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Upgrading blends of microalgae feedstocks and heavy oils in supercritical water

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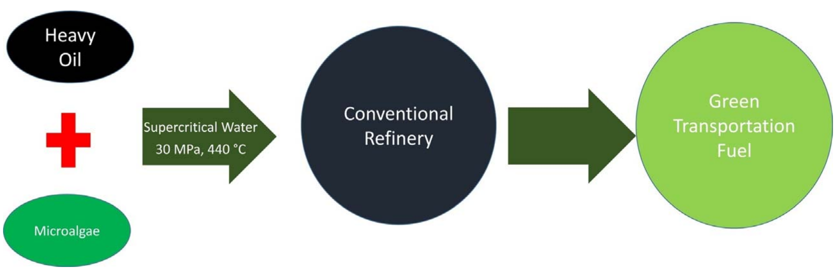
GRAPHICAL ABSTRACT



ABSTRACT

Upgrading of bitumen blended with microalgae *Chlorella vulgaris* was investigated in supercritical water (SCW) at 440 °C and 30 MPa in a home-made batch type bomb reactor. The effects of the water/feed ratio ranging from 2 to 10 and the effects of microalgae fraction in the feeds ranging from 0 (pure bitumen) to 100 wt.% (pure microalgae) were investigated. Pyrolysis experiments in the absence of water were also performed at the same conditions. SCW was found to suppress the coke formation. 25 wt.% microalgae addition to bitumen increased VR conversion 20% with a considerable increase in gas content and diesel yield. Increasing microalgae fraction in the feed to 50 wt.% resulted in increased light liquid yields due to increasing conversion of VR and also led to undesired increases in coke and gas formation. Water/feed ratio of 10 led to increased gas yields with a lower VR conversion.

1. Introduction

Volatile and unpredictable oil prices, primarily due to political factors, are forcing energy policy makers as well as industry to focus on both alternative energy conversion technologies and sustainable feedstocks for energy security. Brent crude oil prices, for example, have fluctuated in a wide range of 40–150 $/barrel with sharp drops and escalations since 2008 [1]. In addition to unstable crude oil prices, there is a continuous increase in the world energy demand accompanied by a sharp decrease in the amount of available light crude oil resources [2]. One third of world's recoverable oil reserves are in some form of heavy oil [3]. Therefore, there is an emerging need to develop alternative oil upgrading technologies with high conversion and improved selectivity towards lighter compounds which are paraffins having high hydrogen to carbon ratios (H/C) and short chain length aliphatic compounds. The value of 2 for H/C suggests high amount of

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light compounds while those approaching to 1 are an indication of unsaturated, heavy and multi-ring aromatic compounds in hydrocarbon mixtures. Knowing the fact that oil streams are complex mixtures, the tendency of being light is measured by the boiling point distribution of the inner compounds (cuts) existing in crude mixtures. Practically the distilled compounds having low boiling points around 200 °C may fall into both gasoline or diesel pools in oil refineries, while those above 350 °C are even out of the heavy diesel pool range.

Moreover, the energy supplied from biobased resources is expected to increase and 27% of transportation fuel could be provided by biofuels by 2050 [4]. Current regulations on greenhouse gas emissions require blending of fossil fuels with biofuels such as bioethanol or biodiesel produced from renewable sources such as sugar cane, corn and various vegetable oils [5]. However, using such edible feedstocks for biofuel production has raised a lot of concerns about food security and arable land conservation [6]. Moreover, it has even been suggested that corn-based ethanol will increase greenhouse gas emissions due to converting forests and grassland into biofuel factories and thus eliminating positive contribution of these lands to carbon dioxide fixation [7]. Microalgae based biofuels, on the other hand, have potential to overcome these concerns. Microalgae which are unicellular, phototrophic microorganisms can be cultivated in saline and waste water, on non-arable land without competing with agricultural crops [8]. Therefore, it may be advantageous to blend biodiesel produced from oil extracted from microalgae or bioethanol produced by fermentation of microalgae with fossil fuels. An alternative would be to use microalgae directly as a refinery feedstock in the conventional refineries. Microalgae can be directly processed together with conventional hydrocarbon feedstocks in existing refineries resulting in fuels, a fraction of which is derived from biomass. Moreover, the components of microalgae such as proteins and carbohydrates can also be converted into useful fuels with improved yields [9]. However, direct utilization of microalgae feedstocks in the existing refinery operations is problematic due to high oxygen, nitrogen and sulfur content of microalgae. Undesired gum formation may occur due to high oxygen content of microalgae whereas high nitrogen and sulfur content of microalgae may lead to the deactivation of the catalyst in hydrocracking unit (HYCU) by exceeding the allowable nitrogen and sulfur limit in the feedstock of HYCU [10]. Therefore, innovative schemes are required for processing of microalgae in refineries.

Supercritical fluids (SCFs) as a reaction medium, on the other hand, possess tunable solvent properties and might provide processing alternatives for refining operations. Mass transfer limitations can be eliminated in some processes by using SCFs since diffusivity of compounds is higher in supercritical fluids than in conventional solvents [11]. Supercritical water (SCW) among other SCFs is the most suitable one for oil upgrading purposes with the critical temperature and pressure of 374 °C and 22.1 MPa, respectively. Under supercritical conditions, the properties of water start to resemble that of hydrocarbons making it an excellent solvent for organic compounds. Increased ionic product of water leads to increased $[H_3O^+]$ concentration and thus promotes the reactions requiring the addition of an acid when the reactions are performed under near critical water. Low dielectric constant and accompanying solvation power enables extraction of lighter compounds while increased hydronium ion concentration makes reactive extractions of heavy hydrocarbons possible. In addition, SCW can form layers between asphaltene micelles and suppress the formation of coke, an undesired by product of refineries' upgrading units [11,12]. Based on the experimental findings, for example, it was suggests that SCW is not only useful for the rapidly transfer (dissolution and diffusion) of newly formed light liquid products towards SCW phase but also for the dispersion of asphalthene micro-emulsions enabling coke suppression, higher surface and reaction area and improved liquid yield [13]. Heavy oil upgrading with SCW was studied by several authors with promising results and optimum process conditions were determined to be around 25–30 MPa and 420–440 °C with varying water/heavy oil ratios [14–16]. Similarly, there are numerous studies including production/upgrading of microalgae based biofuels by using SCW processing [17–20]. Hydrothermal gasification of microalgae at supercritical conditions results in production of a combustible gas mixture consisting of methane and hydrogen by successfully breaking the C—C bonds within microalgae [21]. Several authors [22,23] reported that an increase in temperature resulted in higher gas yields. Effect of water/microalgae ratio on gas yield was also investigated and lower microalgae loading was found to increase gas yield [17]. For understanding the reaction mechanisms involved in upgrading of microalgae, decomposition of long chain saturated fatty acids which are present in microalgae was investigated in SCW environment at 400 °C and alkene production was observed [24]. Upgrading of algal bio-oil produced from hydrothermal liquefaction was also carried out in SCW at 400 °C in the presence of hydrogen with and without catalyst. Improved bio-oil quality as well as coke and gas formation were reported [19]. The process is also attractive since it reduces the costs associated with the energy-intensive drying step. For hydrothermal gasification, slurries of microalgae can be used directly or after removal of some water. The studies in the literature indicate that operating conditions for hydrothermal gasification are 400–700 °C and 25–30 MPa which intersects with the conditions of bitumen upgrading in SCW [25]. In view of such information, it may be advantageous to blend microalgae into conventional heavy oil fractions of refinery such as bitumen. Prospective algae farms can be constructed next to refineries and microalgae can use CO_2 emission of refineries as the carbon source since it has been demonstrated that microalgae can utilize CO_2 from industrial exhaust gases containing 10–20% CO_2 [26]. Using existing infrastructure of refineries as much as possible eliminates high capital investment of microalgae processing. Aqueous phase obtained after supercritical water processing is expected to include nutrients for microalgae cultivation such as ammonium, sodium, potassium which can be recycled to growth media bringing economic benefits [21]. However, it is possible that the aqueous phase may contain toxic compounds which may require further treatment before recycling. Despite such advantages, to the best of our knowledge, there is no study investigating upgrading of bitumen blended with microalgae in SCW.

Among a vast variety of microalgae species, fast growth rate of *Chlorella vulgaris* makes it a very promising candidate for biofuel production [27]. Moreover, commercial large scale cultivation of *Chlorella vulgaris* is performed in many countries in cost effective open ponds enabling high volume applications.

In this study, upgrading of mixtures of microalgae, *Chlorella vulgaris,* with bitumen in SCW was investigated at 440 °C and 30 MPa with water/feed ratios ranging from 2 to 10. Operating conditions were selected by considering optimum conditions for bitumen upgrading. Selected temperature was also close to optimum temperature (430 °C) determined for upgrading of algal oil with SCW with a product having lower oxygen, nitrogen and sulfur content as well as higher heating value [28]. Pyrolysis of pure bitumen and pure microalgae were also studied in the absence of supercritical water for comparison purposes. Morphological analysis of coke samples obtained after upgrading were performed by SEM-EDX analysis to compare conventional and SCW upgrading in terms of type of coke formation.

2. Experimental section

Bitumen was kindly provided by Turkish Petroleum Refineries Corporation (Tüpras).

The SARA (Saturate-Aromatics-Resins-Asphalthenes) fraction of the bitumen like heavy oil feeds was determined, firstly, by removing the maltene (*n*-heptane soluble fraction, i.e. Saturate-Aromatic-Resin groups) from asphaltene (*n*-heptane insoluble fraction) by soxhlet extraction. To remove saturates from the maltene fraction, 5% maltene – heptane solution was prepared. A glass column of length of ~1 m was filled with silica and washed with heptane. Then, 5% maltene – heptane