Chapter 3
Perspective on the Deep Hydrotreating of Renewable and Non–Renewable Oils

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ABSTRACT

To meet not only the increased demand of liquid transportation fuel but also the stringent environmental legislation centered on anthropogenic emissions, renewable resources (i.e., not depleted by use) and low-grade feedstocks need to be processed, since the reserves and quality of the feeds available are markedly declining. In this chapter, an overview on the hydrotreating of renewable and non-renewable feeds for producing ultraclean transportation liquid fuels is given. The fundamentals and factors that affect the generation of ultraclean fuels and bio-fuels are discussed in an integrated perspective. The authors include not only the current understanding of the hydrotreating process but also the challenges for the valorization of non-renewable and renewable feedstocks with high content of heteroatoms and unsaturated poly-aggregate compounds (asphaltenes and lignin). The importance to develop advanced catalysts based on abundant metals, rather than precious metals, and multifunctional properties with sufficient activity and selectivity in hydrodeoxygenation of bio-oils is outlined.

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INTRODUCTION

The increasing market demand for ultraclean transportation fuels in many countries combined with their environmental impact and the increasing consumption of transportation fuels represent a major challenge, not only for the petroleum refinery industry, but also for the nations involved in the agreement reached at the Paris climate Conference of Parties (COP21) to reduce greenhouse gas emissions fast enough to prevent the worst impacts of climate change (King, 2016). Nowadays, the global market for clean fuel is increasing whilst the quality of the feed streams available is markedly declining, low grade feedstocks or even alternative feedstocks may need to be processed in order to meet the additional volume of ultraclean liquid fuel required for transportation. Indeed, the replacement of non-renewable crude oil by renewable sources has been addressed in recent years, particularly in developed countries and its main driving force has been mainly the concerns related to their environmental impact and also the need of securing energy supplies.

The hydrotreating (HDT) process plays a major role not only in the reduction of environmental pollution but also in the upgrading of low grade non-renewable feedstock, in which a number of variables such as catalyst formulation, operating conditions and feed quality (i.e., concentrations and type of aromatics, S-, O- and N-containing compounds, their reactivity, inhibiting effects, etc.) need to be considered to produce ultraclean transportation fuel (Stanislaus, Marafi, & Rana, 2010). Indeed, the feedstock properties are markedly dependent upon their sources (i.e., location, distillation cut and blending components) and play a major role in the selection of the operating conditions to produce clean transportation fuel over a specific hydrotreating catalyst (Al-Barood, & Stanislaus, 2007; González-Cortés, et al., 2014). The HDT process has also been used for the upgrading of renewable feedstock, particularly for pyrolysis bio-oil (Elliott, 2007), which has a complex composition of organic compounds such as acids, alcohols, aldehydes, phenol, sugar, phenol derivatives, components with multifunctional groups, and lignin-derived oligomers emulsified in water (Oasmaa, et al., 2015).

Hydroprocessing mainly involves hydrotreating reactions (i.e., removal of metals and heteroatoms such as S, N and O in presence of hydrogen), partial (or total) hydrogenation of unsaturated hydrocarbons and hydrocracking reactions in the crude oil refining. The processes are often classified according to the severity of the operation. Under relatively mild operating conditions (i.e., hydrotreating, typically at 320-350 °C and 30-50 bar), the main purpose is to saturate the feed molecules and/or to remove the unwanted heteroatoms without significantly changing either the boiling point range or the molecular size distribution. Hydrocracking, on the other hand, is typically carried out at 400-450 °C and 100-150 bar. The primary purpose is to maximize the conversion of a heavy feed to desirable lower boiling-range fractions. A clear distinction between these processes is seldom possible, since the different reactions usually occur simultaneously. In addition, a hydrotreating catalyst may act as a hydrocracking catalyst (under mild hydrocracking conditions) in the presence of another feedstock or under different operating conditions (Topsøe, Clausen, & Massoth, 1996). Currently, it is however well established that for the hydrotreating process a catalyst that provides hydrogenation and hydrogenolysis activity is required, whereas for the hydrocracking process it is desirable to use a bifunctional catalyst which has both acidic and hydrogenation sites that each play a crucial role during the catalytic process (Cornils, et al., 2003).

The relatively high content of both refractory sulfur and nitrogen compounds for the extra-heavy crude oils and the very high oxygen concentration for the bio-oil, together the high concentration of unsaturated component, i.e., asphaltenes for crude oils (Ancheyta, Trejo, & Rana, 2009) and pyrolytic lignin for bio oils (Zakzeski, et al., 2010), present extreme challenges for their upgrading to gasoline/middle distil-