Recent Advances in
Petrochemical Science
ISSN: 2575-8578

Mini Review
Volume 2 Issue 1 - June 2017
DOI: 10.19080/RAPSCI.2017.01.555580

Recent Adv Petrochem Sci

Heavy Oil Refining Processes and Petrochemicals: A Role of Catalysis

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Submission: June 19, 2017; **Published:** June 22, 2017

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Abstract

Heavy crude oil not only difficult to process but also its composition contains large amount of undesirable elements. Considering an eco-friendly approach towards fossil fuel based chemical transformations then one should use an appropriate catalyst process, which may not be economic but intent toward the better environment. However, considering the complexity of feedstock only catalytic method may not be enough to get best commodity product hence, a combination of thermal and catalytic methods can be effectively used. In the case of heavy oil, the primary need is to lower boiling point of complex hydrocarbon along with the removal of hetero-atoms such sulfur, nitrogen, and metals. Hydroprocessing catalyst plays an important role to convert heavy oil into various HC streams with desire products specifications. The cracking of complex hydrocarbons is the most important petroleum-refining process, which is mainly depend on the acidic property of the catalyst. The importance of support to provide enhancing function to catalytic sites as well as participate as acid-base sites. FCC and hydro cracking catalyst usually contains mesoporous synthetic silica-alumina, and/or zeolite. Achieving integration between refining and petrochemicals is considered one of the major pivot that depends to carry out its strategy of achieving growth in value product.

Introduction

The light fossil fuel reserves are getting depleted and heavier, sourer and more complex reserve are being explored, thus, quality is deteriorating. Moreover, environmental regulations are becoming more stringent, which put additional responsibility on the researchers to develop innovative technologies in order to counter viable solutions to processes these heavy crude. Moreover, due to the large amount of sulfur, nitrogen, metals and asphaltenes such feeds are not easy to process [1,2]. On the other hand, about 85% of the global energy demand is being supported by the fossil fuels, which will continue much longer, as there is no immediate replacement or very limited renewable energy (solar, wind and water) resources has been explored. Considering the importance of various processes, the overall future refinery depends on key fundamentals such as choice of crude slate, complexity of the refinery and the product requirement. Heavy crude oil means high yield of residue (350 C^{+}), which is usually > 65%. Hence refinery capability is to process heavier crude oil and its residues that involve mainly upgrading processes. Refiners who are able to convert heavy, high-sulfur crude to light products face prosperous economic benefits. Therefore, biggest winner will be the refining companies that can deal with heavy and high-sulfur crude oil. Atmospheric residue desulfurization (ARDS) process plays an important role in upgrading heavy petroleum oils and residues to more valuable clean environmentally friendly transportation fuels. Hydro cracking process is another flexible refining process, extensively used for heavy oil upgrading that converts large and complex organic molecules into the valuable light petroleum products. Hence it is one of the most leading process along with fluid catalytic cracking (FCC) and thermal cracking. Hydro cracking is a most preferred over the later two options (i.e., FCC and thermal). Considering the significance of clean fuel, hydroprocessing remain one of the most efficient refining process that remove hetero-atoms as well enhance H2/HC ratio [1,3]. Significant work has been also carried out in the last century and as a result, catalysts became one of the most powerful tools in the petroleum refining industry. Zeolites are widely used as a catalyst and catalyst support for a quite broad range of processes, which attracted much interest in catalytic application in petroleum refining industry such as FCC, hydro cracking (HC), reforming, alkylation and isomerization [4,5].

Recently, due feedstock (heavy and extra heavy) refiners are looking forward to use more efficient catalytic or non-catalytic method options to convert heavy component to valuable products. Thus, depending on the products requirement various options can be used where one of the most important process is to prepare petrochemical feedstock.

Moreover, in order to enhance refinery margin by using heavy oil and its residue, the strategy is to integrate refineries with petrochemical, which will be able to produce high price petrochemical feedstock such as styrene, butadiene, benzene-toluene-xylene (BTX), propylene, ethylene [6]. These products are not only cost effective but also returns are extremely attractive [7]. To the integration of refining and petrochemical industries, new technological developments are expected along with the traditional processes such as cracking, steam cracking, hydro cracking, FCC processes will be at high interest to meet the increasing demand for light olefins. A superficial integration of refinery and the petrochemical is shown in (Figure 1).

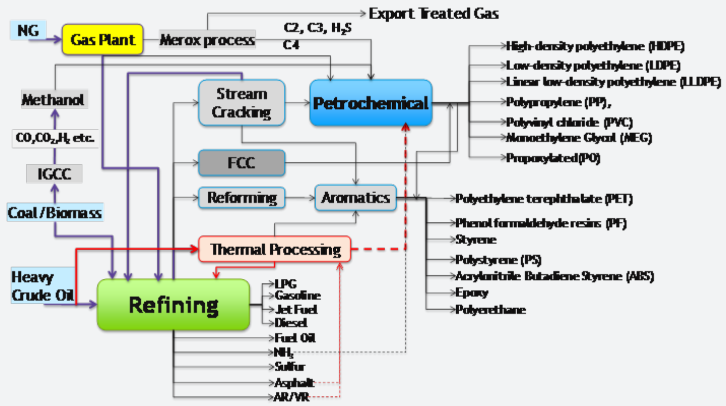

Figure 1: Integrated approach to refining and petrochemicals.

Zeolites are frequently used in the various sectors where their potential use as hydro cracking catalyst, FCC catalyst along with the adsorption as well as separation in the form of membrane. Zeolite has wide scope to further modify in the form of textural geometry (2D,3D linkages), pore diameter, acid-base nature and compositional effect in order to opt newer technologies and more selective products [8,9]. Apart from this, zeolites has potential to replace liquid catalysts (HF, H_2SO_4, $AlCl_3$ etc) used for alkylation, which is one of the common process that link to refinery and petrochemicals. Such integration also open even new route from gas-to-liquid (GTL), methane and coal to methanol high vale products [6].

Challenges in Heavy Oil Processing

Fossil fuels (oil, coal and natural gas) are the major part of the world's energy resources, which are considerably high but their usage often poses a significant challenge to the society and that is the major concern for the researcher as well as refiners [10]. Hence over the past four decades, the refining industry has been challenged by environmental protection agency's (EPA) for its clean burning. The problem even gets more complex or challenging with heavy feed stocks and with decreasing API gravity and increasing contamination [11]. The future refinery feed and products characterized at molecular level rather than measuring bulk properties is the most challenging issue. The end user products will be identified not only environmentally clean (zero sulfur nitrogen) but also will classified high energy efficient fuel, such as high octane, Cetane numbers and improved smoke point along with high H_2/HC ratio, which is demanding task for refiners. The high H_2 to HC ratio is particularly important to burn fossil fuel more efficiently and prevent CO_2 formation [12,13]. However, we may not be completely rule out a possible CO_2 emission as green house gases (GHG) where CO_2 capturing and storage technology has potential challenges for its future endeavor. The development of competitive catalysts and processes that are required to meet these challenges for fossil fuel (oil and gas) and continue to be the world's leading energy resource. The foreseeable future energy demand, which reflect in a safe, socially and environmentally responsible manner, will require massive investments, leading-edge technology, and superior business practices.

On the other hand, petrochemical industry has its own challenges that are usually influenced by the feedstock cost and required feed quality, which is highly sensitive to the economic instability. The most challenge part is to adapt heavy oil processing technologies and its product assimilation to petrochemical industry. However, high crude oil price may not give refinery margin but high demand for polymeric material and plastic consumer goods poses considerable challenges such as inefficient refineries (existing refineries), low refinery margin, excess low value production etc. Therefore, in near future refining industry required flexible with improved technologies and catalysts for refining that should be directed to heavy feedstock upgrading, cleaner transportation fuel production, and the integration of refining and petrochemical [6,14]. Moreover, considering in significant increase in heavy oil it appears petrochemicals investments have become an alternative option to utilize thermal processing option in the form of refinery integration.

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Emerging Trends and Processes Options

It was considered, that there are very limited role for thermal processing in the refinery because it does not give selective product as well as its processed stream has to pass through hydroprocessing. However, due to the production of heavy oil feeds using catalytic refinery process may not be efficient process. Generally, thermal cracking processes are designed to handle heavy residues with high asphaltenes and metal contents [1]. Gasification or Integrated Gasification Combined Cycle (IGCC) is one of the oldest thermal process, used for electricity, which can handle a wide range of poor quality feed stocks (coal, heavy oil, natural gas and even plant waste) and produce a wide range of products such as syngas (H_2, CO, CO_2). The process also crucial for H_2, ammonia, methanol and synthetic fossil fuel (e.g., liquid gasoline, it contains no sulfur or benzene, making it extremely clean-burning) by using Fischer-Tropsch process and methanol to gasoline (MTG) processes. Most of the syn-fuels burn cleaner than conventional fuel but at significantly higher price, i.e. a disadvantage. Hence, syn fuels still remain more expensive to produce than conventional fuels, which have wide scope for technological development in order to make production economically viable. Under gasification, the sulfur in heavy oil can be converted primarily into H2S or carbonyl sulfide (COS) while conversion of fuel bound nitrogen to gaseous nitrogen and ammonia, NH_3. However, in order to use synthetic fossil fuel as transportation may require engine modification. Currently, process mainly used with the association of steam reforming, dry reforming and partial oxidation mainly for the coal, bottom of the barrel, asphalt or petroleum coke [15].

Refining Integration and Petrochemical

The integration of refining and petrochemicals industries is a mutual benefit where utilizing of refinery products and by-products as a feedstock for petrochemicals. Therefore, it is a strategic advantage over decreasing the costs of feed and utilizing in the form of customize products. Not only that, both industries are looking for opportunity to make use of their processing option where refinery can process dirtier feedstock (heavy oil) while commodity supply can be improved in the petrochemical. Particularly this model can be effectively utilize in the refinery for heavy oil processing mainly using cracking [16] or the thermal processes [17] whereas petrochemical benefited from their value products such as refinery off gases, propylene and BTX, surplus coker naphtha, FCC naphtha, etc.

Conclusion

In the refinery, hydroprocessing (hydro treating and hydro cracking) will continue to be crucial processing technology to the modern petroleum refining and petrochemical industry. FCC, due to its flexibility to feed stocks and product yield remain one of the key process that present valuable petrochemical feedstock. Thermal processing likely to enhance their share in the refinery in order to provide energy as well as petrochemical feedstock. Integrating refineries with petrochemical industry offers attractive benefits for commodity products by using refinery waste as well as excess out-put. With integration or without integration refinery need to accustomed with environmental constraints, which are not likely to decrease in the foreseeable future, particular CO2 emissions in atmosphere to be considered at molecular level. Refining as well as petrochemical are expecting more advanced catalytic technologies in the future through improvements in existing catalyst along with new development, particularly emphasis on the acidity and shape selectivity that are exclusive and offered by zeolites. Overall, an integration of refinery with petrochemical is an financially attractive deal, which balance one another.

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