



Review article

Ring opening of hydrocarbons for diesel and aromatics production: Design of heterogeneous catalytic systems



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HIGHLIGHTS

- LCO and Pygas valorization is necessary for approved fuel properties.
- Catalytic ring opening reaction is becoming a suitable industrial option.
- Supported metals, carbides and zeolites are attractive upgrading catalysts.
- The paper examined critical literature on the catalysts design and evaluation.
- Directions for further studies were identified for the benefit of researchers.

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ABSTRACT

The valorization of light cycle oil (LCO) and pyrolysis gasoline (i.e. Pygas) via ring opening reaction (ROR) presents an industrial opportunity for improving the cetane and octane properties of diesel and gasoline fuels, respectively. One major challenge is the design of suitable catalysts that are optimally active, selective and very stable. The paper therefore covered a review of critical studies conducted with the view of achieving these properties. Catalysts based on metals-promoted oxides, carbides, sulfides and modified-zeolites have so far been investigated. The paper therefore discusses the progress made and identified issues for further investigations. Issues such as the role of catalyst compositions, acidity, topology and textural properties on the activity–stability properties were examined.

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1. Introduction

The crude oil otherwise referred to as the petroleum represents a complex composition of hydrocarbon compounds as the major species, in addition to the wide range of O-, S- and N-bearing derivatives [1–5]. The formation of these compounds commonly originates from the breaking down (i.e. decay and decomposition) of molecules of marine species over million of years subject to changes in temperature and pressure conditions [6–10]. Although there are certain indications that the global crude oil reserves will be exhausted in the few decades to come, global energy and petrochemicals production will still rely on crude oil for at least the medium term [11–14]. Therefore, investigations on various valorization techniques are still very relevant for global energy sustainability. According to the statistical information published by the Energy Information Administration (EIA, USA) the Middle East countries have the highest reserves of 48% followed by the countries in Central and South America accounting for 20% of the global crude oil reserves [15]. Countries in the North America possessed 13%, Africa 8%, Eurasia 7% and the European countries account for only 1% of the total reserves of the crude oil. Some 3% deposits have also been attributed to the countries in the Asian region (see Fig. 1). The various deposits include those that are very difficult to be extracted based on the available technologies. Among the total reserves, the conventional crude oil (i.e. the most extractable due to lighter compositions) accounted for only 30%. On the other hand, heavy oil, extra-heavy oil, bitumen (including oil sands) accounted for 15%, 25% and 30%, respectively (see Fig. 2) [15].

According to the above details, the non-conventional deposits are the major deposits for future utilization as fuels and petro-

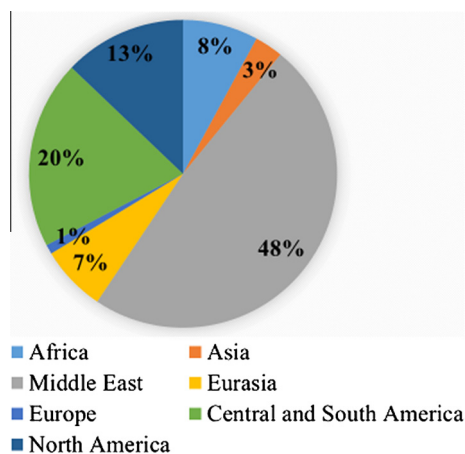


Fig. 1. Percentage global distribution of crude oil reserves. Data source: Ref. [15].

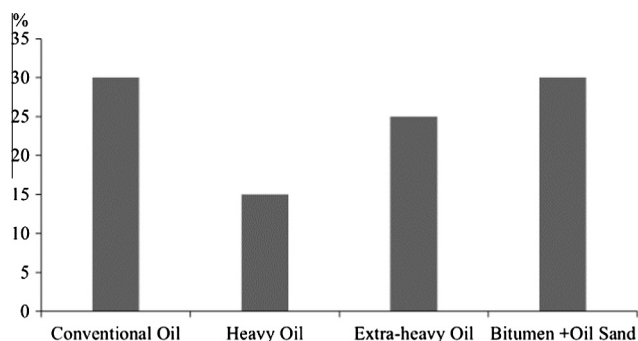


Fig. 2. Reserves share of conventional versus non-conventional crude oils. Data source: Ref. [15].

chemicals. Their compositions, which include asphaltenes, polyaromatics and resins are responsible for low API value and very high specific gravity [16–20]. The asphaltenes, which are very bulky compounds can be found in <1% concentrations in the light/-conventional crude oil, but could be as high as >20% in the unconventional (i.e. heavy oil) deposits [21,22]. To upgrade the heavy fractions into lighter components suitable for fuel usage, different technologies such as aquathermolysis [23–25], sub- and super-critical water cracking [26–29], and solvent extraction processes are been considered by the industries [30–32]. However, there is a recent interest in ring-opening reaction for the transformation of polyaromatic hydrocarbons and their derivatives into the lighter aromatics or even the paraffins. The process generates hydrocarbon compounds like BTEX (i.e. benzene, toluene, ethylbenzenes and xylenes) and aliphatics suitable for incorporation into diesel, gasoline or even the jet fuels. The technology could therefore be very beneficial for the valorization of the heavy oil compounds in the unconventional petroleum resources into fuels. The objective of this paper was to review relevant literature on the ring opening process as related to the production of diesel and gasoline-ranged aromatics (i.e. the BTEX). Emphasis was placed on the design of heterogeneous catalyst systems and their corresponding roles during the process. We have also identified new areas that should be considered for further investigations.

2. Ring opening in diesel production

The production of a very high grade diesel fuel that meets the environmental specifications is an aspect that could be considered very critical from the economic and health points of view [33,34]. Therefore, the targets of modern petroleum refineries include the reduction of sulfur and aromatic compositions in certain fractions like the distillates in order to concede the production of high-quality diesel fuel (i.e. of better cetane properties) [35,36]. The high content (48–70%) of polyaromatic compounds and naphthenes in common diesel fractions failed to comply with the modern specifications applicable to the diesel fuels [37,38]. Although the hydrotreating to remove O-, S- and N-bearing compounds is still applicable [39–41], the ring opening reaction (ROR) is a more prospective upgrading strategy. This is due to the fact that the hydrocarbon compounds dominated the compositions compared to the heteroatoms containing compounds.

The ROR proceeds with the conversion of naphthenic and polyaromatic rings into monoaromatics, linear or branched-paraffins. This in turn improved the cetane index of the diesel fuel (see Fig. 3 for example) [42]. However, the major difficulty with the process is the design of active catalysts that are very selective to the production of the required hydrocarbon compounds. Different authors have investigated the ROR of tetralin using various heterogeneous catalysts as the model reactions for the diesel feedstock [43–45]. Although the application of catalysts such as NiMo, NiW and CoMo supported over alumina and zirconia have been reported [46–49], the metals-promoted zeolite catalysts are the most widely studied for the ROR.

One critical factor that is considered in the catalyst design for the ROR is the possibility of achieving suitable acidity-hydrogenation properties. This is because the mechanism of the process involved hydrogenation, acid-mediated cracking and in some instances isomerization at certain intermediate stages. The catalyst must also possess good dehydrogenation characteristics to fit the process requirements. For example, some authors believed the decalin opening reaction to proceed by dehydrogenation and later protonation. Subsequently, the protonated intermediates could undergo protolytic-dehydrogenation followed by cracking reactions to produce open-structured hydrocarbons of

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