Fischer–Tropsch product as a co-feed for refinery hydrocracking unit

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HIGHLIGHTS

▶ Adding of Fischer–Tropsch (FT) product into petroleum vacuum distillate.
▶ Hydrocracking at 390, 410 and 430 °C.
▶ Distillation of the primary products and evaluation of all products obtained.
▶ FT product in the feed decreased density and sulfur content in all products.
▶ FT product improved cetane index of diesel.

ARTICLE INFO

ABSTRACT

A flow bench scale fix-bed reactor was used for hydrocracking experiments, which were carried out over a commercial Ni-W/alumina catalyst under hydrogen pressure of 18 MPa. Two feeds were separately processed at temperature levels of 390, 410 and 430 °C: vacuum distillate containing 10 wt.% of Fischer–Tropsch (FT) product prepared in separate experiments and neat vacuum distillate used as a reference material. The hydrocracking products were fractionated by distillation into naphtha, diesel oil and residue. All samples were then analyzed using several analytical methods in order to compare properties of the products obtained from different feeds. All products obtained from the feed containing FT product had lower or comparable density and sulfur content to products obtained from neat vacuum distillate. Differences in hydrocarbon group-type composition were observed in both naphtha and diesel fractions. The impact of modification of vacuum distillate by FT product on the properties of its hydrocracking products is discussed in detail.

1. Introduction

The ever increasing demand for liquid transportation fuels (diesel, kerosene, petrol) together with the increasing awareness of the environmental negative impacts of using fossil resources to produce these fuels has initiated search for suitable alternatives [1,2]. The key features of these alternative liquid fuels are that their production relies on renewable resources and can be carried out in sustainable manner. While the application of other energy resources than liquid fuels (e.g. electricity) have been investigated intensively, liquid fuels still remain an indispensable energy carrier for the transportation sector owing to the existing infrastructure (consisting of fuel distribution as well as engine technology in current vehicles) and their high energy density. For instance, the amount of usable energy per unit weight is significantly higher (20–40 times!) than in electrically-driven vehicles and liquid fuels can be also easily stored and handled [3,4].

Fischer–Tropsch synthesis (FTS) is a key technology for production of future liquid transportation fuels as it allows conversion of virtually any organic-carbon-containing raw material, such as coal, natural gas, biomass and waste, into transportation fuels by gasification of these raw materials to afford synthesis gas, a mixture of CO and H_2, followed by FTS and subsequent refining of the primary FTS products [5]. The conventional refining technologies have been developed and adjusted to petroleum-derived feedstocks with their specific properties that of course differ significantly from the Fischer–Tropsch syncrude (i.e. the overall product of FTS). In order to suggest appropriate technologies for efficient refining of Fischer–Tropsch products, these differences have to be taken into account and the existing technologies modified accordingly [6]. In contrast to crude oil, FTS syncrude does not contain any sulfur or nitrogen-containing compounds, but it usually contains a small portion of oxygenates despite their majority is dissolved in the

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aqueous phase. Moreover, FTS syncrude has low concentrations of branched and cyclic hydrocarbons (i.e. iso-alkanes, aromatics and naphthenes), but it contains linear olefins that are not typically present in primary petroleum fractions.

Since petroleum is a finite energy resource, its availability and production will inevitably start declining in future [7]. Consequently, the importance of transportation fuels from other carbon sources will significantly increase, unless there is a considerable development step of other means of transportation. While vegetable oils (lipids) and sugars can be directly converted into liquid fuels, i.e. biodiesel or renewable diesel [8,9] and ethanol [10], respectively, the other carbon-containing raw materials (natural gas, coal, lignocelluloses biomass) require an indirect conversion route. The final step of this route is either conversion of synthesis gas by FTS producing hydrocarbons [11–15] or transformation of synthesis gas into methanol. Methanol can be then transformed to hydrocarbons (e.g. in the methanol-to-gasoline (MTG) process) [11,12,16–18] or directly to dimethyl ether (DME) [19,20] that has been proposed as an alternative diesel fuel [21].

The distribution of FTS products follows the so-called Andersson-Schulz-Flory (ASF) distribution. As a result, a mixture of products, mainly n-alkanes having a wide range of carbon atoms in their molecules is obtained depending on the chain-growth probability (α) (with the exception the two theoretical extremes, i.e. α = 0 and α = 1 that result in formation of methane and an infinite paraffin chain, respectively) [15]. A practical consequence of ASF distribution is that using conventional catalysts the highest directly attainable yields of gasoline and diesel fractions are limited to 42 and 20 wt.% respectively [15], which differs significantly from the current as well as expected liquid transportation fuel demands [22]. Moreover, low octane number of the gasoline fraction and poor cold flow properties of the diesel fraction are yet another obstacle for direct use of these fractions [23] and they have to be further upgraded before being used as automotive fuel blending components.

Apart from upgrading of FTS distillate fractions e.g. by hydrotreating and hydroisomerization [23], FTS waxes can be produced in high yields (at α = 0.95) and then converted into desired products by cracking technologies [6,15,23–28]. Modifications of the conventional FTS catalysts by using acid supports or acid co-catalysts (e.g. zeolites) for partial cracking and isomerization of longer paraffins to enhance the yield and improve the properties of gasoline fraction were suggested as well [29–32]. This article focuses solely on the possibility of converting FTS waxes by catalytic hydrocracking (HCK).

The relatively high flexibility of HCK in terms of raw materials [33] as well as in the distribution and quality of the products [34–36] is its main advantage over other cracking technologies, such as fluid catalytic cracking (FCC). When applied to FTS syncrude, the main purpose of HCK is to obtain products with lower molecular weight (e.g. in diesel fuel range) and to saturate any present olefins and to remove any oxygenates. Hence, the conversion requires mainly C—C bond scission, which involves typically the use of high temperatures and pressures, even in the presence of a catalyst. Hydrocracking catalysts are typically bifunctional ones having both metal (or metal sulfide) and acid sites. Their performance is determined by balance between the metal (metal sulfide) sites and acid sites [37]. The metal (metal sulfide) sites are responsible for heteroatom removal by HDS, HDO and HDN and for hydrogenation/dehydrogenation reactions. In terms of hydrogenation/dehydrogenation function, hydrocracking catalysts can be divided into two classes, namely sulfide-based metal catalysts (NiMo–NiW or CoMo) and noble-metal-based catalysts (Pt, Pd). Since sulfur is a poison for Pt, Pd catalysts, they cannot be used for untreated petroleum feeds, but they are suitable for Fischer–Tropsch syncrude [38,39] as it is sulfur-free. Moreover, the waxes

from low-temperature Fischer–Tropsch (LTFT) synthesis consist mainly of linear paraffins with small amount of olefins and oxygenated products [6] that are easily refined using HCK catalysts. In contrast, high-temperature Fischer–Tropsch (HTFT) waxes contain more than 25% aromatics (although polynuclear aromatics content is as low as 1%). Consequently, they are more similar to conventional hydrocracking feedstocks, which typically contain aromatics and naphthenes, and the same principles employed for hydrocracking of petroleum residue fractions, can be applied in HTFT wax hydrocracking [6].

This work is focused on investigation of co-processing of experimentally prepared FTS product with a petroleum-derived vacuum distillate (VGO, a typical hydrocracking feedstock). The main objective is to assess the influence of FTS product addition in conventional hydrocracking feedstock on (i) overall conversion, (ii) the yields of standard hydrocracking products, i.e. naphtha, middle distillate and hydrocracking residue, and (iii) their composition and properties using a commercial hydrocracking catalyst.

2. Experimental

2.1. Preparation of Fischer–Tropsch product

Fischer–Tropsch (FT) product wax was prepared using an in-house experimental unit for the FT synthesis process. The unit consists of four fixed-bed reactors placed in an oil bath and hence it is possible to operate the unit at nearly isothermal conditions. The catalyst volume of each catalyst bed is up to 250 cm^3. The FT product used for blending of the hydrocracking feedstock consisted of those FT synthesis products that condensed in a hot separator ($\sim$120 °C). These products were collected from the FT synthesis unit working under standard FT synthesis reaction conditions – H$_2$/CO = 2 (mol/mol), 1.9 MPa, GHSV = 750 h^{-1} and temperature 200–240 °C. The FT synthesis catalyst, Co/Al$_2$O$_3$, was prepared by incipient wetness impregnation using Co(NO$_3$)$_2$·6H$_2$O as the source of Co as described previously elsewhere [40]. The amount of the used precursor corresponded to the desired Co concentration, i.e. 15 wt.%. The Co concentration determined by XRF analysis of the catalyst was 15 wt.%. After impregnation with an aqueous solution, the catalyst was dried for 2 h at 105 °C and calcined at 400 °C for 8 h. A commercial γ-alumina support purchased from Sasol Germany (spheres 1.8 mm) was used. The specific surface area and pore volume of the support were 186 m^2 g^{-1} and 0.489 cm^3 g^{-1}, respectively. After impregnation with Co these values dropped to 138 m^2 g^{-1} and 0.317 cm^3 g^{-1}, correspondingly. The catalyst was activated by reduction ex situ at 400 °C for 24 h followed by catalyst passivation using N$_2$/air mixture (0.5–21 vol.% O$_2$) and not allowing the temperature to exceed 60 °C. After loading the catalyst into the reactor, the catalyst was re-reduced in situ at 150 °C for 24 h. Hence, active catalyst phase Co^0 was obtained. The extent of cobalt reduction was estimated to be ca. 70% based on temperature programmed reduction measurements [40].

2.2. Hydrocracking

Two starting materials were used for preparation of two hydrocracking feeds: a straight-run vacuum distillate obtained from a petroleum refinery and a Fischer–Tropsch (FT) product prepared in an experimental reactor. The first hydrocracking feed, referred to as mixed feed, was prepared by blending 90 wt.% of the vacuum distillate and 10 wt.% of FT product. The straight-run vacuum distillate was used as the second feed, referred to as reference feed, for hydrocracking experiments. The chromatograms of both feeds and the chromatogram of the neat FT product are presented in Fig. 1. The distillation characteristics and some