-supported CoMo and NiMo catalysts<sup>103</sup>. When the mesoporous carbon black support was employed to support Mo carbides, the  $\beta\text{-Mo}_2\text{C}$  hexagonal compact crystallographic phase was obtained as the unique active phase, improving HDN of indole<sup>141</sup>. The carbon-supported catalysts also showed high resistance to poisoning<sup>142</sup>, and high hydrodenitrogenation activity/selectivity<sup>143</sup>.

Silica (*e.g.* MCM-41<sup>116</sup>, SBA-15<sup>86, 144</sup>) materials are of interests because of their moderate acidity, high surface area, large pore size, and highly ordered structures. For example, the  $\text{SiO}_2$  supported Mo or W phosphides showed superior HDN but lower HDS activity compared to the sulfides<sup>145</sup>. In addition, silica-alumina<sup>146, 147</sup>,  $\text{TiO}_2$ <sup>148</sup>,  $\text{ZrO}_2$ <sup>149</sup>, and  $\text{CeO}_2\text{-ZrO}_2$ <sup>150</sup> were also tested as supports in hydrotreating catalysts.

To summarize this subsection, a good HDN catalyst support should improve allover thermal and chemical stability and the dispersity of active components, tailor surface chemistry (for example, the HDN performance was related to the Brønsted acidity of some catalysts<sup>147, 151</sup>), and promote the formation of the highly active crystal structure.

#### 4.5 Catalyst Suppliers

Hydroprocessing of algal fuels is a new and very challenging task. Most studies were conducted by using commercial available catalysts. Table 5 gives a list of catalyst suppliers, whose catalysts have been used for hydrotreating algal fuels. The catalysts used for hydroprocessing lignocellulosic bio-oils and their suppliers can be found in<sup>89</sup>.

**Table 5.** Catalyst Suppliers

Company name	Catalysts used by researchers	Company web address	Reference
Sigma-Aldrich	Pt/C, Pd/C, Ru/C, Mo <sub>2</sub> C, MoS <sub>2</sub> , Al, Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> , HZSM-5, Al/Ni, and activated carbon	sigmaaldrich.com	98, 100
Zeolyst International	Zeolite Beta, ZSM-5, Zeolite Y	zeolyst.com	98
Akzo Chemicals Inc.	KF-1001	akzonobel.com	91
Alfa Aesar	CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	alfa.com	100
Johnson Matthey (London, UK)	CoMo/Al <sub>2</sub> O <sub>3</sub> and NiMo/Al <sub>2</sub> O <sub>3</sub>	matthey.com	66
Qilu petrochemical catalyst plant (China)	NiMo/Al <sub>2</sub> O <sub>3</sub>	qpec.cn	25

## 5. Effect of Process Parameters on Hydroprocessing

The ultimate goal of hydroprocessing of algal biofuels is to synthesize drop-in fuels: automobile fuels (gasoline and diesel) and aviation turbine fuels<sup>152</sup>. These fuels are a mixture of different hydrocarbons: The hydrocarbons of gasoline contain typically 4-12 carbon atoms; diesel contains between 12 and 20 carbon atoms per molecule<sup>153</sup>; and the jet fuel has a carbon number distribution between about 8 and 16<sup>154</sup>. Besides the catalyst, the parameters of a hydroprocessing process include the reactor configuration, reaction temperature, initial H<sub>2</sub> pressure, residence time, and etc. These parameters are important to the overall effectiveness of hydrogenation and the product distribution.

### 5.1 Crude Extracted Algal Oil

Normally, laboratory experiments were performed at the batch mode in either a tubular reactor or a high pressure reactor, like autoclaves and Parr reactors<sup>155</sup>. In one case, the algal oil was treated sequentially in a two-reactor system with Pt/C and Pd/US-Y zeolite, respectively, giving a 95% yield of alkanes<sup>75</sup>. The advantages of using two-stage reactors are that each reactor could be operated under different optimal conditions for different catalysts, thus potentially giving a higher hydrocarbon yield.

In terms of reaction time, most experiments were conducted for 6-8 h, and then the catalysts were deactivated due to coking. Only one report showed that when Pd/C was used as the catalyst, their operation could last for 200-h if the algal oil was charged at the rate of 0.177 mL/min<sup>75</sup>. The long catalyst life in this study might be due to the continuous operation mode, the use of two-stage reactors, and/or the catalyst support of carbon.

Compared with other parameters, the product distribution is more likely determined by the reaction temperature and the amount of initial H<sub>2</sub> (*i.e.* the severity of

reaction conditions). Most hydroprocessing processes, which were conducted between 260-360°C with an initial H<sub>2</sub> pressure of 2-5.5 MPa, successfully upgraded the algal lipids to the diesel range (C13-C20). The major alkanes in treated oil have a carbon number range of C15-C18. When a more severe condition of (400°C and 20 MPa H<sub>2</sub>) was applied, the hydrocracking process was able to convert the algal lipids mainly to gasoline (C4-C12), representing 67% of total hydrocarbons<sup>80</sup>.

## 5.2 Bio-Oil

Some successful hydroprocessing experiments for upgrading bio-crude oils were conducted in a two-stage continuous system<sup>90</sup>. Both the continuous operation and the two-stage treatment are important to the quality of the upgraded oil. For example, if the batch reactors were used for the two-stage configuration, the N content of treated oils was still above 2.4%<sup>95</sup>.

Hydroprocessing of bio-oils was often performed for less than 24 h, and the life of catalysts has not been studied systematically. The typical treatment temperature was 350-405°C, while the initial H<sub>2</sub> pressure was around 6 MPa. In order to achieve a good performance, a 10 MPa initial H<sub>2</sub> pressure may be necessary<sup>92, 93</sup>. Most studies were able to obtain the upgraded oil with a carbon number distribution mainly in the diesel range (C14-C18), representing 50-85% of total hydrocarbons<sup>156</sup>.

## 6. Summary

The algal biofuel technology has been accelerated during last decade, especially since 2010. However, in order to commercialize algae-based biofuels, it still requires extensive efforts. The purpose of this review is to bring more research interests, engineers, and catalysis scientists into this field via summarizing and criticizing the state-of-the art in hydroprocessing of algae-based biofuels or biofuel precursors.

From a prospect of the process development, the continuous operation is highly recommended, which might minimize the window that by-products react with the upgraded oil. If it's possible, the multi-stage continuous system is preferred, because each reactor will be operated under different optimal conditions and/or different catalysts. The typical reaction conditions for hydroprocessing of crude algal oil and bio-crude oil are (260-360°C & 3-20 MPa H<sub>2</sub>) and (350-405°C & 6-13.6 MPa H<sub>2</sub>), respectively. To obtain better HDO and HDN results, a higher initial H<sub>2</sub> pressure (*i.e.* the availability of H<sub>2</sub>) is expected.

From the point of view of catalyst development, the traditional HDS catalysts could be efficient enough for deoxygenation of crude algal oils that have low sulfur and nitrogen contents. Meanwhile, an ideal catalyst for hydroprocessing of algal bio-oils should possess high activities towards both denitrogenation and deoxygenation. According to Pacific Northwest National Laboratory's reports, the presulfided catalyst of CoMo supported on fluorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was suggested to be the best candidate for this process, if a continuous operation can be applied. However, the function of this catalyst was only confirmed in a limited number of applications, and it did not show

the same efficiency in the batch reactor. Accordingly, the door is still open to catalysis scientists who are interested in developing effective and cost-effective catalysts.

Up to date, it's shown that bimetallic catalysts could be a promising choice to fulfill the requirement for upgrading algal bio-oils that contain a high amount of nitrogenated chemicals. The active metals of tungsten carbide (WC), molybdenum carbide (Mo<sub>2</sub>C), and molybdenum nitride (MoN) are recommended, while the noble/transition metals of Ru, Pt, Ni, Co, Fe, and Cu could be used to modify the active metal. Because the bio-oil contains 5-10% moisture and hydrotreatment will produce water as a by-product, the supporting material of the catalysts should be more water-resistance. Therefore, the materials, such as carbon, modified Al<sub>2</sub>O<sub>3</sub>, and modified silica, are of interest.

For the long term, following issues shall to be considered: 1) The study on reaction mechanism using model compounds is essential to reveal the catalysis pathway. 2) The expected catalyst life is 2 years. Meanwhile catalysts need to tolerate poisons (such as sulfur, phosphorus, and water), and minimize leaching problems and coke formation. 3) The economics for preparing catalysts are important, so the cost of active metals and regeneration protocols are import factors.

## Acknowledgments

We are grateful for the support from the School of Chemical Engineering and Pharmacy at Wuhan Institute of Technology.

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