



Review

Indirect coal to liquid technologies

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ABSTRACT

Indirect coal liquefaction has enormous potential applications. Increasingly, new synthetic technologies have been concentrating in this area, and a number of new large-scale indirect coal liquefaction plants have been set up during very recent years. Further, a large volume of papers on indirect coal liquefaction have been published over the last two decades, including those on Fischer–Tropsch synthesis, syngas to ethylene glycol, syngas to methanol, dimethyl ether as well as methanol to olefins. In this review, the recent literature of indirect liquefaction, including Fischer–Tropsch and syngas to chemicals, are summarized, with an emphasis on the reaction mechanisms, conditions and novel catalysts.

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1. Introduction

Coal is a material that some people like because of their needs while others hate due to the various emissions resulting from its combustion [1–7]. To overcome the environmental challenges as associated with the conventional utilization approaches, people are

increasingly interested in using alternative approaches including gasification and liquefaction. Liquefaction can be direct or indirect. Indirect coal liquefaction (ICL) processes mainly include two important steps. In the first step, the coal is gasified and converted into hydrogen and carbon monoxide, also called as syngas. In the second step, the syngas is further synthesized into liquid fuel. Coal is the most abundant energy reserve in the world. According to statistics of the International Energy Agency (IEA), of the top 10 coal producers in 2011, China has the highest coal production – 3576 metric tons (Mt) (46%), whereas the United States produces 1004 Mt (13%). Meanwhile, world crude oil demand in

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2012 was approximately 92.0 million barrels per day (mmb/d), slightly higher than the 2011 demand of 91.9 mmb/d; global crude oil production in 2013 (from January to May) was 75.87 mmb/d. Global demand for crude oil continues to rise, which means that improvements in technologies to produce liquid fuels from other sources would be highly beneficial. In addition, because of the abundance and low-price of coal, many countries still use it in large tonnages in traditional way. However, it should not be ignored that emissions of SO_x/NO_x , Hg, CO_2 from coal combustion cause environmental problems. Researchers have been making great effort in recent years to mitigate these environmental concerns, and great progress has been achieved worldwide. Coal energy resources have been developed and commercialized through alternative utilization technologies, such as pyrolysis, gasification and liquefaction. Among these technologies, indirect liquefaction promises to be one of the most effective approaches to convert coal to fuel liquid. Synthetic fuels derived via indirect liquefaction can outperform fuels directly derived from crude oil or from direct liquefaction, with regard to air pollution, and greenhouse gas emissions and other environmental constraints.

In contrast to direct liquefaction, two steps have to be developed in order to make indirect liquefaction possible. The first step is to break down the carbon-based raw material to form syngas. The second step is to catalytically produce hydrocarbon fuels and/or chemicals from syngas. Indirect liquefaction can be classified into two principal areas: (1) conversion of syngas to light hydrocarbon fuels via Fischer–Tropsch synthesis (FTS) and (2) conversion of syngas to oxygenates such as methanol, dimethyl ether (DME), ethylene glycol (EG) and so on. FTS, a gas to liquid technology, is one of the most important processes, which produces synthetic fuel and lubrication oil, mainly from coal, natural gas or biomass resources. Following its invention by Fischer and Tropsch in the 1920s, research has made great strides in adjusting and refining the process. The development of FTS has been greatly influenced by fluctuations in the price of global crude oil. In recent decade, due to global energy-deficiency and the demand for green energy, FTS has received wide recognition. Based on coal gasification to syngas technology, the integrated gasification combined cycle (IGCC) process has also attracted extensive attention, due to its high efficiency and favorable environmental performance. As important chemical intermediates and peak shaving fuels, methanol and DME are the top-priority products of the IGCC process. As a primary part of indirect liquefaction, coal to EG has also been attracting extensive attention in both academic and business circles in the past decades.

Since indirect liquefaction has enormous potential applications, more and more new synthetic technologies have been concentrated in this area, and research on FTS [8–12], syngas to EG [13–25], syngas to DME [18,26–28] and methanol [29–32], as well as methanol to olefins (MTO) [33–38], have resulted in a large number of publications during the past couple of decades. However, most of the papers and reviews mainly focused on one specific detail of the range of subjects relevant to indirect liquefaction. In this review, the recent developments of indirect liquefaction, including FTS, syngas to EG, DME, methanol and MTO are summarized, with an emphasis on the reaction mechanisms, conditions and novel catalysts.

2. The development of catalysts for the Fischer–Tropsch process (FT process)

FTS is one of the most important synthetic processes. This process, which provides an effective gas to liquid technology, produces a broad range of hydrocarbon products, which are converted to synthetic lubrication oil and synthetic fuel in subsequent refining process, mainly from coal, natural gas resources or biomass.

FTS is a collection of chemical reactions, and mainly produces synthetic linear hydrocarbons (alkane and alkene). It also comes with production of oxygenates and utilizes the water–gas shift reaction (WGS). The products from FTS have many outstanding, advantageous properties. FTS produces sulfur free, nitrogen free and few aromatic hydrocarbon components, and thus is which are environmentally friendly. FTS is also an important path for industrial materials manufacture, due to its production of chemicals with high value, especially waxes and light olefins [39]. FTS has a long history. After it was firstly invented by Fischer and Tropsch in the 1920s, researchers working on FTS have made great strides in adjusting and refining the process. Many prominent large-scale coal to liquid companies have been established, including Sasol South Africa plant (the world's largest oil-from-coal plant) and Sasol Qatar plant [40]. The development of FTS has been greatly influenced as a result of the fluctuation in the price of global crude oil. In recently decades, due to global the energy-deficiency and the demand of green energy, FTS has been widely recognized as an alternative path to liquid fuels. Currently there are two FT operating modes. The high-temperature (HTFT, 300–350 °C) process with iron-based catalysts is used for the production of gasoline and linear low molecular mass olefins [41]. The low-temperature (LTFT, 200–240 °C) process, with either iron or cobalt catalysts, is used for the production of high molecular mass linear waxes.

Only the metals Fe, Ni, Co and Ru have the required FT activity for commercial application. On a relative basis, taking the price of scrap iron as 1.0, the approximate cost of Ni is 250, of Co is 1000 and of Ru is 50,000 [42]. However, Ni produces too much CH_4 while Ru has really high price and the amount available is insufficient for large-scale application. So, only Fe and Co can be used as viable catalysts. Various types of reactors have been developed for the FTS process, such as fixed-bed (FBR), slurry bubble column reactor (SBCR, or CSTR in bench scale testing) and fluidized-bed reactor [43]. However, the selection of type of product in FTS is still the one of the most important issues. Chain growth in FTS follows the principles of stepwise polymerization and the product distribution of hydrocarbons follows an Anderson–Schulz–Flory distribution [44]. But the selectivity for methane and heavy hydrocarbon is higher than the selectivity for gasoline and diesel (C_{5-11} and C_{12-20}).

For maximum gasoline production the best option is high capacity fixed fluidized bed (FFB) reactors operating at about 340 °C, with an iron catalyst. This produces about 40% straight run gasoline. Twenty percent of the FT product is propene and butene [45]. These can be oligomerized to gasoline and because the oligomers are highly branched it has a high octane value. The straight run gasoline, however, has a low octane value because of its high linearity and low aromatic content. The C_5/C_6 cut needs to be hydrogenated and isomerized and the $\text{C}_7\text{--}\text{C}_{10}$ cut requires severe platinum reforming to increase the octane value of these two cuts [46].

Mild hydrocracking of wax was investigated at the Sasol R&D division during the 1970s [47]. The product heavier than diesel was recycled to extinction. The overall yields were about 80% diesel, 15% naphtha and 5% $\text{C}_1\text{--}\text{C}_4$ gas. When the decision to construct the third Sasol plant was made, the wax hydrocracking proposal was rejected because at that time making gasoline was the more economic option, and the straight duplication of the second plant resulted in huge savings in time and capital. Also at that stage, the FT slurry reactors had not yet been developed. About 20 years later the same concept of wax hydrocracking was implemented at the Shell Bintulu plant where multi-tubular FT reactors are used and currently Sasol/Chevron are designing a slurry FT plant with wax hydrocracking in Nigeria [48].

The high-temperature fluidized bed FT reactors with iron catalyst are ideal for the production of large amounts of linear-olefins. As petrochemicals they sell at much higher prices than fuels. The olefin content of the C_3 , $\text{C}_5\text{--}\text{C}_{12}$ and $\text{C}_{13}\text{--}\text{C}_{18}$ cuts are typically

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