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Hydrothermal liquefaction of algae and bio-oil upgrading into liquid fuels: Role of heterogeneous catalysts

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ABSTRACT

The numerous challenges attributed to fossil fuels and the transformation of food crops for energy production necessitate the search for better energy options. Algae valorization via liquefaction under hydrothermal conditions is one of the re-ignited areas of interest for liquid fuels production. Their cultivation and processing feasibilities could infer good benefits for future energy sustainability. The paper explored the role of catalytic systems, especially the heterogeneous catalysts during the liquefaction process. Solid catalysts such as supported metals, zeolites and silica-alumina are so far given preference as catalytic materials for improving bio-oil and associated hydrocarbon fuels yields. The paper therefore analyzed critical literature on the process catalysis and simultaneously discussed new directions for further investigations.

1. Introduction

The fossil fuels are composed of those categories of fuels derived from decayed plants and animals over many centuries (usually many million years). There are indications that these non-renewable fuels being used globally today have their initial formation stages traced to the geological Carboniferous Period [1–3]. Since many decades, the world population relied on these fossil fuels for the production of transportation, industrial and household fuels and petrochemicals. In fact, there are indications that up to 90% of global energy relied on the fossil fuels [4,5]. However, the numerous problems associated with the fossil fuels exploration and utilization have accounted for the search for new, reliable and better options [6,7].

Among the major identified challenges, environmental pollution is a forefront issue. Right from the production fields (i.e. oil and gas fields), spillage of the crude oil products into the marine habitats have caused serious concerns over the years [8,9]. Thousands of tonnes of oil have been spilled into the marine and nearby terrestrial areas, damaging agricultural land (see Fig. 1), killing aquatic habitats and in some instances rendering the fresh water unsuitable for human consumption [10–12]. Gas flaring and combustion of the refined crude oil fuels on the other hand emit serious environmental pollutants. The emissions of CO_2 and CH_4 as well as hydrogen sulfide, nitrous oxide and polyaromatic hydrocarbons are very dangerous for the planet (i.e. earth) [13]. The global warming problems are associated with these emissions and are with continuous effect of global degradation [14,15]. The agricultural lands are poorly yielding, plant and animal species are going into extinction, the level of sea ice is declining and the marine organisms are suffering [16,17]. Human exposures to some of the pollutant gases are associated with serious health degradation including the development of cancer and psychological disorders [18–20].

In addition to the environmental pollution problems, the fossil fuels are declining in reserves in most depositing areas (see Fig. 2) [21,22]. They are similarly unevenly distributed (i.e. large deposits in some regions with little or no deposits in other regions). According to the statistical information recently published by British Petroleum (BP), the total world reserves of fossil fuels are 1688 bbl, 186tcm and 892 bt of crude oil, natural gas and coal, respectively [23]. The crude oil in particular is expected to be completely exhausted by 2067, whereas the natural gas by 2069. In fact, the disadvantages of fossil fuels are too numerous and very dangerous for global sustenance.

The shift to biofuel alternatives have in the recent years became an important issue of interest in the world [24,25]. Their environmental sustainability, abundance, distribution pattern and processing feasibilities have accounted for their strong potentials as fuels for the future [26]. Like the fossil fuels, biofuels can be derived in the liquid, solid and gaseous forms for various household and industrial applications [27,28]. They can be utilized in existing infrastructure and automobiles without the need for re-configuration [29]. They are not associated with destruction to marine organisms because biomass would be produced and processed into fuels using 100% onshore infrastructure. Similarly, the issue of gas flaring can be eradicated completely. However, the used

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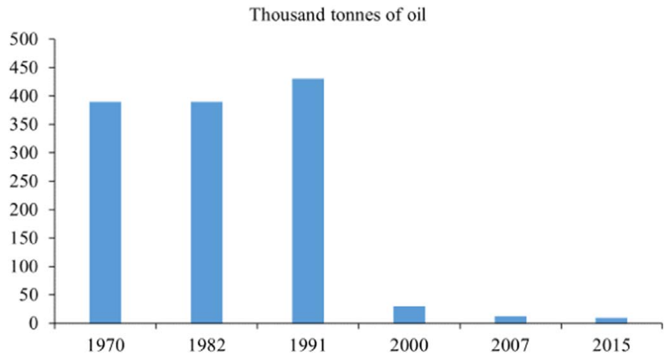

Fig. 1. Thousands of tons of oil spill into the environment over the years 1970–2015). Data source from ITOPF. Ref: [19].

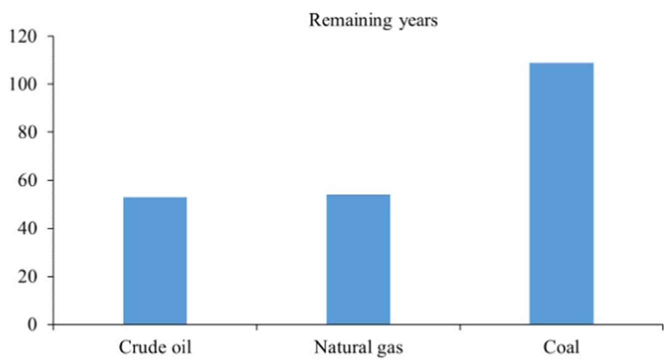

Fig. 2. Estimated period (in years) for exhausting the remaining reserves of fossil fuels from 2014. Data sourced from BP. Ref: [21].

of edible biomass feedstock (e.g. vegetable oils, corns and cereals) for the biofuels production had been classified as unsustainable due to possibility of hunger and price control challenges [30,31]. Therefore, a shift to non-edible sources would be the most appropriate choice. There is in the recent times a special consideration for algae and algae-biomass as the affordable sources of biofuels. This can be attributed certain considerable advantages [32]. Algae species could be cultivated throughout the year, and are similarly higher yielding in terms of oil composition. For example, the yielding biodiesel potential of algae oil is 12,000 l/ha compared to 1190 l/ha for the best vegetable oil crop [33]. The ability of the algae species to be grown, requiring lesser water supply, implies a positive advantage for freshwater conservations when compared to the situation involving seed crops [34]. Similarly, algae species can be cultivated even in brackish water (i.e. salty waters) producing commercially good yields. Another important environmental benefit is the ability of the algae species to fix CO_2 gas and prevent it from escalating the problems of global warning [35,36].

The advantages identified above are certainly crucial for the current and future world generations that are already into energy and environmental crisis. To this scale, authors have studied the upgrading of algae and algae-biomass into different fuel products under different conditions, especially for the production of biodiesel and biogas [37–42]. However, catalytic thermal liquefaction is a recent issue of interest.

1.1. Objectives of the review

The main objective of the current paper was to review a wide range of literature on the progress made regarding the exploitation of algae as sources of fuels (i.e. both liquid and gaseous fuels). Therefore, details on the biofuels potentials of algae were first presented in Section 2, and in the subsequent sections emphasis was given to the role of catalysts and catalytic parameters during algae liquefaction into liquid fuels (i.e. gasoline, diesel and jet) via hydrothermal process. We have carefully identified and analyses literature on heterogeneous catalyst systems preferentially due to their advantages that include availability, reusability and established prospects in biogas, biodiesel and bioethanol production from biomass substrates. Post-liquefaction valorization of algae-based bio-oil was also substantially covered. The ability of the heterogeneous catalyst systems to produce hydrocarbon compounds (including the gasoline scale BTEX aromatics) that are in the fuels range was the central focus of the paper. The paper simultaneously identified and discussed areas requiring further investigations for the benefit of other researchers in the field.

2. Biofuels potential of algae

Algae are commonly described as non-flowering plants that are mostly found in aquatic environment. However, they can be cultivated in almost all the types on environments suitable and no-suitable for agricultural crops production [43]. The algae species, which could be multi- or singled-cell organisms are characterized by chlorophyll like other plant species, but are lacking in some features like true stems and vascular tissues. The diversity of the algae species (i.e. millions of species) is a forefront issue in realizing their potentials in addressing the challenges of environment and fuels production facing the world today. The marine algae are accounting for the fixation of at least 40% of CO_2 gas through the carbon fixation cycle [44,45]. They are similarly very fast growing plants [46]. In fact, there are evidences that the average growth rate for algae is more than twice that of most other biofuel-crops. They possessed 20–50% of extractable oil that can be upgraded into biodiesel with less-difficulty [47,48]. Some dry algae biomass can possess more than 50% of long-chained hydrocarbons that can be processed into gasoline, diesel or even the jet fuels [49]. Fig. 3 provides a schematic representation of some of the fundamental routes for algae valorization. After development of the suitable algae strains for production and harvesting, the derived algae species are subjected to extraction and refining processes for the production of liquid fuels. The residues can also be transformed into biogas or utilized as feed for animals.

Recent studies have documented a good prospect for the algae species (i.e. both macro- and micro-alage) as biodiesel feedstock, especially due to high lipid content and economics of production. A model study by Speranza et al. [50], demonstrated that algae cultivation for biodiesel production had been economically very profitable for countries in the Europe, USA and Brazil. They found the production efficiency to range between 90% and 100%. Similarly, the production was projected to be successful without recourse to the food land. Similar findings were also reported by other authors from many parts of the world, including the African countries [51–56]. An acid-catalyzed upgrading of oil extracted from algae species (*Spirulina*sp. and *Chlorella*sp.) with H_2SO_4 as catalyst at 60 °C for a period of 1 h by Nautiyal et al. [57] showed that up to 80% yield of biodiesel could be achieved. Chen and co-workers [58] found 62% yield of oil from *Scenedesmus* sp. when transesterified with KOH as catalyst at 65 °C. The biodiesel yield reached 100% within 30 min of reaction period. Infact, the

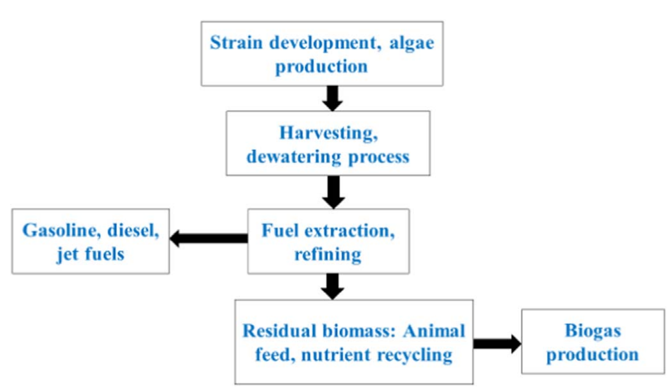

Fig. 3. Routes for algae valorization into biofuels and useful residues.