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Hydroconversion of heavy residues in slurry reactors: Developments and perspectives

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ABSTRACT

Slurry-phase hydrocracking is the most suitable technology for the conversion of heavy oils/residues. However, with conventional processes, the production of low-quality by-products is unavoidable. The newly developed Eni Slurry Technology (EST) process reaches total conversion of the feedstock to distillates. A nanosized MoS_2 catalyst provides hydrogenation activity, while cracking is mainly of thermal origin. An acid catalyst alone, which would enhance the cracking reaction, is rapidly deactivated under the severe process conditions, but the presence of nanosized MoS_2 protects the acid catalyst long enough for potential practical applications, thus allowing a more effective exploitation of unconventional oil resources.

1. Introduction

The global energy demand is increasing steadily, despite efforts to improve energy efficiency and to save energy. This trend will continue in the near future. For example, projections made by the International Energy Agency (IEA) consider a *Current Policies Scenario*, which encompasses the effects of government policies and measures up to mid 2012 [1]. An annual increase in energy demand of 1.5% was predicted for 2010–2035 (Fig. 1). The *New Policies Scenario* takes into account broad policy commitments and plans that have already been implemented to address energy-related challenges. New forecasts include targets for renewable energy and energy efficiency, programs related to nuclear energy, national targets to reduce greenhouse gas and the phasing out of inefficient fossil-fuel subsidies. Even so, the *New Policies Scenario* predicts an increase of 35% from 2010 to 2035, an average of 1.2% per year. This represents a sharp decrease in the rate of energy demand in the past two decades; nevertheless, the rate of increase is still significant.

The dynamics of energy markets will be determined mainly by emerging economies. The non-OECD share of the global primary energy demand, which has increased from 36% in 1973 to 55% in 2010, will continue to increase. This reflects the increasing of population growth, economic activity, urbanization and industrial production, as well as saturation effects that curb increases in the demand for energy in mature economies. The share of the global energy demand in non-OECD countries will average 64% in 2035.

Even though the importance of renewable sources is growing, in the medium-term (tens of years) fossil energy sources will continue to meet most of the global energy requirements. Fossil fuels represented 81% of the primary fuel mix in 2010 and remain the dominant source of energy through 2035 in every foreseen scenario (Fig. 2).

Thus, it is crucial that, in the short to medium term, it is necessary to rationalize the efficient use of raw materials to enable a "smooth" transition to "low-carbon" energy systems. In this framework, the total conversion of the oil barrel to distillates, avoiding the formation of fuel oil, tarry residues, and coke, has gained overwhelming relevance. Moreover, it is important to exploit the so-called unconventional resources, which are at present, not being exploited fully and efficiently. Among these resources, heavy and ultra-heavy oils, tar sands, and oil shale are of great importance because of their abundance and their potential to transform them into liquid transportation fuels. The conversion of oil residues and low-quality heavy feedstocks to transportation fuels was studied extensively in the first half of the last century, with the works of Bergius, Bosch, Mittasch, and Pier [2,3]. However, today none of the existing commercially available

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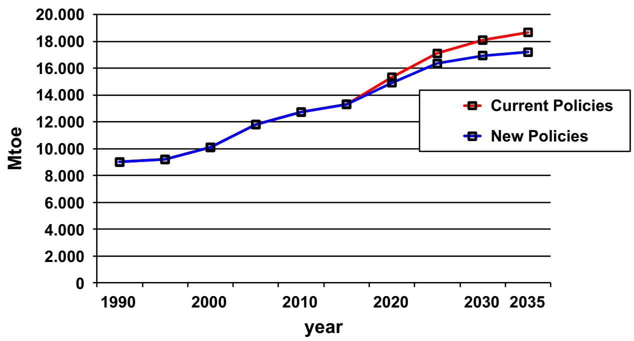

Fig. 1. Primary global energy demand.

technologies achieves total conversion, which would avoid the production of undesirable low-quality side products such as coke or fuel oil.

2. Overview of residues hydroconversion

Hydroconversion is the most efficient way to convert heavy oily feeds to distillates suitable for use as transportation fuels. From a chemical point of view, this process consists of breaking the largest molecules in heavy oils or unconverted residues and reorganizing primary fragments and molecules to maximize the fraction in the range of the desired boiling points. A general increase in the H/C ratio is obtained by adding hydrogen.

Several technologies for the hydrocracking of heavy residues have been developed [4]. Those based on fixed-bed reactors are, in principle, simpler and result in a stable and reliable performance [5–7]. However, they have strong limitations in feedstocks characteristics, because fixed bed catalyst is quite sensible to poisons contained in the feed and to coke formation [8,9]. Inefficiency due to fast deactivation of the catalyst and an uneven temperature profile in the bed have prevented the wide use of these technologies for the hydroconversion of heavy feeds. Hydroconversion processes in ebullated bed reactors are more flexible with respect to the feedstock, and they usually results in better performance, even in the processing of highly polluted feeds [10,11]. In particular, ebullated bed hydrocrackers can handle greater amounts of metals and coke, but they are limited as far as overall conversion is concerned usually achieving less than 80% conversion. The inability to convert asphaltenes without encountering severe fouling, the necessity to introduce aromatic solvents, and the production of a low-quality residue are just a few of the drawbacks of this technology.

Slurry processes are much more reliable to achieve high conversions of heavy feedstocks and to minimize the yield of low-value by-products (e.g. gas, coke, fuel oil). For instance, they combine flexibility with regards to the feedstock, typical of carbon rejection processes, with the high upgrading achieved with the hydrogen addition technologies. However, the complexity of the heavy feedstock, in a high range of boiling points of the components makes it almost impossible, to reach full conversion of the feed to high-value distillates in a single step, even with slurry reactors.

The slurry process is operated in the presence of a finely dispersed catalyst, the particle size of which is usually submicron. The reactants are well-mixed and kept in suspension in hydrogen flowing upward in the reactor. A major role of the catalyst in slurry technologies is to suppress coke formation in the hydroconversion step, which typically occurs at temperatures well above the thermal cracking temperatures (>400 °C). The catalyst is typically a transition metal sulfide (such as Mo, W, Fe or other elements), with an intrinsic stability higher than that of conventional hydrocracking catalysts [12]. Thanks to its high stability maximum interaction with oil and hydrogen is possible. The high degree of catalytic metal utilization enables the approach of large complex molecules (heavy hydrocarbons) to reach active sites rather than plug the pores, as is the case of supported catalysts, with an effective and strong inhibition of coke formation. For these reasons, the catalyst can be used with greater ease in the presence of much heavier feedstocks than over a supported hydrotreating catalyst and, as a consequence, slurry processes will be more suitable than other hydroconversion technologies in treating more "difficult" feedstocks (i.e. high content of metals, carbon residues, and asphaltenes).

The catalyst can be prepared *ex situ* and then dispersed into the oil, or *in situ* by converting an oleo-soluble precursor that is added to the feed. After the reaction and the separation processes, the catalyst remains in the residue of the vacuum distillation unit together with the nickel and vanadium sulfides derived from the organo-metallic compounds in the feedstock.

3. Slurry hydroconversion processes

In the last few decades, several slurry hydroconversion has been studied mainly in industrial research centers [13,14]. Most of the process schemes reported in the published literature refer to once-through processes. For economical reasons, this limits the use of the catalyst to inexpensive and less active materials (i.e. iron sulfide) or to low concentrations of more effective salts (i.e. few hundreds ppmw of molybdenum sulfide).

The Exxon MRC process operates at 420–450 °C and 10–15 MPa. Conversion is essentially driven by thermal cracking, but coke formation is minimized by the action of the catalyst as well as by reactor design and operating conditions. The catalyst is formed by 1–2 μm diameter particles comprised of single layer of

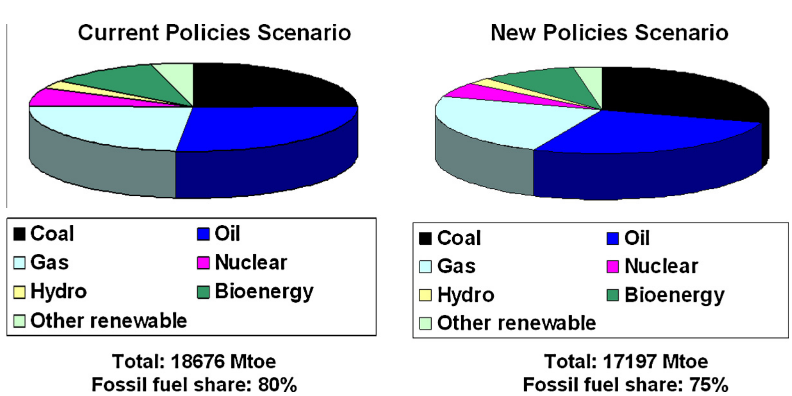

Fig. 2. Primary global energy demand by source: projections at 2035.