ASEAN Journal for Science and Engineering in Materials

Journal homepage: https://ejournal.bumipublikasinusantara.id/index.php/ajsem

Uncovering the Full Potential Utilization of Petroleum Reserves Residue for Sustainable Energy Supply

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ABSTRACT

In the framework of international efforts to achieve carbon neutrality, this research investigates the potential of petroleum reserve residue as a sustainable energy source, focusing on unconventional crude oils. The discovery of alternative resources, such as bitumen, heavy crudes, and high-acid crudes—which combined make up almost two-thirds of the world's oil reserves—has become necessary due to the depletion of traditional oil stocks. This study looks at the difficulties in processing these non-conventional oils, especially their high acidity, which poses environmental risks and severely corrodes refinery equipment. The article discusses a revolutionary method for upgrading and treating these unconventional crudes without the need for external catalysts or molecular hydrogen, utilizing supercritical fluids (supercritical methanol and water). The evaluation emphasizes how well this process works to produce synthetic crude oil that is appropriate for use in refineries that are currently in operation by lowering asphaltenes, contaminants, and total acid numbers (TAN). There are suggestions for more study into low-temperature, low-pressure catalytic alternatives, although the economic feasibility of high-temperature, high-pressure processes is questioned. One important step in striking a balance between technical growth and environmental preservation is the emphasis on the potential of this methodology in promoting sustainable energy production and lowering environmental pollution.

ARTICLE INFO

Article History:

Submitted/Received 02 Jun 2024
First Revised 29 Jul 2024
Accepted 09 Sep 2024
First Available online 10 Sep 2024
Publication Date 01 Mar 2025

Keyword:

Supercritical fluids,
Sustainable energy,
Total Acid Number (TAN),
Unconventional crude oils.

1. INTRODUCTION

Energy and the environment are becoming increasingly a concern not only for researchers and industrialists but also for all living organisms in this ecosystem (Raihan et al., 2022; Buechler & Martinez, 2021). The temperature increase nowadays is a serious threat with news of many deaths every day in hotter areas because of climate change. Now there is a dire need to take some steps on an emergency basis to save living organisms and human beings from this burning situation (Ahmed et al., 2024; Asif et al., 2023; Asif et al., 2022). The worldwide average atmospheric CO2 concentration rose from 285 ppm in 1850 to 424 ppm by 2024 (Chen, 2021). From 1850 to 2024, the worldwide average surface temperature rose 1.2 °C (McCulloch et al., 2024). Even if we stop carbon emissions immediately, the greenhouse effect from extra CO2 in the atmosphere will warm the Earth. Carbon neutrality by 2050 aims to restrict temperature rise to 1.5–2.0 °C from preindustrial levels. Moreover, as a result of global warming, the sea level might increase up to 0.3–1.5 m at a different area of different coastal areas depending on the fossil fuel emissions. The absolute change in the energy and rapid decrease in carbon emissions can also result from many other problems such as deficiency of infrastructure, cost management, resources management, and huge manpower consumption because of the lack of automation setup. So, on an emergency basis, we need to introduce an energy mix that can overcome this issue without disturbing the sustainable development process and reducing environmental pollution (Asif et al., 2020; Hassan et al., 2023; Kareem et al., 2022).

Carbon neutrality can reduce global warming and solve our energy crisis, with accompanying benefits to air quality, ecological recovery, and the beauty of the landscape (Zhao et al., 2022). It may, therefore, be regarded as an industrial revolution that would mark an important milestone in human development. Following the previous four industrial revolutions, carbon neutrality could be the fifth revolution in the history of mankind as shown in **Figure 1**. These industrial revolutions raised living standards but depleted natural resources, many of which are non-renewable. Our use of fossil fuels, which causes global warming and environmental destruction (Asif et al., 2023; Asif et al., 2021), is at the heart of the human-nature conflict (Asif et al., 2024; Donald et al., 2022; Khan et al., 2024). However, it is imperative to use depleting crude oil reserves to maintain the life cycle of human beings. To replace conventional fuel, unconventional and heavy crude oil are also important to maintain the energy balance between technological advancement and environmental disorder (Khan et al., 2017; Khan et al., 2019). Moreover, new technologies such as green hydrogen production (Sharma et al., 2024; Shen et al., 2024; Asif et al., 2023), renewable energy technologies (Batel, 2020; Suman, 2021; ALevenda et al., 2021) , energy devices (Liang et al., 2021; Olabi et al., 2022; Chen et al., 2020), nuclear energy (Kim et al., 2022), Fuel cells (Pramuanjaroenkij & Kakac, 2023; Kahraman & Akin, 2024; Zhang et al., 2024), and waste-to-energy (Rubio-Jimenez et al., 2023; Ahmad et al., 2024) are important areas for energy production to mitigate greenhouse gas emissions (Al Khourdajie et al., 2024).

The global endeavors to neutralize carbon may be the largest ever. This is a sign of international social development but also a desperate attempt to protect ourselves from our own mistakes. The fruitful discussion of many experts and from our point of view, there should be three areas which need to be focused and commercialized. The first one could be carbon capture and conversion technologies which can reduce CO2 emissions and replace fossil fuel consumption (Talapaneni et al., 2020; Shao et al., 2022; Podder et al., 2023; Xia et al., 2023). The second option could be the complete utilization of explored and extracted fossil fuel resources. Opening a new exploration and extraction site for fossil fuel may emit a

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

huge amount of global warming gases. So already extraction-initiated fossil fuel sites should be utilized with their full potential and many fractions of such crude oil should be processed and converted into commercial products and fuel through proper processing and hydrogenation (Hosseini et al., 2021; Isaac et al., 2022).

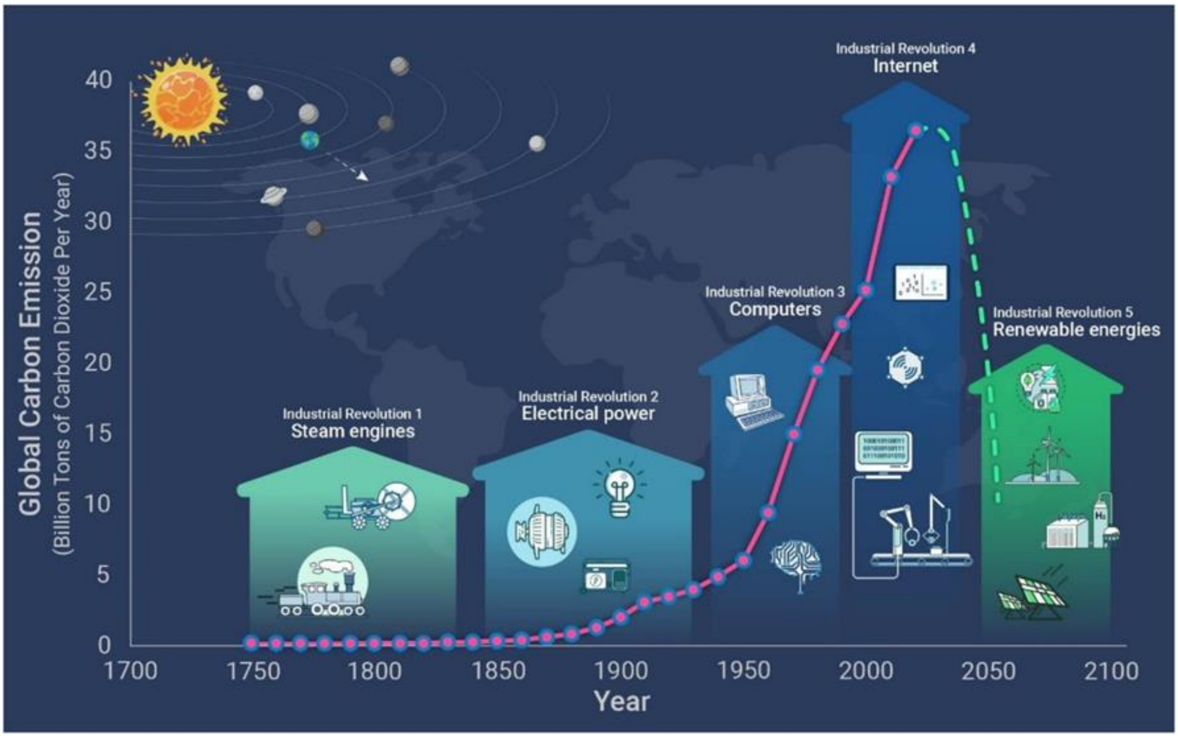

Figure 1. The Industrial Revolution from 1750 to 2100, showed renewable energy might be the fifth industrial revolution to mitigate global warming globally (Chen, 2021).

2. METHODS

This study is a literature review, in which the data was obtained from literature in international journals. We selected the data, analyzed it, summarized, and concluded to construct the paper.

3. RESULTS AND DISCUSSION

Unconventional crude oils are a viable alternative that can be utilized to satisfy the growing need for energy and fuel on a global scale, as well as to locate more cost-effective resources. Because of the rapid depletion of conventional oil reserves, the utilization of unconventional crude oils, such as high acid crudes, heavy and extra-heavy crudes, and bitumen, which account for about two-thirds of the total oil reserves in the world, is an alternative that has a great deal of promise (Khan et al., 2017). When it comes to the recovery, transportation, and treatment of existing refineries, one of the most significant challenges is the easy formation of a multiphase complex layer at the interface between the oil and water phases. This layer is also referred to as oily sludge, petroleum emulsion, or rag layer. The existence of intrinsic naphthenic acid, also known as carboxylic acid, is the cause of the high acidity of petroleum emulsions and high acid crudes (Khan et al., 2017). These acids are particularly damaging to the equipment used in refineries, as well as to the environment and aquatic species inside it.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

An approach that is safe for the environment and makes use of supercritical fluids (supercritical methanol and supercritical water) has been developed for demulsifying and treating highly intractable petroleum emulsions and unconventional crude oils as shown in **Figure 2a.** These types of crude oils contain hazardous acidic compounds, heavy fractions, heteroatoms, and metallic impurities. Through this method, there is no requirement for the utilization of molecular hydrogen or external catalysts. Because of its low asphaltene fractions and low quantities of impurities, the synthetic crude oil that is produced from both feedstocks has the potential to be suitable for use in petroleum refineries that are under operation at present (Kwek et al., 2017; Kwek et al., 2018; Khan et al., 2019).

High acid crudes contain significant quantities of naphthenic acids (NAs), which are directly responsible for the severe corrosion that occurs in oil refinery equipment as well as the considerable environmental issues that arise. The primary objective of the initial research was to devise a method that utilizes non-catalytic supercritical methanol (scMeOH) for the efficient deacidification of NA mixes and high-acid crude petroleum products (Khan et al., 2016). At a temperature of 400°C, the efficiency was in the range of 92-97% in terms of the total acid number (TAN). Several model compounds, including hexadecenoic acid, octadecanoic acid, and 2-naphthoic acid, were subjected to treatment in the presence of supercritical methanol (scMeOH) and supercritical water (scH2O), to gain an understanding of the process behind the decrease of TAN. With the assistance of DFT calculations, it was shown that the esterification and thermal decarboxylation reactions were the most important reaction pathways in scMeOH and scH2O, respectively. In addition, several studies investigated the possibility of upgrading unconventional crude oils and extra heavy fractions by employing supercritical methanol (scMeOH) and contrasting it with upgrading techniques that are based on supercritical water (scH2O) and pyrolytic upgrading. Using high-acid crude oils (Laguna and Bachaquero-13), a heavy crude oil (Rubiales), and a vacuum tower bottom (VTB), the yields and qualities of upgraded oil are investigated as functions of operational parameters (temperature, pressure, and concentration). Additionally, feedstocks for upgraded oil are also investigated as shown in **Figure 2b**. By upgrading unconventional crude oils with scMeOH at a temperature of 400°C and a pressure of 30 MPa, the asphaltene component of these oils was efficiently decreased to ~0%, while the naphtha-diesel fraction was enhanced to between 30 and 40 wt%. On the other hand, oil upgrades that utilized scH2O and pyrolysis exhibited a significant quantity of asphaltenes, which ranged from 8.8 to 10.0 wt%.

The presence of intrinsic naphthenic acids (NAs) in high acid crudes (HACs) causes significant corrosion of refinery equipment. To deacidify the HACs in the absence of a catalyst or exogenous hydrogen, efficient removal of the NAs present in HACs was obtained using methanol at moderate temperature and pressure. To optimize the removal of NAs from HACs, various process variables such as temperature, crude concentration, and reaction time are investigated. Under the conditions of 250 °C temperature, 6.4 MPa pressure, and 33.3 wt% crude concentration, a remarkably low total acid number (TAN) of 0.08mg-KOH/g-oil is obtained, indicating a reduction efficiency of 96.9%. Additionally, a high oil yield of 95wt% is attained.

Petroleum emulsions are formed excessively in the refinery desalters; therefore, a representative sample of petroleum emulsion was prepared in the lab to check the viability of supercritical fluids towards the simultaneous breaking and upgrading of toxic and intractable emulsion without the utilization of external catalysts. The petroleum emulsion underwent efficient conversion into synthetic crude oil, resulting in a significant reduction in impurities using supercritical water (scH2O) and supercritical methanol (scMeOH). This

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

approach holds potential for application in existing petroleum refineries [21]. The level of reduction in asphaltenes is 98.5%, while the non-distillate percentage has been reduced by 94.0%. This comprehensive research offered a valuable understanding of the pre-treatment techniques for efficiently using petroleum emulsions and unconventional crude oils in the existing refinery system, without the need for external catalysts and molecular hydrogen.

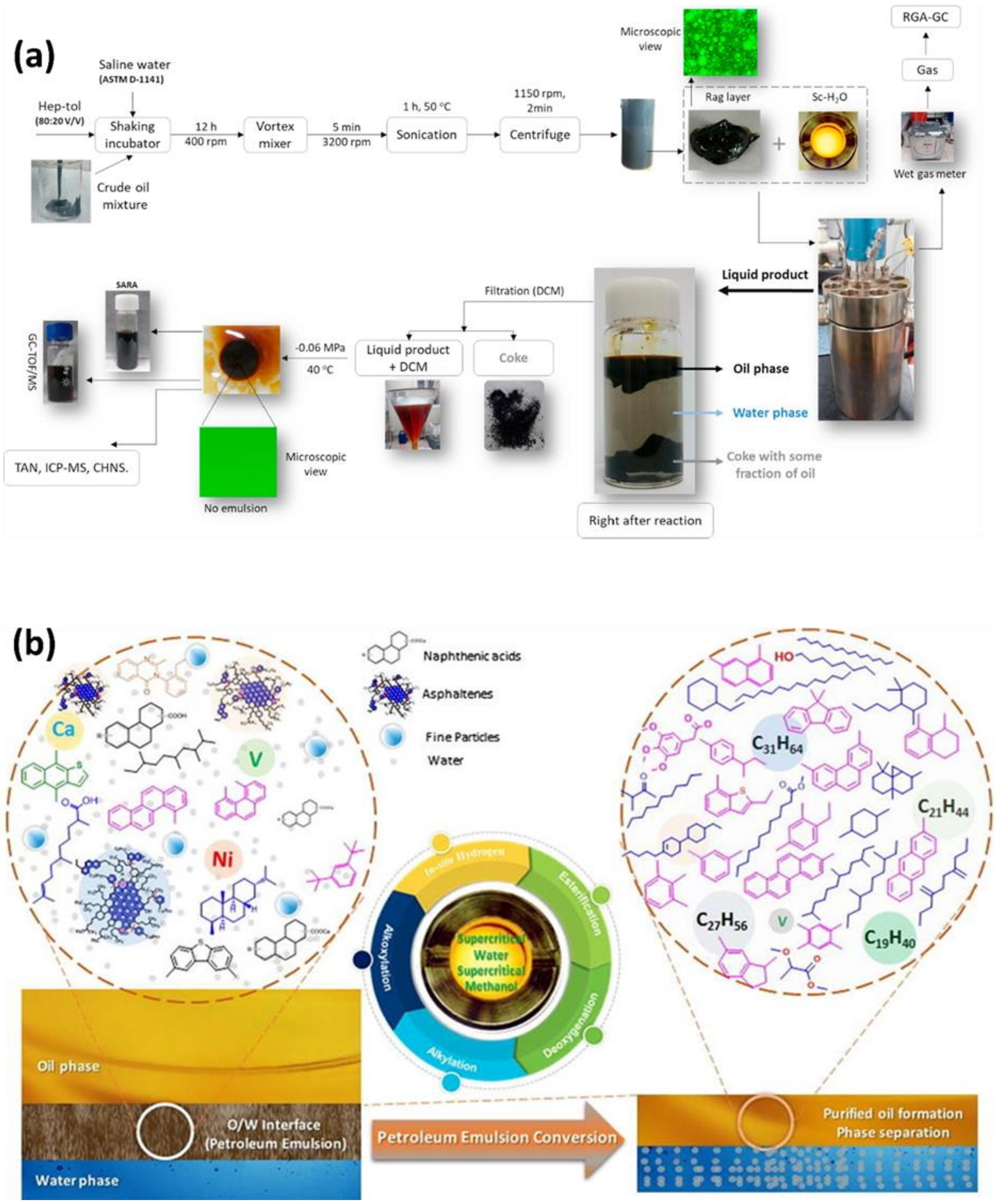

Figure 2. (a) The supercritical fluids upgrading reaction system for unconventional heavy crude oil and petroleum emulsions with separation protocol (Khan et al., 2019), Copyrights 2019, Elsevier, (b) graphical representation of oily sludge demulsification to upgraded crude oil I supercritical fluids (Khan et al., 2017), Copyrights 2017, Elsevier.

4. CONCLUSION

Utilization of supercritical fluids proved to be an effective pre-treatment methodology for upgrading unconventional crude oils and petroleum emulsions without external catalysts and molecular hydrogen. Reduction of asphaltenes, oil viscosity, non-distillable fraction, metallic (V, Ni, Ca, Fe), and non-metallic impurities (S, N, O) are major achievements of these studies. The simultaneous breaking and upgrading of highly toxic and stable petroleum emulsions is one of the key findings which was never been explored before. TAN reduction of high acid crudes, oily sludge, and complex naphthenic acid mixtures was also achieved.

However, several questions remain in current studies that need to be answered regarding the upgrading of petroleum emulsion and unconventional crude oil in supercritical fluids. The high temperature (400 °C) and high pressure (20 MPa) supercritical process is somehow less economically viable because of the huge reactor and auxiliary component cost. Therefore, low-temperature and low-pressure catalytic processes can be a more attractive option for commercializing such processes in current refinery systems for upgrading unconventional crude oils. The proposed methodology can be an attractive option regarding the upgrading of petroleum emulsion if we can further enhance the quality of upgraded crude oil in terms of sulfur, coke, and metallic impurities reduction. Numerous aspects of the above-mentioned studies are further needed to explore for a better understanding of petroleum feedstock upgrading in the presence of supercritical fluids. The main points are listed below, why are asphaltenes preferably converted into coke instead of liquid hydrocarbons, what structural and chemical properties of asphaltenes are responsible for generating problems in refinery feedstock upgrading, why sulfur-containing benzo-thiophene are so recalcitrant, why nitrogen reduction is good in supercritical fluids as compared to pyrolysis, why are metals selectively transformed into coke instead of the liquid phase, what is the effect of different types of asphaltenes structures on the coke formation, detailed analysis of coke formation in terms of structural and chemical aspects, what is the effect of different supercritical fluids during the transformation of asphaltenes into coke?

To obtain the answers to the inquiries above, it may be necessary to undertake extensive research to gain a comprehensive grasp of the various components involved in the intricate process of upgrading crude oil mixtures in supercritical fluids. One can examine the stubborn characteristics of asphaltenes, benzo-thiophene, and its derivatives, nitrogenated compounds, and metal-porphyrins by using heterogeneous catalysts. This can help enhance the quality of upgraded crude oil derived from petroleum emulsion and unconventional crude oils.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951