Review

Catalyzed hydrothermal treatment of oily sludge: A review

Jie Zhang[1,*], Lingling Zhang[2], Hulin Li[2], Xinyue Tian[2], Rongpu Huang[2], Jinling Lu[2]

[1] Shaanxi Key Laboratory of New Transportation Energy and Automotive Energy Saving, Chang'an University, Xi'an 710064, Shaanxi Province, China

[2] State Key Laboratory of Eco-hydraulics in Northwest Arid Region of China, Xi'an University of Technology, Xi'an 710048, Shaanxi Province, China

* Corresponding author: Jie Zhang, jiezhang28@chd.edu.cn

Abstract: Oily sludge is a common by-product of the petroleum exploration industry, which is rich in resources and has strong toxicity. It is categorized as hazardous waste in many nations worldwide. Owing to the distinct physical and chemical characteristics of sub/supercritical water, the application of hydrothermal conversion technology, which uses sub/supercritical water as a medium, has been growing in the utilization of resources and the safe disposal of oily sludge. In this article, the research on the oxygen-free hydrothermal transformation of oil sludge, including hydrothermal carbonization, hydrothermal liquefaction, hydrothermal upgrading, and supercritical water gasification, is reviewed. Due to the significant impact of nitrogenous and sulfurous compounds in sludge on hydrothermal conversion products, the hydrogenation conversion, reaction path, and kinetics for these two compounds were discussed. Finally, a summary and comparison of the studies conducted on carriers and catalysts in hydrothermal processes are provided. This review can offer recommendations for future studies, as well as guidance for the hydrothermal catalytic treatment of oily sludge.

Keywords: oily sludge; hydrothermal; sub/supercritical water; catalyst

1. Introduction

As a common by-product in the processes of mining, storage, transportation, and refining [1] in the petroleum industry, oily sludge has the dual characteristics of petroleum resources and hazardous waste. According to different sources, the oily sludge produced is mainly divided into four categories: oilfield oily sludge (OOS), storage and transportation oily sludge (STOS), refinery oily sludge (ROS), and accident oily sludge (AOS). Crude oil tank bottom sludge is the most widely studied oily sludge in the literature. Before being refined into petroleum products, crude oil is temporarily stored in storage tanks, where it will be separated into heavier and lighter petroleum hydrocarbons (PHCs). Heavy petroleum hydrocarbons often settle with solid particles and water. This mixture of oil, solids, and water deposited at the bottom of the tank is called oily sludge. Generally speaking, the higher the refining capacity, the greater the output of oily sludge. According to statistics, each ton of oily sludge can produce about 0.15–0.5 tons of crude oil, and the quality of the crude oil recovered from oily sludge is generally higher than that of biodiesel extracted from renewable biomass. In China, according to the statistics of relevant enterprises, the annual output of oily sludge exceeds 6 million tons, and the total historical inventory reaches 143 million tons [2]. Therefore, it can be predicted that the output of oily sludge will continue to increase.

It is estimated that in 2020, imports accounted for 73.5% of China's crude oil consumption [3]. Thus, using oily sludge as a resource is feasible in China. However, oily sludge is regarded as a hazardous waste, since it contains dangerous and poisonous materials, such as dioxins, benzene, phenol, heavy metals, anthracene, pyrene, polychlorinated biphenyls, etc. [4]. As a result, if oily sludge is not updated, it will not only result in a significant loss of oil resources but also pose a substantial risk to residents' safety and quality of life.

Excessive petroleum hydrocarbons in oily sludge will reduce the activity of various beneficial soil enzymes and soil microorganisms, thus hindering seed germination and limiting crop growth [5]. Polycyclic aromatic hydrocarbons (PAHs) are one of the most threatening components of hydrocarbons contained in oily sludge. Due to their genotoxicity to humans and other organisms, PAHs can cause lesions in organs, such as the kidney and liver, and lead to the occurrence of cancer when they are transmitted into the human body through the food chain [6]. In addition, oily sludge also contains a variety of heavy metals, and the comprehensive impact of PAHs and heavy metals is greater than that of PAHs [7]. PAHs and heavy metals that migrate into the water through the soil will further expand pollution, resulting in a reduction in the diversity and abundance of fish in the aquatic system. It causes irreversible harm to soil, water, and the human body. Moreover, volatile organic compounds contained in oily sludge will pollute the surrounding air, make the total hydrocarbon concentration exceed the standard, and further endanger human health [8]. Therefore, oily sludge is classified as hazardous waste by the Ministry of Environmental Protection of the People's Republic of China [9], the United States Environmental Protection Agency [10], and other countries [11]. Due to the harm of oily sludge and the continuous increase in its output, its effective treatment has become a worldwide problem.

Generally, oily sludge with an oil concentration higher than 50% and a solid concentration lower than 30% is easier to recover. However, some studies have shown that even if the oil content of oily sludge is relatively low (>10%), it is still worthy of quality improvement and recovery. Traditional treatment methods, such as pyrolysis [12], incineration [13], and solvent extraction [14], have been widely used to treat oily sludge and recover oil or natural gas. Pyrolysis and incineration can effectively reduce the volume of oily sludge, but the high moisture content of oily sludge makes it difficult to directly burn, seriously affecting its combustion efficiency, and auxiliary fuel needs to be added before incineration. Solvent extraction treatment of oily sludge, although the operation is simple and the recovery efficiency is high, the large amount of organic solvent consumption makes it difficult for large-scale application; in addition, because the extractant is often highly volatile and toxic, the solvent volatilized in the extraction process and the extractant residues in the extracted sludge will cause secondary pollution to the environment. It has been found that oily sludge is a water-in-oil emulsion [15], and this stable emulsion structure and flocculating structure will significantly reduce its dewatering performance. Therefore, traditional dewatering methods cannot effectively reduce the water content of oily sludge. The hydrothermal upgrading technology using sub/supercritical water as a green medium is an alternative method to treat oily sludge without dehydration. In addition, as a

solvent with adjustable polarity, subcritical or supercritical water can also be used to extract and recover hydrocarbons from petroleum and play a variety of roles in chemical reactions, such as hydrogen donors, oxygen donors, and catalysts [16]. At present, the research on hydrothermal deoxidation of biological crude oil [17] and its model compound [18] has attracted more and more researchers' attention, but there are few studies on the mechanism of nitrogen and sulfur removal of oil sludge under hydrothermal conditions, the reaction kinetics of model compounds in the hydrothermal catalytic process, and the role of catalysts.

Hydrothermal treatment of oily sludge refers to the process of cracking the hydrocarbons, colloids, and asphaltenes in the sludge into light components under subcritical or supercritical water conditions, thus achieving a higher recovery rate of petroleum hydrocarbons. Hydrothermal treatment is emerging as a powerful means for scientists to produce clean and efficient energy from biomass. Subcritical or supercritical water has unique properties, such as high solubility of organic matter, extremely low viscosity, high diffusivity, and zero surface tension [19], and has become an effective medium for recovering crude oil from oily sludge. The content of interfacial active substances, heavy fractions, and impurities in oily sludge decreases significantly during the reaction with subcritical or supercritical water, and the interfacially active asphaltene and naphthenic acid are converted into non-interfacially active substances. Therefore, the separation between oil and water phases occurs naturally, and the recovery of refined oil can be achieved by simple liquid-liquid separation. Khan et al. [20] explored the demulsification and destabilization of oily sludge under hydrothermal conditions. Under the reaction conditions of 400 °C, 30 MPa, 16.7 wt%, and 60 min, the asphaltene content (23.7 wt%) and total acidity (15.4 mg-KOH/g) were significantly reduced to 3.4 wt% and 2.8 mg-KOH/g, while the ratio of naphtha to diesel increased from 9 wt% to 21 wt%. The results show that the macromolecular organic matter with interfacial activity was transformed under hydrothermal conditions, forming non-toxic and non-interfacial active substances, thus realizing the demulsification and destabilization of the oil sludge emulsification system, realizing oil-water separation, and promoting the improvement of the quality of the recovered oil.

In this review, firstly, four hydrothermal technologies for oily sludge treatment according to different reaction temperatures are classified, introduced, and compared (Section 2). In Section 3, the main components of oily sludge are classified and summarized. In Section 4, the hydrodenitrogenation and hydrodesulfurization of the main nitrogen/sulfur compounds in oily sludge were summarized and compared. Secondly, the denitrification/desulfurization pathways and kinetics of these compounds were also studied. In Section 5, various heterogeneous catalysts that can be used for hydrothermal catalytic hydrodenitrogenation/desulfurization of oily sludge are introduced and summarized and their performances are compared. In this review, a comprehensive introduction to each hydrothermal technology is provided for non-professional readers, the hydrodenitrogenation/hydrodesulfurization characteristics of nitrogen/sulfur-containing model compounds in oily sludge were studied, and suggestions for further basic research and industrial development are provided.

2. Hydrothermal treatment

At present, hydrothermal treatment technologies for oily sludge treatment mainly include supercritical water gasification (SCWG), hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal upgrading (HTU). The reaction temperatures required by these hydrothermal technologies and their main products are shown in **Figure 1**. Since hydrothermal technology is mainly used to recover fuel (charcoal, coke, oil, and H_2-rich syngas) and purify or mineralize organic pollutants, it is only necessary to change the temperature (T), pressure (P), residence time (t), catalyst, and other parameters in the reaction process to achieve the multiple purposes of reducing volume, recovering fuel, and harmless treatment. SCWG technology is the earliest application of hydrothermal technology. In recent years, HTL and HTU have gradually been favored by more and more researchers.
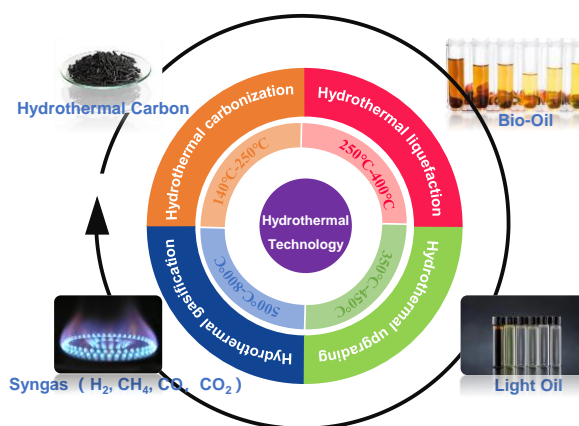
Figure 1. Types of hydrothermal technologies, reaction temperatures, and products.

2.1. Hydrothermal carbonization (HTC)

The operating temperature range of HTC is 140–250 °C, and the reaction time is 2–4 h. Dehydration and carbonization are the main reactions in this process, which can improve fuel characteristics, increase energy density, and reduce the O/C ratio [21]. HTC treatment mainly requires three steps: The first step is to preheat the wet raw material to hydrolyze it into fragments at a low temperature and then to dehydrate and decarboxylate; the fragments need to stay and polymerize at a high temperature for a long time in the maintenance step; and the final main product is coke [22]. HTC is very suitable for dewatering or pretreating sludge and other substances containing a large amount of water before pyrolysis, gasification, and other processes. Hygroscopic substances and sewage sludge with a water content of 75%–85% can be directly treated via HTC without pretreatment steps. The functional groups in a coke can improve its performance as a carbon-based material, which can be used not only as a catalyst to directly remove H_2S but also as a metal carrier to catalyze deoxidation; as an adsorbent to adsorb small molecular gases (such as CO_2 and SO_2), other organic pollutants, or heavy metals; and even as an electrode material for a supercapacitor [23].

In the process of HTC, the form of nitrogen-containing substances in coke is changed, proteins in the sludge are hydrolyzed, amino acids are decarboxylated to form amines, and heterocyclic substances, such as pyridine, pyrrole, and quaternary

nitrogen, also appear [24]. Pauline and Joseph [25] applied HTC technology to the oily sludge of a refinery in India. The results show that the structure of the oily sludge was destroyed after dehydration, decarboxylation, and the condensation reaction, and finally, coke with an energy recovery rate of 75.7%–78.9% was obtained, and the obtained coke was rich in linear long chain alkane (C7–C20). High ecotoxicity was found in the identification of heavy metals in oily sludge via the BCR extraction method, and the ecotoxicity was significantly reduced after hydrothermal carbonization at 250 °C, which indicated that hydrothermal carbonization had a positive effect on the solidification of heavy metals. The reason may be that several heavy metals were dissolved in the liquid phase and recombined with other chemical substances to form stable precipitation. In addition, after the hydrothermal carbonization of the oily sludge, the risk coefficient RI decreased from 101.46 to 7.09, indicating that the potential ecological risk after hydrothermal carbonization was significantly reduced. At present, there are still some urgent problems to be solved in the industrial application of HTC. There are strong hydrolysis reactions of proteins and nucleic acids in the process of HTC, and so a large amount of nitrogen is transferred from the solid phase to the aqueous phase. The analysis of coke characteristics after HTC showed that the nitrogen content in microalgae decreased from 10% to 8% [26], which is more significant for sludge. The nitrogen content decreased from 5.5% to 2.1%–2.2%, which is more conducive to the preparation of clean fuel [27]. However, if coke after HTC is to be further utilized as a renewable energy source, it is still necessary to deeply denitrify it.

2.2. Hydrothermal liquefaction (HTL)

HTL as a new technique for treating "wet" biomass feedstock in high-temperature and high-pressure water (250–400 °C, 4–22 MPa) can convert macromolecular substances into biofuels through a series of chemical reactions, such as hydrolysis and depolymerization [28]. The feedstock water content in the HTL process is mostly over 90%, and the abundant water can dilute biomass or sludge to produce more H^+ and OH^- ions under subcritical water conditions, further promoting hydrolysis reactions, while hindering polymerization reactions [29].

Nazem et al. [30] designed a method to produce bio-oil from oily sludge in a refinery via HTL technology. The optimum operating conditions of hydrothermal liquefaction were determined using response surface methodology. Under the condition of 290 °C, 65 min, and subcritical water with 16 wt% oily sludge, the yield of bio-oil reached 45.52%. The main components were fat, saturated and unsaturated fatty acids, and mono-aromatic and multi-aromatic compounds. Islam et al. [31] used HTL technology to remove harmful substances from oily sludge and recover the oil in it. Under the experimental condition of 260 °C, 8 MPa, cement ratio of 3:1, and extraction time of 90 min, the oil removal rate of sludge residue was about 86% and the recovery rate of crude oil was about 39%. According to FTIR analysis and GC-MS analysis, the main components of recovered oil were various aromatic and aliphatic hydrocarbons, and the fuel characteristics of the recovered oil were similar to those of commercial crude oil. The heavy metal content of the recovered oil was lower than that of commercial crude oil. Although HTL treatment has great potential

and is suitable for the production of high-energy bio-oil from algal biomass, the bio-oil obtained via HTL treatment has high oxygen/nitrogen content. During HTL treatment, 20%–40% of the nitrogen in biomass is converted into the oil phase, resulting in a very high content of nitrogen-containing compounds (8–10 wt%) [32], much higher than that of petroleum crude oil (0.1–1.5 wt%) [33]. It cannot be directly commercialized and requires further process upgrades to reduce the oxygen/nitrogen content in the oil phase.

2.3. Hydrothermal upgrading (HTU)

Compared with the operating temperature of HTL, the temperature required for HTU is higher, reaching a near supercritical range (350–450 °C). This is because the upgrading reaction of heavy compounds becomes significant only above 350 °C [34]. In 2007, Güngören et al. [35] carried out the HTU treatment of oily sludge for the first time. Toluene was selected as the contrast solvent, and the operating temperature and pressure selected were between 300–450 °C and 8.5–20 MPa. The results show that water treatment was superior to toluene treatment in three aspects: high yield of total products (liquid and gas), low yield of heavy compounds in the residue, and no drying pretreatment required. Khan et al. [36] studied the upgrading and recovery of oil sludge in supercritical water. The results show that the oil recovery rate reached 79.8% at 400 °C and 30 MPa for 60 min. The content of saturated hydrocarbons and aromatic hydrocarbons in the recovered oil increased from 40.6% to 74.3%, and the asphaltene content decreased from 46.3% to 7.5%. The acid value of the oil decreased from 15.4 mg-KOH·g-oil^{-1} to 2.8mg-KOH·g-oil^{-1}. The quality of the upgraded oil was significantly improved, and the gas yield was 0.06%. The main components were H_2, CH_4, and CO_2, and no harmful gas was generated, but the coke yield reached 7%.

Water is an excellent dispersant and solvent for pyrolysis, decarboxylation, and demetallization in hydrothermal processes, but its hydrogen supply capacity is very low [37]. To remove nitrogen, sulfur, and other heteroatoms from oily sludge by hydrogenation, additional hydrogen sources need to be provided. The traditional hydrodeoxygenation/nitrogen/sulfur process of bio-oil requires a large amount of hydrogen, and the water in the product will also cause the quality of bio-oil to decline. Since hydrogen itself is a high-quality gas fuel, the economics of the whole process is not ideal. As in other hydrothermal processes, the main parameter of HTU treatment is temperature. With the increase in temperature, the oil production rate also increases, but the improvement of oil quality will also lead to the accelerated formation of coke. Therefore, selecting other in-situ hydrogen sources instead of hydrogen and researching new stable catalysts to reduce reaction temperature and coke formation should be the main research direction in the future.

Adding a catalyst is an effective method to improve the efficiency of HTU. Previously, metal oxide (MO_n) has been the most commonly used catalyst in heavy oil HTU [38]. However, MO_n is vulnerable in subcritical and supercritical water environments [39], where it is corroded and inactivated by heteroatoms (mainly N and S) in oily sludge and sub/supercritical water.

2.4. Supercritical water gasification (SCWG)

In the 20th century, the world's demand for clean and renewable energy continued to increase, but it was not until the beginning of the 21st century that SCWG began to attract the attention of many scholars. SCWG refers to the conversion of biomass into syngas rich in H_2 and CH_4 through various reactions. Oily sludge will undergo a series of complex chemical reactions in supercritical water, such as hydrolysis, dehydration, decarboxylation, pyrolysis, condensation, polymerization, hydrogenation, dehydrogenation, and the generation of H_2, CO, CH_4, CO_2, and other gases. SCWG has several advantages, including the ability to treat raw materials with water contents greater than 50%, produce H_2 under high pressure with a higher yield, improve the possibility of recovering energy from high-temperature product gas, and reduce tar and coke yields. Compared with other hydrothermal technologies, SCWG requires a higher temperature. Catalytic SCWG needs to be in the range of 374–500 °C, while non-catalytic SCWG needs to be in the range of 500–800 °C. Catalysts are crucial to SCWG because they can reduce operating temperature, improve gasification efficiency, and increase H_2 yield [40].

Temperature changes may have a huge impact on the effectiveness of SCWG's treatment of oily sludge. Because the molecular structure of organic matter in oily sludge is more stable than that of other biomass, the gasification efficiency of oily sludge after supercritical water treatment is lower than that of biomass after supercritical water treatment. Peng et al. [41] concluded that asphaltene in oily sludge was the main reason for the reduction of gasification efficiency after experiments. Not only that, up to 50% of organic matter in oily sludge can be converted into aqueous products in SCWG [42], which increases the difficulty of wastewater post-treatment. The main organics in the liquid-phase products of SCWG are oxygenated compounds, such as phenols and organic acids. Zhang et al. [43] studied the SCWG reaction of the oxygen-containing model compound phenol on a Ni-Ru bimetal catalyst in oily sludge and concluded that saturated compounds are generally easier to gasify in supercritical water than aromatic hydrocarbons. For commercial applications, sludge SCWG is more attractive because of the higher concentration of sludge gas production. However, high feed concentration will produce more tar and coke, reduce gasification efficiency, and cause reactor blockage and other problems.

As of 21 December 2023, this study retrieved a total of 1240 relevant articles from the Web of Science. The search focused on two major topics: petroleum waste (oily sludge, petroleum hydrocarbons, heavy oil, PAHs, and asphaltenes) and hydrothermal conditions (HTL, HTC, HTU, and SCWG). Since two or more keywords may be used in the same publication, the retrieved articles may be repeated. However, the string diagram is still meaningful (as shown in **Figure 2**). Although only 51 articles were retrieved when "oily sludge" was used as a keyword search, the relevant research has been very extensive when the keywords of the main components of oily sludge (petroleum hydrocarbon, heavy oil, and polycyclic aromatic hydrocarbons) were used, especially "heavy oil" because it is the most polluting hydrocarbon in petroleum and it is easy to extract from petroleum, coal, and other biomass. In recent years, the HTL method has been gradually used by researchers to treat oily sludge. The reason is that under the operating conditions of HTL, not only can bio-oil be extracted from

microalgae and other biomass but harmful substances in oily sludge can be effectively removed and the quality of oil products can be improved. In contrast, there are relatively few studies on the treatment of oily sludge using SCWG because this method is only suitable for the harmless treatment of harmful substances and cannot upgrade oil products. In addition, it was found that the research on the hydrothermal treatment of oily sludge and its main harmful components began after 2010, and the research results in recent years have significantly improved. However, there is no research review on the catalytic hydrothermal conversion of nitrogen and sulfur compounds in oily sludge.
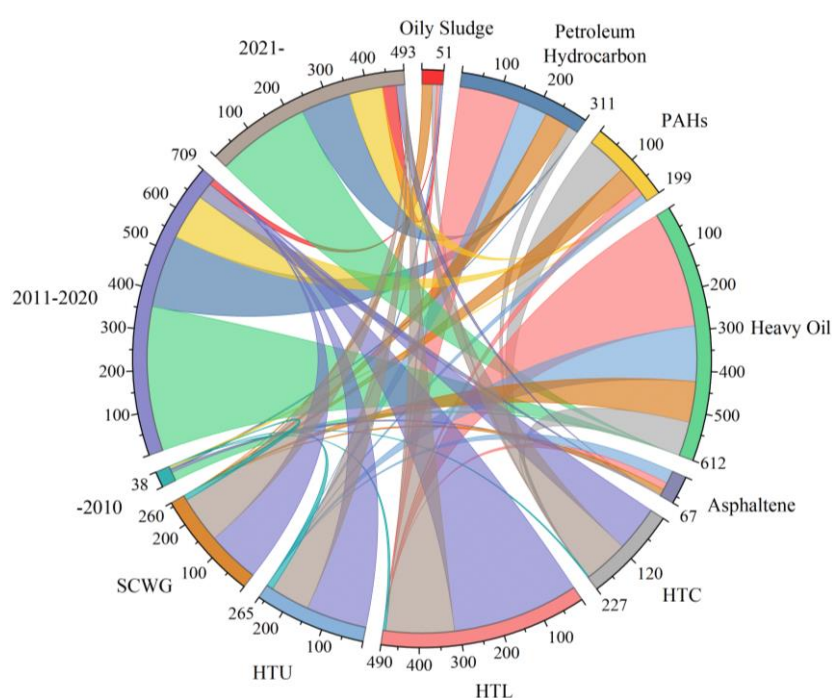
Figure 2. Oily sludge and its harmful components, hydrothermal treatment method, and publication year. Data was gathered from the Web of Science on 21 December 2023.

3. Component analysis of oily sludge

Oily sludge is a kind of semi-solid waste, and its main components are petroleum hydrocarbons, water, and solid particles [5], and its specific contents are shown in **Table 1**. The pH value of oily sludge is usually between 6.5 and 7.5. Organic compounds, such as petroleum hydrocarbons, are generally composed of aliphatic and aromatic hydrocarbons, nitrogen-containing sulfur-oxygen compounds (NSO), and asphaltenes. Alkanes, cycloalkanes, benzene, toluene, xylene, naphthalene, phenol, and various PAHs (such as methylated derivatives of fluorine, phenanthrene, anthracene, kerosene, benzofluorene, and pyrene) account for approximately 75% of petroleum hydrocarbons in oily sludge. The most common NSO components are thiols, thiophene, pyridine, indole, phenol, and other polar compounds. Asphaltene is a mixture of pentane-insoluble and colloidal compounds, mainly including aromatic and alicyclic molecules containing alkyl substituents (usually methyl). Because asphaltenes and colloids contain hydrophilic functional groups and can thus be used

as lipophilic emulsifiers, they are primarily responsible for the stability of oily sludge emulsions. Petroleum hydrocarbons in oily sludge can also be divided into light components and heavy components according to their densities. The light components are generally aliphatic compounds and aromatic hydrocarbons, and the heavy components are divided into colloids and asphaltenes. The light components gradually migrate to the heavy components as storage time passes. Light components and heavy components also determine the type of crude oil in oily sludge and the difficulty of sludge treatment. The main content is shown in **Table 1**.

Generally, nitrogen (N) content in oily sludge accounts for less than 3%, and most nitrogen atoms exist in heterocyclic compounds as part of asphaltene and colloidal distillate [44], which mainly include the homology of pyridine, indole, quinoline, etc. Sulfur (S) content is usually in the range of 0.3 to 10 wt%, with a small amount in the form of elemental sulfur and hydrogen sulfide and most in the form of organic sulfides [45]. Oxygen (O) content is typically less than 4.8 wt%, and it is all in the form of organic matter, the majority of which is colloidal or asphaltene. Oxygen-containing compounds can be divided into acidic oxides and neutral oxides. Naphthenic acids, fatty acids, and phenols are all acidic oxides, collectively known as petroleum acids. Neutral oxides include aldehydes, ketones, and esters, which are extremely rare in oily sludge. Among oxygenated compounds, naphthenic acid and phenols are the most important, especially naphthenic acid, which accounts for about 90% of total petroleum acid [46].

Table 1. Properties and composition of oily sludge.

Project	Composition	Content	Reference
Composition analysis (wt%)	Moisture content	30−85	[47]
	Oil content	15−50	[48,49]
	Solid content	5−46	[47]
Four-component analysis (wt%)	Aliphatic group	40–52	[50]
	Aromatic hydrocarbon	28–31	[50]
	Colloidal	7–22.4	[50]
	Asphaltene	8–10	[50]
Elemental analysis (wt%)	C	31−87	[46,51]
	H	9−13	[51,52]
	O	0.1−4.8	[46,52]
	N	0.9−3	[5,46]
	S	0.3−10	[45,52]
	P	0.77−3.9	[46,52]
Heavy metal analysis (mg·kg^{-1})	Ni	17−25	[5]
	Cr	27−80	[5]
	Zn	7−80	[5]
	Pb	0.001−0.12	[5]
	Cu	32−120	[5]

4. Nitrogenous/sulfurous compounds and kinetics

Studies have found that in addition to lipids and hydrocarbons, there are also a large number of proteins in oily sludge, which can be converted into nitrogen-containing aliphatic (amide, nitrile, etc.) and heterocyclic (indole, pyrimidine, pyridine, etc.) compounds in the thermochemical conversion process [53]. These nitrogen-containing compounds are not only a potential source of pollution but can also lead to catalyst poisoning during subsequent upgrades. In addition, nitrogen-containing compounds inhibit the hydrodesulfurization of sulfur-containing compounds through competitive adsorption, limiting the supply of available hydrogen [54], which is the main reason for the poor stability and the blackening of fuel oil. The nitrogen/sulfur content in light oil obtained using the hydroheat treatment of oily sludge is still significantly higher than that in crude oil. The NO_x and SO_x produced by these nitrides and sulfides during combustion and treatment not only cause serious pollution to the environment but also have a strong toxic effect on the catalysts used in subsequent hydroreforming, hydrodesulfurization, and hydrocracking processes. Under conventional hydrothermal conditions, nitrogen/sulfur compounds, such as pyridine, quinoline, and thiophene, in oily sludge cannot be completely removed. Therefore, it is necessary to hydrogenate nitrogen/sulfur compounds in oily sludge. Hydrodenitrogenation refers to the process in which nitrogen-containing compounds react with hydrogen under the action of a catalyst and are converted into ammonia and water to achieve denitrification. Most of the nitrogen in crude oil exists in the form of five-membered ring or six-membered heterocyclic compounds, and most of them are unsaturated. Non-heterocyclic nitrogen-containing compounds include aniline, aliphatic amines, and acrylonitrile. Hydrodenitrogenation is the process of converting organic nitrogen compounds into easily removed ammonia through a hydrogenolysis reaction to prevent catalyst poisoning and deep denitrification.

Duan et al. did not add hydrogen, water, or catalyst to the reactor when conducting thermal decomposition experiments with pyridine [55]. Around 90%±5% of pyridine did not react after 90 min at 420 °C. When the hydrolysis of pyridine in SCW was studied, 92%±2% of pyridine did not react at 450 °C ($\omega/\rho_w = 0.10$ g/cm^3). These results suggest that the thermal and hydrolytic decomposition of pyridine may contribute at most a few percentage points of conversion. At present, to remove as many of these nitrogen-containing compounds as possible, most researchers will use external hydrogenation sources. The traditional hydrogenation process requires excessive (orders of magnitude) high-pressure fossil source hydrogen, which is not only difficult to control and dangerous but also often leads to excessive hydrogenation products. On the contrary, formic acid (FA) has a high hydrogen content (4.4 wt%), which can be used as a safe and convenient hydrogen source and can replace gaseous H_2 in many reactions [56]. Compared with hydrogen, the yield of upgraded oil by formic acid is generally higher [57], indicating that the hydrogen or hydrogen radicals generated in situ by formic acid are more active in the reactions of hydrogenolysis and hydrogen deoxygenation [58], and the TAN value and viscosity of oil produced by formic acid are significantly lower than those of oil prepared using hydrogen. FA can be completely decomposed into in-situ H_2 in only 40 s under hydrothermal conditions at 341 °C, and the molar yield of in-situ H_2 is 100% [56]. More importantly, FA is

easily obtained by the oxidation or hydrolysis of biomass. Previously, the difficulty of recycling and the use of various additives or organic solvents had limited its practical application on a large scale. Now, the application of heterogeneous catalysts has made up for these shortcomings.

Liu et al. [59] studied the effect of FA on Spirulina bio-oil HTL. The results show that adding FA to the bio-oil reduced the nitrogen content from 10.13 wt% to 5.14 wt%. Li et al. [60] conducted hydrodenitrogenation (HDN) on quinoline, a typical nitrogen-containing model compound in oily sludge, and found that the conversion of quinoline significantly increased from 33.1% of gaseous H_2 to 98.8% in the presence of FA, and they pointed out that FA not only acted as a hydrogen donor in HDN reactions but also reacted with the basic quinoline to form 1,2,3,4-tetrahydroquinoline. Moreover, the conversion of quinoline is very low in the absence of an external hydrogen source, indicating that quinoline cannot be effectively converted using sub/supercritical water alone without an external hydrogen source. Zhang et al. [57] compared the effects of hydrogen sources (hydrogen as a migration hydrogen source and FA as an in-situ hydrogen source) on the upgrading of supercritical ethanol hydrodeoxygenation (HDO) pyrolysis oil. The results show that the in-situ hydrogen source (FA) has better HDO performance at mild temperatures (260 °C, 300 °C). The reason for this situation may be that formic acid rapidly decomposed into CO_2 and H_2 at high temperatures and cannot produce active hydrogen radicals for the HDO reaction.

Although the application of hydrogen sources has been very extensive, the specific reaction mechanism of hydrogen radicals and active hydrogen in the hydrogenation process is not clear, and further research is needed.

4.1. Pyridine

Pyridine, as the smallest nitrogen-containing heterocyclic molecule in oily sludge, has been considered the simplest probe molecule to study HDN in the past. Duan and Savage [55] believed that nitrogen is eventually removed in the form of ammonia, after conducting experiments on hydrothermal catalytic conversion of pyridine into hydrocarbons. Guo et al. [61] studied the kinetic simulation of pyridine HDN under hydrothermal conditions (400 °C) and found that piperidine derivatives are the main nitrogen-containing intermediates of pyridine HDN, which can be further converted into 1-pentanol and 2-methylpentanol. Wang et al. [62] studied the reaction network and mechanism of 2-methylpyridine and 2-methylpiperidine under low-pressure hydrothermal conditions (280–340 °C, 1-3 MPa): 2-ethylpiperidine had a strong retardation effect on the hydrogenation reaction of 2-methylpyridine at low pressure but promoted denitrification; however, the denitrification was inhibited at high partial pressure. It was also proved that H_2S and H_2 had strong denitrification.

4.2. Indole

Indole is the main nitrogen-containing product of algae after hydrothermal treatment. Indole is more hydrothermal stable than other nitrogen-containing compounds (pyrrole or pyridine), and because of the high strength of its carbon-nitrogen bonds, it cannot provide delocalized electrons, making more difficult the

removal of nitrogen from indole. Under the hydrothermal condition of 350 °C, indole only shows ring opening phenomenon, but no nitrogen removal phenomenon, and only a small amount of aniline and 2-methylaniline are produced [63]. Luo et al. [64] compared the effects of carbon-supported and γ-Al$_2$O$_3$-supported precious metal catalysts (Pt, Pd, and Ru) on the hydrodenitrification performance of indole, where Pd/γ-Al$_2$O$_3$ showed the greatest effect on hydrocarbon yield, and the authors proposed two methods for hydrodenitrification of indole to produce hydrocarbons: one is direct hydrodenitrification of indole to produce hydrocarbons, and the other is indole hydrolysis to produce oxygen-containing intermediates and further hydrodeoxygenation to produce hydrocarbons. Guo et al. [65] studied the gasification reaction of indole in supercritical water and believed that under the action of Ni-Ru/CeO$_2$ catalyst, the conversion rate of indole was greater than 80% at 650 °C. In addition, they also found that indoline is the main product of indole hydrogenation, and alkyl aniline is the main ring-opening product of indole [66].

4.3. Quinoline

Quinoline is composed of a benzene ring and a nitrogen heterocyclic ring and has been regarded as a representative of six-membered heterocyclic nitrogen compounds in refinery feedstock and widely studied as an alkaline nitrogen model compound. The bond energy of the C=N double bond (615 kJ/mol) is about twice that of the C-N bond (305 kJ/mol) in the heterocyclic ring. Hydrogenation of heterocyclic ring can weaken the bond energy of the C-N bond and promote nitrogen removal. Therefore, the nitrogen heterocyclic ring needs to be hydrogenated before C-N cleavage can occur. The hydrogenation of quinoline includes all the reactions involved in the hydrogenation of nitrogen-containing compounds, including hydrogenation of nitrogen-containing heterocyclic rings, hydrogenation of benzene rings, and fracture of C$_{sp2}$-N and C$_{sp3}$-N [67], which can fully reflect the hydrogenation denitrification characteristics of the catalyst, helping to explore the mechanism of hydrogenation denitrification and design highly active catalysts. He et al. [68] obtained three main reaction ways of isoquinoline denitrification in supercritical water through experiments, and the rate-limiting steps of the three reaction ways were all N-position addition reactions. Tian et al. [69] compared the HDN of quinoline (Q) and decahydroquinoline (DHQ) on Ni$_2$P catalysts containing sulfur and Ni$_2$P catalysts prepared using the temperature programming reduction (TPR) method and confirmed that the introduction of sulfur can improve the hydrogenation activity and C-N bond cracking activity of NI$_2$P. Xie et al. [70] believed that the hydrogenation of quinoline to decahydroquinoline is a key step in hydrodenitrification under hydrothermal conditions (300 °C, 350 °C, and 400 °C).

4.4. Dibenzothiophene

The world's energy supply mainly comes from oil and, in the next few decades, oil will remain the world's most important energy source. Hydrodesulfurization (HDS) is the most widely used desulfurization technology for petroleum and oily sludge. It is also a catalytic chemical process and widely used to remove sulfur atoms from sulfur-containing molecules in petroleum raw materials. Dibenzothiophene and its alkylated

derivatives, especially the alkyl derivatives at 4 and 6 (4, 6-dimethyl dibenzothiophene), are the most difficult sulfur-containing compounds to deal with in oil and gas and the most problematic molecules in deep hydrodesulfurization. HDS is performed through two parallel paths: direct desulfurization (DDS) and hydrogenation (HYD). DDS leads to the formation of biphenyls (BPs), while HYD produces tetrahydro (TH), hexahydro (HH), and dodecahydro (DH) sulfur-containing intermediates, which are desulfurized into cyclohexylbenzene (CHB) and dicyclohexyl (DCHs) molecules [71]. Deep HDS has become an increasingly important topic due to the need to treat low-quality crude oil raw materials with high sulfur content, coupled with increasing restrictions on the sulfur content of transportation fuels.

Adschiri et al. [72] investigated the catalytic hydrodesulfurization of dibenzo thiophene and Ni-Mo/Al$_2$O$_3$ catalysts under different atmospheres (H$_2$-SCW, CO-SCW, CO$_2$-H$_2$-SCW, and HCOOH-SCW) in a tube reactor at 673 K and 30 MPa. The results show that the hydrogenation of dibenzothiophene in supercritical water was better than that in gaseous hydrogen. In addition, they found that dibenzothiophene performed an efficient hydrogenation reaction even in the presence of oxygen.

4.5. Reaction pathway

In general, when oily sludge is in hydrothermal upgrading conditions alone, the nitrogen and sulfur compounds in the oily sludge cannot be effectively removed, resulting in the nitrogen and sulfur content of the upgraded crude oil being much higher than that of the crude oil. To effectively reduce the nitrogen and sulfur content in oily sludge, researchers carried out the HDN and HDS of nitrogen and sulfur compounds by adding heterogeneous catalysts and hydrogen sources, such as formic acid, during the hydrothermal process. The main HDN and HDS pathways of nitrogen and sulfur compounds are shown in **Figure 3** and **Figure 4**.

According to **Figure 3**, whether the nitrogen-containing compound contains a benzene ring or not, the first step reaction after hydrogenation is to saturate the molten pyridine ring and generate amines, and the process is reversible. For nitrogen-containing compounds without a benzene ring, the further reaction after the pyridine ring is saturated will mainly produce the following four products: piperidine continues to be hydrogenated to form 1-piperidinol; the H on the N atom of pyridine undergoes a substitution reaction with the hydrogen source to form 1-piperidine aldehyde; the derivative reaction produces other piperidines; and the piperidine ring was opened to generate 1-alkyl alcohol, which combined with the piperidine generated by pyridine hydrogenation to generate 1-alkyl piperidine. Subsequently, 1-piperidol and 1-piperidine aldehydes are further hydrogenated to form 1-alkylpiperidine. These alkylpiperidines are converted into amine compounds after ring opening with other piperidines, which then undergo hydrolysis reactions. The hydrolysates are further hydrogenated to form short-chain alkanes. These short-chain alkanes and the previously generated 1-alkyl alcohols can undergo thermal decomposition reactions to generate gas products under hydrothermal conditions.

For nitrogen-containing compounds containing a benzene ring, four main products, which are aniline, alkylaniline, alkylbenzene, and alkylcyclohexane, are

formed after the hydrogenation of the pyridine ring. Aniline and alkylbenzene are formed by alkylaniline through dealkylation and deamination, respectively. The formation rate of alkylaniline is faster than that of alkylbenzene [66]. Polycyclic aromatic hydrocarbons can be obtained by deep hydrogenation of aromatic amines or direct hydrogenation of aromatic nitrogen-containing compounds. Aniline and alkylaniline undergo thermal decomposition under hydrothermal conditions at high temperatures to form olefins, which are further decomposed to produce syngas. Aromatic amines and polycyclic aromatic hydrocarbons also produce syngas at high temperatures. It can be seen that the final products of pyridine-ring nitrogen-containing compounds are syngas, while the final products of aromatic nitrogen-containing compounds contain both gases and hydrocarbons.
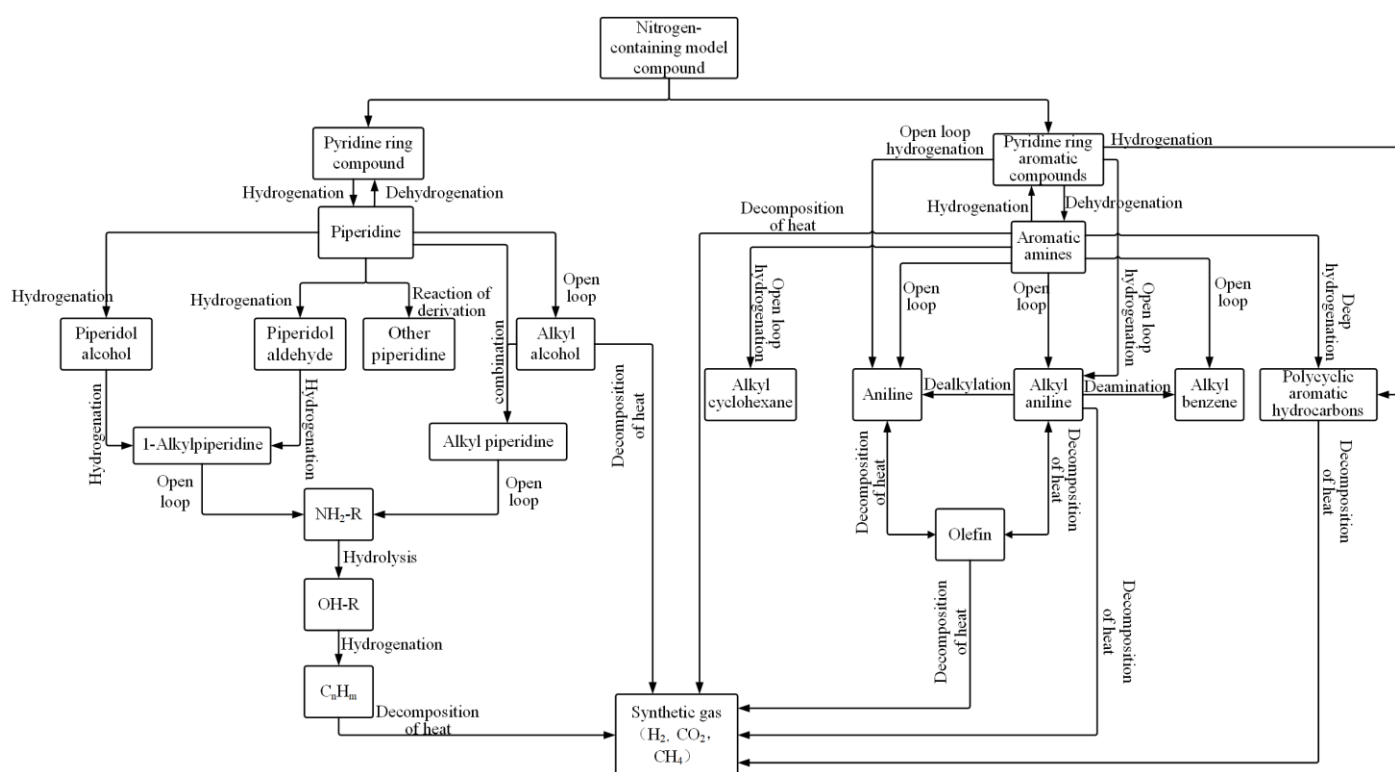

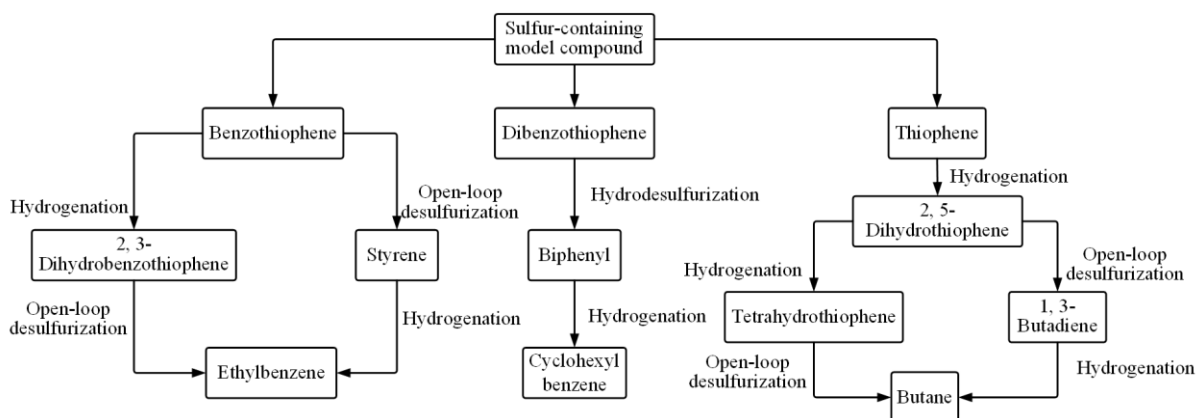**Figure 3.** Reaction pathways of nitrogen-containing compounds in oily sludge.

Figure 4. Reaction pathways of sulfur-containing compounds in oily sludge.

For the main reaction path of sulfur-containing compounds, since the sulfur element in oily sludge mainly comes from thiophene, this paper mainly summarizes the hydrodesulfurization of thiophene and its homologs. It can be seen from **Figure 4** that the main reactions of thiophene and its homologs are hydrogenation reactions or ring-opening desulfurization reactions, and the final products are hydrocarbons.

Because nitrogen and sulfur compounds in oily sludge are difficult to remove in a separate hydrothermal environment, researchers carried out hydrodenitrogen and hydrodesulfurization in a hydrothermal environment by adding catalysts and hydrogen sources. As a result, research into various types of catalysts and hydrogen sources has advanced rapidly in recent years.

4.6. Reaction kinetics

Studying the reaction kinetics of nitrogen-containing model compounds in oily sludge is helpful to determine the intermediate products, final products, and reaction mechanisms in the reaction process in order to adjust the harmful or favorable reactions in the reaction. Massoth et al. [73] used the Langmuir-Hinshelwood equation in a fixed-bed reactor to study the kinetics of gaseous hydrodenitrification of quinoline at 613 K and 3.4 MPa, and the kinetic results show that nitrogen-containing intermediates had a significant inhibitory effect on hydrodenitrification. A complete kinetic analysis of each pathway for quinoline hydrodenitrification requires three different types of active sites: one for C-N bond cleavage, one for aromatic hydrogenation, and one for olefin hydrogenation. Xie et al. [70] established a first-order kinetic model for the hydrodenitrification of quinoline under hydrothermal conditions (300–400 °C, 25 MPa). The model fitted well, with R^2 values exceeding 0.99. The kinetic simulation results show that the conversion rate of quinoline increased with the increase in temperature and reaction time, and the activation energy was 41.72 kJ/mol. The dehydrogenation of 1,2,3,4-tetrahydroquinoline to quinoline was found to be a rate-determining step, with an energy barrier of up to 174.6 kJ/mol. Guo et al. [61] developed a kinetic model for pyridine HDN that mathematically described the hydrothermal HDN reaction of pyridine on a $Ni_{50}Ru_{50}/C$ catalyst. The model captured all data trends and fit the time changes of all major products. The kinetic simulation results show that the formation rate constants of the 1-piperidine ethanol reaction and 1-ethyl piperidine reaction were significantly higher than those of other reactions, which may indicate that the hydroxyl groups of saturated nitrogen heterocyclic compounds were relatively easy to attach and remove under hydrothermal conditions. The sensitivity analysis showed that the dehydrogenation of piperidine to pyridine had a great influence on the whole reaction path. Guo et al. [66] investigated the kinetics of hydrothermal denitrification of indole by Ni-Ru bimetallic catalyst supported on activated carbon. They believed that the hydrogenation of indole to indoline was the main way, and the ring-opening of indoline to alkylaniline was faster than the formation of the HDN product (alkylbenzene).

5. Catalysts and carriers

To verify the hydrodenitrogenation effect of nitrogen-containing compounds without a catalyst, Duan et al. [55] reacted pyridine in supercritical water at 450 °C

and high-pressure H_2 for 1 h (without any catalyst), and no HDN product with C4 or C5 compounds as the main product was observed. This experiment shows that the C4 and C5 detected in the HDN experiment were entirely derived from the catalytic reaction. Combined with previous thermal decomposition and hydrolysis decomposition experiments, the results obtained in the catalytic experiments were due to catalytic HDN rather than some competitive thermal or hydrothermal reaction pathways. Studies have shown that the type of catalyst has a great influence on the percentage of nitrogen and sulfur compounds remaining in treated oil [74]. At present, metal catalysts and phosphorus/sulfide metal salt catalysts are the most studied heterogeneous catalysts. Metal catalysts can be divided into non-precious metal catalysts and precious metal catalysts. Metal catalysts can be used alone or in combination with polymetallic catalysts. The specific catalytic effects are shown in **Table 2**. In this section, different types of metal catalysts and their supports are reviewed.

Table 2. Catalytic effect of different types of catalysts.

Catalyst type	Metal	Carrier	Compound	Hydrothermal condition	Catalytic effect	Ref.
Monometal	Pd	γ-Al$_2$O$_3$	Indole	450 °C, 5 MPa	Indole was completely converted at 90 min, and the maximum yield of hydrocarbons was reached at 120 min.	[64]
	Pt	γ-Al$_2$O$_3$	Pyridine	400 °C, 5. 5MPa	Pyridine is completely converted into hydrocarbons. The main products are n-butane and n-pentane.	[55]
Polymetallic	Ni-Ru	γ-Al$_2$O$_3$	Quinoline	400 °C, 20 MPa	The conversion of quinoline increased with the increase in temperature and reaction time, and the maximum value was 94.99%.	[70]
	Ni-Ru	C	Pyridine	400 °C, 20 MPa	The total yield of nitrogen-containing compounds was 11%.	[61]
	Ni-Ru	AC	Indole	350 °C, 20 MPa	The indole HDN product had the highest molar yield (31%).	[66]
Metal phosphorus/sulfide	Sulfide-Ni-Mo	γ-Al$_2$O$_3$	Quinoline	350–450 °C, 25–35 MPa	The denitrification pathway consisted of two consecutive steps: in-situ generated H_2 and quinoline hydrogenation. The total nitrogen reduction rate reached about 85%.	[44]
	Ni$_2$P	SiO$_2$	Cazole	275–400 °C, 3.0 MPa	The metal phosphating catalyst showed higher HDN activity of carbazole and produced more cyclohexylbenzene.	[75]
	Ni$_2$P	-	1,2,3,4-Tetrahydrodibenzothiophene, 1,2,3,4,4a,9b-Hexahydrodibenzothiophene	340 °C, 4 MPa	The hydrogenation and dehydrogenation activities of Ni$_2$P were low, but the desulfurization activity was high.	[76]

5.1. Non-noble metal catalysts

With the gradual improvement of people's environmental awareness and the increasingly stringent environmental regulations, the production of low-sulfur and low-nitrogen fuels has become one of the most important tasks of the petroleum industry. HDS and HDN are typical hydrogenation processes, in which the reaction between raw materials and hydrogen mainly occurs on the catalyst. Because of the importance of HDS and HDN processes, as well as the associated economic and environmental issues, researchers have conducted extensive research and made significant efforts to develop new high-yielding catalysts. Ni-Mo and Co-Mo catalysts on different supports are the most studied catalysts at present.

Studies have shown that the addition of Mo to a Ni catalyst can improve the dispersion of Ni on the carrier material, increase the pre-sulfidation degree of the metal, and significantly increase the activity of the Ni/Al$_2$O$_3$ catalyst for FCC gasoline etherification [77]. Kordouli et al. [78] found that in the case of an alumina-supported catalyst, the addition of Mo increased the conversion rate of phenol by 18%. When amorphous-silica-alumina (ASA)-supported catalysts were used, the corresponding increase was 38%, and therefore they believe that adding Mo to a Ni catalyst improved the activity of the catalyst, regardless of the carrier. Most researchers believe that the enhanced activity of bimetallic catalysts over single-metal catalysts is due to the synergistic effect between the two metals [79]. Duan et al. [80] found that Co-Mo/Al$_2$O$_3$ had a specific desulfurization performance for bio-oil and can also reduce O/C, thereby increasing the calorific value. Li et al. [81] also studied the effect of Ni-Mo/Al$_2$O$_3$ on the products of halophytic green algae HTL. The results show that Ni-Mo/Al$_2$O$_3$ significantly increased bio-oil yield, while also being capable of denitrification. Rinaldi et al. [82] investigated the role of boron and citric acid in thiophene HDS over a Co-Mo/γ-Al$_2$O$_3$ catalyst. They observed that the activity of HDS increased after citric acid and boron were added to the Co-Mo catalyst.

5.2. Noble metal catalysts

Traditional catalysts, such as sulfides Ni-Mo and Co-Mo, deactivate quickly due to sulfur leaching [83], whereas supported noble metal (Ir, Pt, Pd, and Rh) catalysts perform better in removing oxygen-containing substances in the bio-oil phase [84]. Snåre et al. [85] screened a series of noble metal catalysts (Pd, Pt, Ir, Ru, and Rh) on Al$_2$O$_3$, Cr$_2$O$_3$, MgO, SiO$_2$, and activated carbon for the deoxygenation of stearic acid in a batch reactor. It was found that Pt/C was the most active catalyst, and the selectivity of deoxygenated C17 products exceeded 95%. Pt/C had the best deoxidation performance, according to Duan and Savage, and can reduce the content of oxygenated compounds in biocrude oil from 8.07 wt% to 0.68 wt% [86]. Duan and Savage [55] also studied the hydrothermal catalytic conversion of pyridine, a nitrogen-containing compound. They screened several noble metal catalysts (Pt/C, Pd/C, Ru/C, Rh/C, sulfurized Pt/C, Pt/γ-Al$_2$O$_3$, Mo$_2$C, MoS$_2$, and PtO$_2$). It was confirmed that the Pt/γ-Al$_2$O$_3$ catalyst was most effective for the pyridine hydrothermal HDN reaction, but the catalyst showed a certain degree of activity loss when reused. When conducting hydrothermal HDN for indole, Luo et al. [64] screened carbon-supported and Al$_2$O$_3$-supported noble metal catalysts (Pt, Pd, or Ru). The results show that 5wt% Pt, Pd, or Ru noble metal catalysts supported on porous solids (such as carbon and alumina) promoted the conversion of indole to hydrocarbons, and Pd/γ-Al$_2$O$_3$ had the greatest effect on hydrocarbon yield. Guo et al. [66] studied the activity and selectivity of activated-carbon-supported Ni, Pt, Ru, and Ni-Ru bimetallic catalysts for hydrothermal denitrification of indole and found that when FA was added, ruthenium-containing catalysts promoted the production of hydrocarbons (HDN products). Subsequent DFT calculations further confirmed the experimental activity trend, indicating that the noble metal Ru was more active than the non-noble metal Ni in the ring opening of indole and the deamination of o-toluidine. They also compared the catalytic performances of commercial Pd/C catalysts and self-made Ni-Ru bimetallic

catalysts for pyridine under a hydrothermal condition (400 °C) [61]. It was found that commercial Pd/C had higher pyridine conversion at 350 °C, while self-made Ni-Ru bimetallic catalysts had a significant denitrification activity at 400 °C. Zhang et al. [43] gasification phenol in supercritical water after adding Ru to a Ni catalyst. Compared with the case without a catalyst, Ni and Ni-Ru catalysts effectively reduced the formation of cyclohexanone and oligomer products. With the increase in the Ru/Ni ratio, the yields of H_2 and CH_4 increased, and the yields of carbon and hydrogen in gas products also increased.

5.3. Phosphide/sulfide catalysts

In addition to ordinary metal catalysts, traditional hydrogenation catalysts also include supported molybdenum sulfide and tungsten sulfide catalysts with cobalt and nickel as additives. Adschiri and colleagues [72] found that dibenzothiophene could be effectively removed in the presence of sulfided Ni-Mo/γ-Al$_2$O$_3$ by introducing O_2 into systems of supercritical water and hydrocarbons. The desulfurization pathways are partial oxidation of hydrocarbons, water-gas transfer reaction (WGTR), and sulfide tandem hydrogenation. Yuan et al. [44] found that HDN activity was usually higher when sulfide catalysts were used.

Many researchers believe that phosphide catalysts are superior to sulfide catalysts not only because of their higher activity but also because of their unique behavior in HDS reactions. In the first few hours, as the running time increases monotonously, the HDS activity of phosphide catalysts will also increase. Bowker et al. [75] pointed out that nickel phosphide and nickel-rich bimetallic phosphide catalysts produced a large amount of partially hydrogenated hydrocarbon products compared with sulfide catalysts, thus consuming less hydrogen and achieving a higher HDN conversion. Eijsbouts et al. [87] also believed that phosphorus had a more positive effect on HDN activity. For nickel-based phosphide catalysts, the addition of phosphorus can reduce the formation of inactive nickel aluminate and make more nickel available at the active site. Moreover, phosphorus has a strong adsorption effect on the OH group on the surface of alumina, reducing the number of basic OH groups available to the molybdenum oxygen group and also reducing the interaction between the active metal and the carrier, which is conducive to the active metal's complete vulcanization or reduction [88]. Many theories have been proposed to explain the promoting effect of P on HDN activity, including the formation of highly dispersed Ni or Mo phosphides (or phosphorus sulfides) at the edge of MoS$_2$ under reaction conditions and morphological changes of MoS$_2$ crystals (increased accumulation of MoS$_2$ layers), leading to increased hydrogenation activity [89]. Phosphorus is usually added to an impregnation solution in the form of phosphate (such as H_3PO_4 or $NH_4H_2PO_4$), which increases the solubility of molybdate by forming phosphomolybdate species.

Transition metal phosphides (such as Ni$_2$P, MoP, and WP) are metallic covalent compounds. They have been proven to be not only a new type of highly active catalyst for HDS and HDN of petroleum feedstocks [90] but also have good resistance to carbon deposition. Researchers discovered that Ni$_2$P is particularly active in simultaneous HDS and HDN reactions in phosphides [90]. In addition to HDS and HDN, Ni$_2$P can also be used in many important reactions, such as hydrodeoxygenation

(HDO) [91], hydrogenation [92], and hydrogen evolution [93]. Ni_2P is very likely to become the next generation of hydrofining catalysts after metal sulfides.

The effect of phosphorus on hydrogenation activity mainly depends on the concentration of phosphorus and the preparation method. Comparing co-impregnation with sequential impregnation, Maity et al. [94] suggested that catalysts prepared using co-impregnation had a higher hydrogenation activity for diesel oil. They also reported that increased activity was observed as the phosphorus concentration increased, which reached the maximum at 1wt% load. Further increases in concentration reduced the dispersion of the active metal, leading to the formation of MoO_3 crystal clusters, which reduced catalytic activity.

5.4. Effect of H_2S

It has been reported that the introduction of sulfur can improve the hydrogenation activity and carbon-nitrogen bond cleavage activity of Ni_2P. In the upgrading process of heavy oil and asphalt, HDN and HDS always occur at the same time, producing H_2S. A small amount of H_2S, such as about 0.3%, can significantly promote the HDN of quinoline in oily sludge, and the denitrification rate increases from about 40% to about 75% because the presence of sulfur can weaken the adsorption of nitrogen-containing compounds.

Nucleophilic substitution, which requires the participation of sulfur, is an important mechanism leading to C-N bond cleavage. In this mechanism, after the reaction of aliphatic amines with H_2S, the NH_2 group is replaced by the SH group, and the generated alkane thiol reacts with hydrogen to form alkane, which then reacts with H_2S for desulfurization. H. Wang and colleagues [62] reported that using the sulfided $Ni-Mo/\gamma-Al_2O_3$ catalyst in the presence of H_2S, the C-N bond cleavage of alkylamines formed alkyl thiols only through a nucleophilic substitution mechanism. Gutiérrez et al. [96] found that nickel was beneficial to the adsorption of H_2S and H_2 and the migration of hydrogen. In the HDN of quinoline, H_2S can promote the reaction of decahydroquinoline (DHQ) to propylcyclohexylamine (PCHA) and delay the pathway of o-propylaniline (OPA) to propylcyclohexylamine (PCHA). At low concentrations, the promotion effect of H_2S is better than the inhibition effect, increasing hydrocarbon yield.

After the addition of heterogeneous catalysts, the nitrogen and sulfur content of bio-oil significantly reduces. Moreover, in the hydrothermal reaction of nitrogen/sulfur model compounds, the conversion rate also significantly improves after a catalyst and a hydrogen source are added. In addition to adding catalysts and hydrogen sources, some researchers also added a small amount of H_2S during the hydrothermal treatment of model compounds. The reason is that a small amount of H_2S can accelerate the cleavage of C-N bonds and promote hydrogenation activity. At present, an important factor hindering the upgrading effect of bio-oil and the catalytic conversion effect of nitrogen/sulfur compounds is the life of the catalyst. Because of the high sulfur content, the activity of most catalysts is greatly reduced after repeated use, resulting in a poor subsequent upgrading effect. Therefore, the future research direction should focus on the improvement and development of new catalysts and the selection of various types of hydrogen sources.

5.5. Carrier

5.5.1. AC/BC/molecular sieve

Commonly used catalyst carriers in the laboratory are usually activated carbon (AC), molecular sieves, etc. Researchers mainly improved bio-oil yield by adjusting the pore size distribution, specific surface area, and other parameters of the catalyst. Nevertheless, some carriers also play an active role in the production of bio-oil. Guo et al. [61] created a $Ni_{50}Ru_{50}/AC$ catalyst using AC as a carrier and investigated the catalyst's catalytic denitrification performance for pyridine under hydrothermal conditions. The results show that the self-made NiRu bimetallic catalyst had a significant denitrification activity at 400 °C. Li [97] used an HZSM-5 molecular sieve to catalyze nano-green algae under hydrothermal conditions and found that the contents of N, O, and other heteroatoms in the prepared bio-oil significantly reduced. When no catalyst was added, the contents of O and N in the produced bio-oil were 8.35 wt% and 5.32 wt%, respectively. The content of O and N in the crude oil produced after the use of the catalyst was reduced to 0.75 wt% and 2.71 wt%, respectively. Although AC as the support for HDN has certain catalytic activity, its catalytic activity is much lower than that of biological carbon (BC) as the catalyst support. First, the main source of BC is the solid residue after algae HTL, which is not only low-cost but also environmentally friendly. Second, the preparation of BC does not necessitate the drying of raw materials, which reduces the process cost. Finally, the surface of BC is highly aromatized and contains a large number of functional groups, which may promote oil phase formation. Ormsby et al. [98] found that BC showed a better performance than AC in the catalytic hydrolysis of carbohydrates. Wang et al. [99] studied the performance of biochar-based catalysts on HTL by loading Co, Ni, and their oxides on BC with low-fat microalga Spirulina as the raw material. The results show that the BC catalyst can significantly improve the yield of bio-oil at low temperatures (260–280 °C) and that Ni/BC had a good denitrification effect on bio-oil. Compared with the non-catalytic case, the N content was reduced by nearly 2 wt%. Furthermore, under the assumption of an equal mass yield, BC had a higher energy density [100].

5.5.2. γ-Al$_2$O$_3$

γ-Al$_2$O$_3$ has become the most widely used catalyst carrier for its excellent structure and mechanical properties. It not only contributes to the dispersion of the active metal but also changes the electronic properties of the active phase, thus greatly improving catalytic activity. In addition, γ-Al$_2$O$_3$ can easily be formed into desired shapes and contains both acidic and alkaline sites [101]. Duan et al. [55] reported the catalytic activity of several catalysts supported by 5wt% precious metals (Pt/C, Pd/C, Ru/C, Rh/C, sulfide Pt/C, and Pt/γ-Al$_2$O$_3$) for the hydrothermal conversion of pyridine into hydrocarbons. They believed that γ-Al$_2$O$_3$-supported Pt was the most effective pyridine HDN catalyst in the hydrothermal reaction because γ-Al$_2$O$_3$ was likely involved in the cleavage of the C-N bond, and this could explain why the Pt/γ-Al$_2$O$_3$ catalyst is more active than the Pt/C catalyst.

6. Conclusion

Hydrothermal treatment provides a new idea for the resource utilization of oily sludge. Compared with traditional methods, which require dehydration and then treatment, hydrothermal treatment simplifies the operation steps because the reaction medium is water. The main conclusion of this paper is as follows:

1) Various hydrothermal technologies for the treatment of oily sludge were introduced, including the development, principles, and application scenarios of supercritical water gasification, hydrothermal carbonization, hydrothermal liquefaction, and hydrothermal upgrading. The summary is helpful for beginners to understand the similarities and differences between oily sludge treatment using different hydrothermal technologies. Supercritical water gasification can produce H_2-rich syngas, hydrothermal carbonization can produce coke, hydrothermal liquefaction can produce bio-oil, and hydrothermal upgrading can transform heavy oil into light oil.

2) The removal effects of various types of catalysts and carriers on nitrogen and sulfur compounds in oily sludge were introduced. Noble metal catalysts can remove nitrogen/sulfur and other heteroatoms in oily sludge more effectively than non-noble metal catalysts. In addition, using formic acid as a hydrogen source for nitrogen/sulfur removal is better than using hydrogen directly as a hydrogen source.

3) This paper introduced the kinetics of the hydrogenation of nitrogen-containing model compounds in oily sludge by some researchers. Most researchers believe that the destruction of C=N hydrogenation in nitrogen-containing compounds is a prerequisite for nitrogen removal. Secondly, some nitrogen-containing intermediates have an obvious inhibitory effect on hydrodenitrification. In future studies, the formation of these nitrogen-containing intermediates should be minimized.

Although hydrothermal treatment of oily sludge has been widely used by researchers, there are few large-scale commercial applications so far. To narrow the gap between experimental research and industrial production, this paper puts forward some suggestions for future research.

1) When using the hydrothermal method to treat oily sludge, the probability of coking is larger, which will not only have adverse effects on the hydrothermal effect but also weaken the catalytic effect of the catalyst. Therefore, the coking phenomenon should be reduced as much as possible in future research.

2) Poor reusability is a problem of most metal catalysts at present. The catalytic performance of most catalysts decreases sharply after three times of use, and the problem of plugging the catalyst's active site is easy to occur. Therefore, the development and selection of suitable catalysts is also an important issue to be solved in the future.

3) Most researchers focused on the yield and quality of bio-oil after the hydrothermal treatment of oily sludge, but few studied the gas phase and solid phase products, especially the heavy metal content in solid-phase products. Excessive heavy metals will continue to pollute the environment after discharge.

Future research should also focus on the transfer process of heavy metals in oily sludge conversion.

4) The kinetics of denitrification reaction of nitrogen-containing heterocyclic compounds in oily sludge have been studied extensively, but there is little research on model compounds containing sulfur (such as thiophene). Kinetics studies can understand the reaction path of its transformation and guide further effective desulfurization in the future.

Conflict of interest: The authors declare no conflict of interest.

References

1. Hochberg SY, Tansel B, Laha S. Materials and energy recovery from oily sludges removed from crude oil storage tanks (tank bottoms): A review of technologies. Journal of Environmental Management. 2022, 305: 114428. doi: 10.1016/j.jenvman.2022.114428

2. Li J, Lin F, Li K, et al. A critical review on energy recovery and non-hazardous disposal of oily sludge from petroleum industry by pyrolysis. Journal of Hazardous Materials. 2021, 406: 124706. doi: 10.1016/j.jhazmat.2020.124706

3. Wang Y, Fan D, Li W. Analysis and prospect of domestic and foreign oil and gas resources in 2020. China Mining Magazine. 2021, 30(1): 18-23. doi:10.12075/j.issn.1004-4051.2021.01.035

4. Duan H, Huang Q, Wang Q, et al. Hazardous waste generation and management in China: A review. Journal of Hazardous Materials. 2008, 158(2-3): 221-227. doi: 10.1016/j.jhazmat.2008.01.106

5. Hu G, Li J, Zeng G. Recent development in the treatment of oily sludge from petroleum industry: A review. Journal of Hazardous Materials. 2013, 261: 470-490. doi: 10.1016/j.jhazmat.2013.07.069

6. Robertson SJ, McGill WB, Massicotte HB, et al. Petroleum hydrocarbon contamination in boreal forest soils: a mycorrhizal ecosystems perspective. Biological Reviews. 2007, 82(2): 213-240. doi: 10.1111/j.1469-185x.2007.00012.x

7. Naz A, Chowdhury A, Chandra R, et al. Potential human health hazard due to bioavailable heavy metal exposure via consumption of plants with ethnobotanical usage at the largest chromite mine of India. Environmental Geochemistry and Health. 2020, 42(12): 4213-4231. doi: 10.1007/s10653-020-00603-5

8. Wake H. Oil refineries: a review of their ecological impacts on the aquatic environment. Estuarine, Coastal and Shelf Science. 2005, 62(1-2): 131-140. doi: 10.1016/j.ecss.2004.08.013

9. Teng Q, Zhang D, Yang C. A review of the application of different treatment processes for oily sludge. Environmental Science and Pollution Research. 2020, 28(1): 121-132. doi: 10.1007/s11356-020-11176-2

10. Ubani O, Atagana H I, Thantsha MS. Biological degradation of oil sludge: A review of the current state of development. African Journal of Biotechnology. 2013, 12(47): 6544-6567. doi: 10.5897/AJB11.1139

11. Qu Y, Li A, Wang D, et al. Kinetic study of the effect of in-situ mineral solids on pyrolysis process of oil sludge. Chemical Engineering Journal. 2019, 374: 338-346. doi: 10.1016/j.cej.2019.05.183

12. Gao N, Kamran K, Quan C, et al. Thermochemical conversion of sewage sludge: A critical review. Progress in Energy and Combustion Science. 2020, 79: 100843. doi: 10.1016/j.pecs.2020.100843

13. Zhao Y, Yan X, Zhou J, et al. Treatment of oily sludge by two-stage wet air oxidation. Journal of the Energy Institute. 2019, 92(5): 1451-1457. doi: 10.1016/j.joei.2018.08.006

14. Al-Doury MMI. Treatment of oily sludge using solvent extraction. Petroleum Science and Technology. 2019, 37(2): 190-196. doi: 10.1080/10916466.2018.1533859

15. Gao N, Duan Y, Li Z, et al. Hydrothermal treatment combined with in-situ mechanical compression for floated oily sludge dewatering. Journal of Hazardous Materials. 2021, 402: 124173. doi: 10.1016/j.jhazmat.2020.124173

16. Wei N, Xu D, Hao B, et al. Chemical reactions of organic compounds in supercritical water gasification and oxidation. Water Research. 2021, 190: 116634. doi: 10.1016/j.watres.2020.116634

17. Duan P, Zhang C, Wang F, et al. Activated carbons for the hydrothermal upgrading of crude duckweed bio-oil. Catalysis Today. 2016, 274: 73-81. doi: 10.1016/j.cattod.2016.01.046

18. Liu X, Yang M, Deng Z, et al. Hydrothermal hydrodeoxygenation of palmitic acid over Pt/C catalyst: Mechanism and kinetic modeling. Chemical Engineering Journal. 2021, 407: 126332. doi: 10.1016/j.cej.2020.126332

19. Fomo G, Madzimbamuto TN, Ojumu TV. Applications of Nonconventional Green Extraction Technologies in Process Industries: Challenges, Limitations and Perspectives. Sustainability. 2020, 12(13): 5244. doi: 10.3390/su12135244

20. Khan MK, Cahyadi HS, Kim SM, et al. Efficient oil recovery from highly stable toxic oily sludge using supercritical water. Fuel. 2019, 235: 460-472. doi: 10.1016/j.fuel.2018.08.003

21. Huang J, Wang Z, Qiao Y, et al. Transformation of nitrogen during hydrothermal carbonization of sewage sludge: Effects of temperature and Na/Ca acetates addition. Proceedings of the Combustion Institute. 2021, 38(3): 4335-4344. doi: 10.1016/j.proci.2020.06.075

22. Wang T, Zhai Y, Zhu Y, et al. A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. Renewable and Sustainable Energy Reviews. 2018, 90: 223-247. doi: 10.1016/j.rser.2018.03.071

23. Demir M, Ashourirad B, Mugumya JH, et al. Nitrogen and oxygen dual-doped porous carbons prepared from pea protein as electrode materials for high performance supercapacitors. International Journal of Hydrogen Energy. 2018, 43(40): 18549-18558. doi: 10.1016/j.ijhydene.2018.03.220

24. Leng L, Yang L, Chen J, et al. A review on pyrolysis of protein-rich biomass: Nitrogen transformation. Bioresource Technology. 2020, 315: 123801. doi: 10.1016/j.biortech.2020.123801

25. Pauline AL, Joseph K. Hydrothermal carbonization of oily sludge for solid fuel recovery – Investigation of chemical characteristics and combustion behaviour. Journal of Analytical and Applied Pyrolysis. 2021, 157: 105235. doi: 10.1016/j.jaap.2021.105235

26. Ekpo U, Ross AB, Camargo-Valero MA, et al. A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate. Bioresource Technology. 2016, 200: 951-960. doi: 10.1016/j.biortech.2015.11.018

27. Fang J, Tang Q, Li Y, et al. Morphology of phosphorus and metal extraction behavior in sewage sludge during hydrothermal carbonization treatment. CIESC Journal. 2020, 71: 3288-3295. doi: 10.11949/0438-1157.20200042

28. Valdez PJ, Tocco VJ, Savage PE. A general kinetic model for the hydrothermal liquefaction of microalgae. Bioresource Technology. 2014, 163: 123-127. doi: 10.1016/j.biortech.2014.04.013

29. Lachos-Perez D, César Torres-Mayanga P, Abaide ER, et al. Hydrothermal carbonization and liquefaction: Differences, progress, challenges, and opportunities. Bioresource Technology. 2022, 343: 126084. doi: 10.1016/j.biortech.2021.126084

30. Nazem MA, Tavakoli O. Bio-oil production from refinery oily sludge using hydrothermal liquefaction technology. The Journal of Supercritical Fluids. 2017, 127: 33-40. doi: 10.1016/j.supflu.2017.03.020

31. Islam MN, Jung SK, Jung HY, et al. The feasibility of recovering oil from contaminated soil at petroleum oil spill site using a subcritical water extraction technology. Process Safety and Environmental Protection. 2017, 111: 52-59. doi: 10.1016/j.psep.2017.06.015

32. Zhang J, Zhang Y. Hydrothermal Liquefaction of Microalgae in an Ethanol–Water Co-Solvent To Produce Biocrude Oil. Energy & Fuels. 2014, 28(8): 5178-5183. doi: 10.1021/ef501040j

33. Jena U, Das KC, Kastner JR. Effect of operating conditions of thermochemical liquefaction on biocrude production from Spirulina platensis. Bioresource Technology. 2011, 102(10): 6221-6229. doi: 10.1016/j.biortech.2011.02.057

34. Al-Muntaser AA, Varfolomeev MA, Suwaid MA, et al. Hydrothermal upgrading of heavy oil in the presence of water at sub-critical, near-critical and supercritical conditions. Journal of Petroleum Science and Engineering. 2020, 184: 106592. doi: 10.1016/j.petrol.2019.106592

35. Güngören T, Sağlam M, Yüksel M, et al. Near-Critical and Supercritical Fluid Extraction of Industrial Sewage Sludge. Industrial & Engineering Chemistry Research. 2007, 46(4): 1051-1057. doi: 10.1021/ie0614780

36. Khan MK, Cahyadi HS, Kim SM, et al. Efficient oil recovery from highly stable toxic oily sludge using supercritical water. Fuel. 2019, 235: 460-472. doi: 10.1016/j.fuel.2018.08.003

37. Radfarnia HR, Khulbe C, Little EC. Supercritical water treatment of oil sludge, a viable route to valorize waste oil materials. Fuel. 2015, 159: 653-658. doi: 10.1016/j.fuel.2015.06.094

38. Yeletsky PM, Zaikina OO, Sosnin GA, et al. Heavy oil cracking in the presence of steam and nanodispersed catalysts based on

different metals. Fuel Processing Technology. 2020, 199: 106239. doi: 10.1016/j.fuproc.2019.106239

39. Jocz JN, Thompson LT, Savage PE. Catalyst Oxidation and Dissolution in Supercritical Water. Chemistry of Materials. 2018, 30(4): 1218-1229. doi: 10.1021/acs.chemmater.7b03713

40. Abdpour S, Santos RM. Recent advances in heterogeneous catalysis for supercritical water oxidation/gasification processes: Insight into catalyst development. Process Safety and Environmental Protection. 2021, 149: 169-184. doi: 10.1016/j.psep.2020.10.047

41. Peng P, Guo S, Li L, et al. Supercritical water gasification mechanism of polymer-containing oily sludge. International Journal of Hydrogen Energy. 2021, 46(53): 26834-26847. doi: 10.1016/j.ijhydene.2021.05.161

42. Wang C, Wu C, Zhang H, et al. Hydrothermal treatment of petrochemical sludge in subcritical and supercritical water: Oil phase degradation and syngas production. Chemosphere. 2021, 278: 130392. doi: 10.1016/j.chemosphere.2021.130392

43. Zhang J, Dasgupta A, Chen Z, et al. Supercritical water gasification of phenol over Ni-Ru bimetallic catalysts. Water Research. 2019, 152: 12-20. doi: 10.1016/j.watres.2018.12.030

44. Yuan PQ, Cheng ZM, Zhang XY, et al. Catalytic denitrogenation of hydrocarbons through partial oxidation in supercritical water. Fuel. 2006, 85(3): 367-373. doi: 10.1016/j.fuel.2005.07.006

45. Patwardhan PR, Timko MT, Class CA, et al. Supercritical Water Desulfurization of Organic Sulfides Is Consistent with Free-Radical Kinetics. Energy & Fuels. 2013, 27(10): 6108-6117. doi: 10.1021/ef401150w

46. Kriipsalu M, Marques M, Maastik A. Characterization of oily sludge from a wastewater treatment plant flocculation-flotation unit in a petroleum refinery and its treatment implications. Journal of Material Cycles and Waste Management. 2008, 10(1): 79-86. doi: 10.1007/s10163-007-0188-7

47. Ramaswamy B, Kar DD, De S. A study on recovery of oil from sludge containing oil using froth flotation. Journal of Environmental Management. 2007, 85(1): 150-154. doi: 10.1016/j.jenvman.2006.08.009

48. Liu W, Luo Y, Teng Y, et al. Bioremediation of oily sludge-contaminated soil by stimulating indigenous microbes. Environmental Geochemistry and Health. 2009, 32(1): 23-29. doi: 10.1007/s10653-009-9262-5

49. Biswal BK, Tiwari SN, Mukherji S. Biodegradation of oil in oily sludges from steel mills. Bioresource Technology. 2009, 100(4): 1700-1703. doi: 10.1016/j.biortech.2008.09.037

50. Van Hamme JD, Odumeru JA, Ward OP. Community dynamics of a mixed-bacterial culture growing on petroleum hydrocarbons in batch culture. Canadian Journal of Microbiology. 2000, 46(5): 441-450. doi: 10.1139/w00-013

51. Shi Q, Zhao S, Zhou Y, et al. Development of heavy oil upgrading technologies in China. Reviews in Chemical Engineering. 2019, 36(1): 1-19. doi: 10.1515/revce-2017-0077

52. Lin B, Huang Q, Ali M, et al. Continuous catalytic pyrolysis of oily sludge using U-shape reactor for producing saturates-enriched light oil. Proceedings of the Combustion Institute. 2019, 37(3): 3101-3108. doi: 10.1016/j.proci.2018.05.143

53. Brown TM, Duan P, Savage PE. Hydrothermal Liquefaction and Gasification of Nannochloropsis sp. Energy & Fuels. 2010, 24(6): 3639-3646. doi: 10.1021/ef100203u

54. Ho TC, Qiao L. Competitive adsorption of nitrogen species in HDS: Kinetic characterization of hydrogenation and hydrogenolysis sites. Journal of Catalysis. 2010, 269(2): 291-301. doi: 10.1016/j.jcat.2009.11.012

55. Duan P, Savage PE. Catalytic hydrothermal hydrodenitrogenation of pyridine. Applied Catalysis B: Environmental. 2011, 108-109: 54-60. doi: 10.1016/j.apcatb.2011.08.007

56. Bi QY, Lin JD, Liu YM, et al. Gold supported on zirconia polymorphs for hydrogen generation from formic acid in base-free aqueous medium. Journal of Power Sources. 2016, 328: 463-471. doi: 10.1016/j.jpowsour.2016.08.056

57. Zhang M, Wu Y, Han X, et al. Upgrading pyrolysis oil by catalytic hydrodeoxygenation reaction in supercritical ethanol with different hydrogen sources. Chemical Engineering Journal. 2022, 446: 136952. doi: 10.1016/j.cej.2022.136952

58. Nie R, Tao Y, Nie Y, et al. Recent Advances in Catalytic Transfer Hydrogenation with Formic Acid over Heterogeneous Transition Metal Catalysts. ACS Catalysis. 2021, 11(3): 1071-1095. doi: 10.1021/acscatal.0c04939

59. Liu C, Kong L, Wang Y, et al. Catalytic hydrothermal liquefaction of spirulina to bio-oil in the presence of formic acid over palladium-based catalysts. Algal Research. 2018, 33: 156-164. doi: 10.1016/j.algal.2018.05.012

60. Li G, Yang H, Zhang H, et al. Encapsulation of nonprecious metal into ordered mesoporous n-doped carbon for efficient quinoline transfer hydrogenation with formic acid. ACS Catalysis. 2018, 8(9): 8396-8405. doi: 10.1021/acscatal.8b01404

61. Guo Y, Liu X, Duan P, et al. Catalytic Hydrodenitrogenation of Pyridine under Hydrothermal Conditions: A Comprehensive Study. ACS Sustainable Chemistry & Engineering. 2020, 9(1): 362-374. doi: 10.1021/acssuschemeng.0c07389

62. Wang H, Liang C, Prins R. Hydrodenitrogenation of 2-methylpyridine and its intermediates 2-methylpiperidine and tetrahydro-

methylpyridine over sulfided NiMo/γ-Al₂O₃. Journal of Catalysis. 2007, 251(2): 295-306. doi: 10.1016/j.jcat.2007.08.005

63. Katritzky AR, Shipkova PA, Allin SM, et al. Aqueous High-Temperature Chemistry. 24. Nitrogen-Containing Heterocycles in Supercritical Water at 460 °C. Energy & Fuels. 1995, 9(4): 580-589. doi: 10.1021/ef00052a003

64. Luo L, Liu S, Liu C, et al. High Yield of Hydrocarbons from Catalytic Hydrodenitrogenation of Indole under Hydrothermal Conditions. Energy & Fuels. 2017, 31(11): 12594-12602. doi: 10.1021/acs.energyfuels.7b02322

65. Guo Y, Wang S, Yeh T, et al. Catalytic gasification of indole in supercritical water. Applied Catalysis B: Environmental. 2015, 166-167: 202-210. doi: 10.1016/j.apcatb.2014.11.033

66. Guo Y, He H, Liu X, et al. Ring-opening and hydrodenitrogenation of indole under hydrothermal conditions over Ni, Pt, Ru, and Ni-Ru bimetallic catalysts. Chemical Engineering Journal. 2021, 406: 126853. doi: 10.1016/j.cej.2020.126853

67. Nguyen MT, Tayakout-Fayolle M, Chainet F, et al. Use of kinetic modeling for investigating support acidity effects of NiMo sulfide catalysts on quinoline hydrodenitrogenation. Applied Catalysis A: General. 2017, 530: 132-144. doi: 10.1016/j.apcata.2016.11.015

68. He F, Wang J, Li Y, et al. Quantum Chemistry Calculations on the Mechanism of Isoquinoline Ring-Opening and Denitrogenation in Supercritical Water. Industrial & Engineering Chemistry Research. 2017, 56(7): 1782-1790. doi: 10.1021/acs.iecr.7b00307

69. Tian S, Li X, Wang A, et al. Hydrodenitrogenation of Quinoline and Decahydroquinoline Over a Surface Nickel Phosphosulfide Phase. Catalysis Letters. 2018, 148(6): 1579-1588. doi: 10.1007/s10562-018-2370-z

70. Xie D, Liu X, Lv H, et al. Products, pathways, and kinetics for catalytic hydrodenitrogenation of quinoline in hydrothermal condition. The Journal of Supercritical Fluids. 2022, 182: 105509. doi: 10.1016/j.supflu.2021.105509

71. Girgis MJ, Gates BC. Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing. Industrial & Engineering Chemistry Research. 1991, 30(9): 2021-2058. doi: 10.1021/ie00057a001

72. Adschiri T, Shibata R, Sato T, et al. Catalytic Hydrodesulfurization of Dibenzothiophene through Partial Oxidation and a Water−Gas Shift Reaction in Supercritical Water. Industrial & Engineering Chemistry Research. 1998, 37(7): 2634-2638. doi: 10.1021/ie970751i

73. Massoth FE, Kim SC. Kinetics of the HDN of Quinoline under Vapor-Phase Conditions. Industrial & Engineering Chemistry Research. 2003, 42(5): 1011-1022. doi: 10.1021/ie020390t

74. Duan P, Savage PE. Catalytic treatment of crude algal bio-oil in supercritical water: optimization studies. Energy & Environmental Science. 2011, 4(4): 1447. doi: 10.1039/c0ee00343c

75. Bowker RH, Ilic B, Carrillo BA, et al. Carbazole hydrodenitrogenation over nickel phosphide and Ni-rich bimetallic phosphide catalysts. Applied Catalysis A: General. 2014, 482: 221-230. doi: 10.1016/j.apcata.2014.05.026

76. Li X, Bai J, Wang A, et al. Hydrodesulfurization of Dibenzothiophene and its Hydrogenated Intermediates Over Bulk Ni2P. Topics in Catalysis. 2011, 54(5-7): 290-298. doi: 10.1007/s11244-011-9663-4

77. Shen Z, Ke M, Yu P, et al. Catalytic activities of Mo-modified Ni/Al2O3 catalysts for thioetherification of mercaptans and di-olefins in fluid catalytic cracking naphtha. Transition Metal Chemistry. 2012, 37(6): 587-593. doi: 10.1007/s11243-012-9625-0

78. Kordouli E, Pawelec B, Kordulis C, et al. Hydrodeoxygenation of phenol on bifunctional Ni-based catalysts: Effects of Mo promotion and support. Applied Catalysis B: Environmental. 2018, 238: 147-160. doi: 10.1016/j.apcatb.2018.07.012

79. Liu Q, Wang S, Zhao G, et al. CO2 methanation over ordered mesoporous NiRu-doped CaO-Al2O3 nanocomposites with enhanced catalytic performance. International Journal of Hydrogen Energy. 2018, 43(1): 239-250. doi: 10.1016/j.ijhydene.2017.11.052

80. Duan P, Savage PE. Hydrothermal Liquefaction of a Microalga with Heterogeneous Catalysts. Industrial & Engineering Chemistry Research. 2010, 50(1): 52-61. doi: 10.1021/ie100758s

81. Li H, Hu J, Zhang Z, et al. Insight into the effect of hydrogenation on efficiency of hydrothermal liquefaction and physico-chemical properties of biocrude oil. Bioresource Technology. 2014, 163: 143-151. doi: 10.1016/j.biortech.2014.04.015

82. Rinaldi N, Usman, Al-Dalama K, et al. Preparation of Co–Mo/B2O3/Al2O3 catalysts for hydrodesulfurization: Effect of citric acid addition. Applied Catalysis A: General. 2009, 360(2): 130-136. doi: 10.1016/j.apcata.2009.03.006

83. Gong S, Shinozaki A, Qian EW. Role of Support in Hydrotreatment of Jatropha Oil over Sulfided NiMo Catalysts. Industrial & Engineering Chemistry Research. 2012, 51(43): 13953-13960. doi: 10.1021/ie301204u

84. Han Y, Gholizadeh M, Tran CC, et al. Hydrotreatment of pyrolysis bio-oil: A review. Fuel Processing Technology. 2019, 195: 106140. doi: 10.1016/j.fuproc.2019.106140

85. Snåre M, Kubičková I, Mäki-Arvela P, et al. Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons. Fuel. 2008, 87(6): 933-945. doi: 10.1016/j.fuel.2007.06.006

86. Duan P, Savage PE. Catalytic treatment of crude algal bio-oil in supercritical water: Optimization studies. Energy & Environmental Science. 2011, 4: 1447-1456. doi: 10.1039/C0EE00343C

87. Eijsbouts S. The effect of phosphate on the hydrodenitrogenation activity and selectivity of alumina-supported sulfided Mo, Ni, and Ni-Mo catalysts. Journal of Catalysis. 1991, 131(2): 412-432. doi: 10.1016/0021-9517(91)90276-a

88. Rayo P, Ramírez J, Torres-Mancera P, et al. Hydrodesulfurization and hydrocracking of Maya crude with P-modified NiMo/Al2O3 catalysts. Fuel. 2012, 100: 34-42. doi: 10.1016/j.fuel.2011.12.004

89. Furimsky E, Massoth FE. Hydrodenitrogenation of Petroleum. Catalysis Reviews. 2005, 47(3): 297-489. doi: 10.1081/cr-200057492

90. Lee YK, Oyama ST. Sulfur resistant nature of Ni2P catalyst in deep hydrodesulfurization. Applied Catalysis A: General. 2017, 548: 103-113. doi: 10.1016/j.apcata.2017.06.035

91. Peroni M, Lee I, Huang X, et al. Deoxygenation of Palmitic Acid on Unsupported Transition-Metal Phosphides. ACS Catalysis. 2017, 7(9): 6331-6341. doi: 10.1021/acscatal.7b01294

92. Carenco S, Leyva-Pérez A, Concepción P, et al. Nickel phosphide nanocatalysts for the chemoselective hydrogenation of alkynes. Nano Today. 2012, 7(1): 21-28. doi: 10.1016/j.nantod.2011.12.003

93. Popczun EJ, McKone JR, Read CG, et al. Nanostructured Nickel Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction. Journal of the American Chemical Society. 2013, 135(25): 9267-9270. doi: 10.1021/ja403440e

94. Maity S, Flores G, Ancheyta J, et al. Effect of preparation methods and content of phosphorus on hydrotreating activity. Catalysis Today. 2008, 130(2-4): 374-381. doi: 10.1016/j.cattod.2007.10.100

95. Zhao Y. Mechanisms of the hydrodenitrogenation of alkylamines with secondary and tertiary α-carbon atoms on sulfided NiMo/Al2O3. Journal of Catalysis. 2004, 222(2): 532-544. doi: 10.1016/j.jcat.2003.12.013

96. Gutiérrez OY, Hrabar A, Hein J, et al. Ring opening of 1,2,3,4-tetrahydroquinoline and decahydroquinoline on MoS_2/γ-Al_2O_3 and Ni–$MoS2/\gamma$-Al_2O_3. Journal of Catalysis. 2012, 295: 155-168. doi: 10.1016/j.jcat.2012.08.003

97. Li Z, Savage PE. Feedstocks for fuels and chemicals from algae: Treatment of crude bio-oil over HZSM-5. Algal Research. 2013, 2(2): 154-163. doi: 10.1016/j.algal.2013.01.003

98. Ormsby R, Kastner JR, Miller J. Hemicellulose hydrolysis using solid acid catalysts generated from biochar. Catalysis Today. 2012, 190(1): 89-97. doi: 10.1016/j.cattod.2012.02.050

99. Wang B, He Z, Zhang B, et al. Study on hydrothermal liquefaction of spirulina platensis using biochar based catalysts to produce bio-oil. Energy. 2021, 230: 120733. doi: 10.1016/j.energy.2021.120733

100. Kambo HS, Dutta A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. Renewable and Sustainable Energy Reviews. 2015, 45: 359-378. doi: 10.1016/j.rser.2015.01.050

101. Azizi N, Ali SA, Alhooshani K, et al. Hydrotreating of light cycle oil over NiMo and CoMo catalysts with different supports. Fuel Processing Technology. 2013, 109: 172-178. doi: 10.1016/j.fuproc.2012.11.001