

# Clean Diesel Production from Coal Based Syngas via Fischer-Tropsch Synthesis: Technology Status and Demands in China

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## ABSTRACT

Production of fuels/chemicals from syngas ( $\text{CO} + \text{H}_2$ ) derived from coal is receiving increasing attention under the background of the resource depletion and the unstable prices of petroleum oil. The fuels, especially diesel obtained from the syngas conversion via Fischer-Tropsch synthesis (FTS), are proved to be of very high quality that will contribute much in environmental protection and raising the energy efficiency in the transportation sector when modern diesel engines are massively applied in vehicles. FTS technology developed in recent years has reached the stage for the feasibility of construction of large-scale complexes to reach economical goals in many cases. Due to lack of petroleum and natural gas reserves, China has to go with coal utilization in this direction. The main frame of the coal to liquid strategy is that coal is gasified with modern gasification technologies at large scale to produce syngas, and syngas is firstly purified, catalytically converted to hydrocarbons, and then refined to high quality fuels by using slurry phase FTS as the core technology using low cost iron catalysts developed in the Institute of Coal Chemistry (ICC), Chinese Academy of Sciences (CAS). The optimization of the coal to liquid (CTL) processes is on the basis of the massively laboratory development of the key technologies in syngas conversion and syncrude upgrading and the scaling-up validation in pilot plant tests. The final products from the integrated syngas conversion technology show excellent quality with cetane number typically above 70 and sulphur below 5 ppm. The recent case studies show that the cost of the products in a large scale CTL plant are well below 23 \$ /b (oil equivalent), projecting an attractive option in the oil replacement frame.

## 1. Introduction

Technological achievement in converting syngas into clean diesel fuels via advanced FTS routes has attracted industrial application interests under the background of the unstable oil price that has imposed sensitive concerns for many countries. Currently production of liquid fuels is based predominantly on petroleum oil in the world. Stringent environmental regulations have pushed conventional refineries to use more costly deep hydrogenation technologies to remove the impurities causing environmental pollution in the raw oil and to improve the fuel quality, especially of diesel fuels, which has successfully been combined with modern diesel engine technology, gaining benefits from both high energy efficiency and improved environmental effects as practiced in the west European countries in the last decades. However, sustainable development of current frame of fuel supply has greatly been menaced by the depletion of crude oil. Under this background, production of syngas from natural gas,<sup>1</sup> coal,<sup>2</sup> and biomass<sup>3</sup> and conversion of syngas to high quality fuels/chemicals via FTS become increasingly of interest.<sup>4</sup>

China is considering establishing a new field using its relatively rich coal resource to partially fill the oil gap. In fact, this trend is not only politically but also economically feasible regarding to the rapidly increasing liquid

fuel demands due to the fast development of the economy of this country. Comparing to other options in formulating the energy frame using oil replacements, production of liquid fuels from FTS provides a seeable way that is viable both technologically and economically.<sup>1-4</sup> FTS can be applied to convert the syngas from various non-petroleum resources, particularly coal in China. In addition, super clean fuels from FTS are believed to contribute to the environmental improvements in comparison with the best fuels available from conventional oil refineries. Recent development in the advanced FTS technology has greatly been enhanced under the frame of coal utilization program in China. This includes the development of efficient and low cost synthesis catalysts,<sup>5,6</sup> the slurry phase reaction process at a pilot scale, and related process integration on the basis of a systematic development of Fischer-Tropsch reaction engineering.<sup>7</sup> Extensive investigation of fundamental kinetics of the complex FTS system has imposed great impact on the better understanding in the Fischer-Tropsch catalysis, reactors, and the way to apply them in view of an overall process performance optimization.<sup>8</sup> The technology developed in the Institute of Coal Chemistry has reached a level that allows consideration of formulating a practical production process.

The technological development in the Fischer-Tropsch synthesis in ICC mentioned above will be summarized, proposing a systematic establishment of CTL complexes by using coal under the economic conditions in China.

## 2. CTL Process Frame

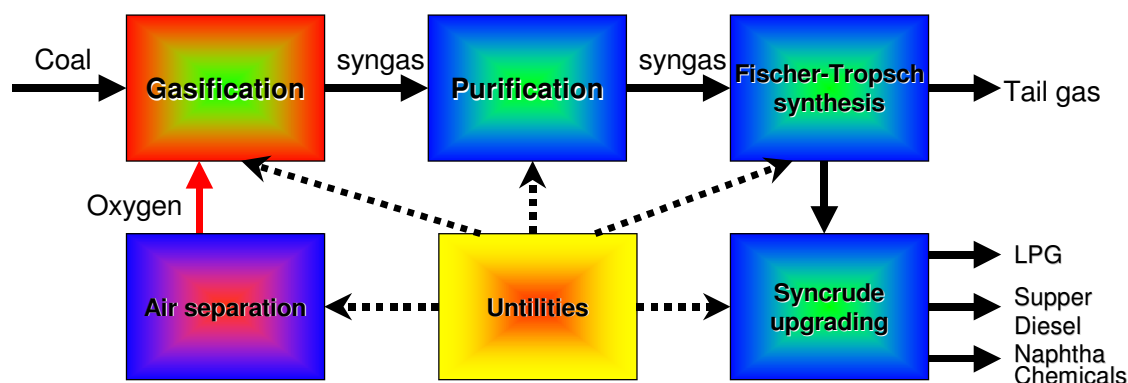
A coal to liquid process needs in principle several major sub-processes:

- (1) oxygen production;
- (2) coal preparation and gasification;
- (3) syngas purification;
- (4) Fischer-Tropsch synthesis;
- (5) syncrude upgrading.

Oxygen production via air separation is a major power consumption part in a CTL plant, and it needs high fixed capital cost. Gasification associated with coal preparation is another major capital demanding part in CTL plants. Syngas purification at large scale covers moderate capital cost and power consumption in typically cooling down the syngas to about  $-40$  degree C. In a Fischer-Tropsch synthesis sub-process, the construction of the reactor and heat exchangers is main capital cost, and replacing catalyst may become a main operation cost in this part depending on the catalyst technology. Syncrude upgrading will cover similar capital cost as the FTS process if the final products are limited to fuels and raw chemical feed stocks. It should be mentioned that high-pressure steam or electricity generation plant as major utilities must be presented and this cost will be divided into the above listed sub-processes on the basis their demands. A very brief frame of the CTL plant is illustrated in Fig. 1. In this section, the gasification and FTS will be summarized for a clear picture of technological status in CTL applications, considering the other parts are matured technologies and can be mentioned whenever necessary.

### 2.1 Coal gasification technologies

Coal gasification technology could be a most importantly decisive factor for a successful CTL plant. This of course is determined firstly by the reliability of selected gasification technology regarding to that selection of a gasification technology is not only dependent on the technology itself but also on the properties of desired coal to use for syngas production. In a practical case, decision makers of a planned CTL plant have to be aware whether the gasification technologies can be applied for the coal feed in a very early stage. This normally is done with the help of the providers of gasification technologies. In some specific cases, tests using the desired coal must be done in a test facility or in a working gasifier to be selected. It is therefore necessary to summarize the experiences in using the available gasification technologies.



**Figure 1.** CTL plant frame

Among available gasification technologies for large-scale production of syngas, there are actually only a few of them have commercially been proved: (1) Lurgi fixed bed gasification, (2) Texaco entrained flow gasification using coal-water slurry, and (3) Shell entrained flow gasification using dry powder of coal.

Lurgi fixed bed gasification has been operated in SASOL's CTL plant. This kind of gasification technology is suitable for gasifying coal with sufficiently low sticky index and  $T_2 > 1200$  degree C. The syngas produced from this kind of gasification technology contains significant methane that must be carefully utilized in a CTL plant design.

Texaco gasification has also been commercially demonstrated for quite long time. It is suitable for gasification of coal with relatively low content and low melting point ( $< 1350$  degree C) of ash. Texaco can produce high quality syngas with  $CO+H_2$  content over 96% after removing acidic gases.

Shell gasification technology has been successfully applied in IGCC plant in Europe, and there are tens of installations in construction stage in China. This gasification technology may work at a bit higher temperature than Texaco, and the  $CO+H_2$  in raw gas is higher too. Syngas quality is as good as that of Texaco gasification.

For a typical CTL plant, purified syngas production normally accounts for 60-70% of costs of the end products.<sup>4</sup> A critical analysis for predicting economics of the syngas production is therefore very important. Analyses in our CTL study show that gasification technologies with pressure about 30 bar (or higher) and as high as possible the  $CO + H_2$  content in purified syngas may be very competitive. Normally this is true if the capital costs for producing syngas for a certain quantity of final Fischer-Tropsch products that can be converted to useful products are at the same level.

## 2.2 Fischer-Tropsch technologies

Sasol has experienced for more than 50 years of applying FTS technology in production of fuels and chemicals.<sup>1,4,9</sup> The core synthesis technologies used in Sasol are known as low temperature Fischer-Tropsch (LTFT) and high temperature Fischer-Tropsch (HTFT). In LTFT, a precipitated iron catalyst is used in multitubular reactors, and spray dried iron and/or cobalt catalysts are used in Sasol's slurry phase reactors. These reactors are operated at 240 degrees C and 25-45 bars, favoring production of heavy hydrocarbon products with a low methane selectivity of typically about 4%. In HTFT, a melted iron catalyst is used in gas-solid fluidized bed reactors at 25 bars and 340 degrees C to produce light fractions consisting of mainly unsaturated hydrocarbons with methane selectivity of typically 6-7%. The total capacity of Sasol CTL complexes is well above 160000 barrels/day. Recent open domain news shows that Sasol is expanding application of its LTFT (cobalt catalyst) for converting natural gas into typically clean diesel fuels in Africa.

Shell has been working on the commercialization of its SMDS technology of Fischer-Tropsch synthesis using the cobalt catalyst in multitubular fixed bed reactors. An about 12500 barrels/day plant was put into operation using

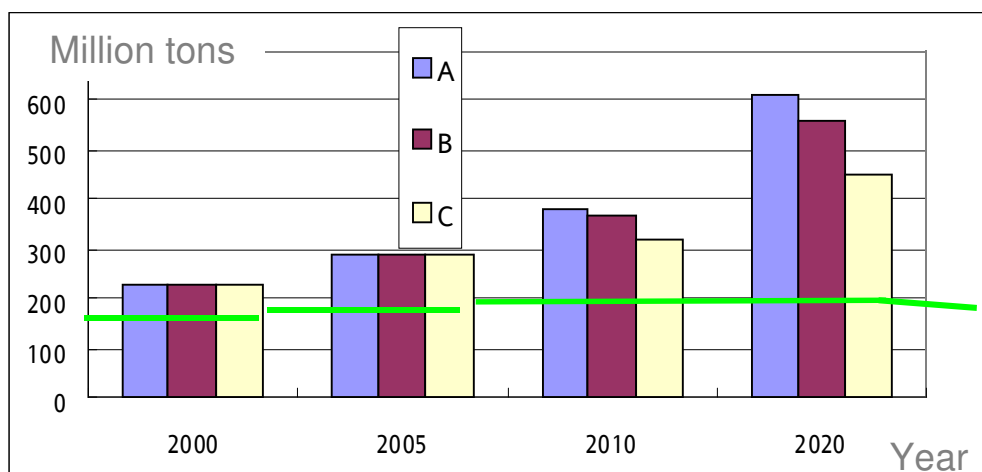
natural gas derived syngas in Malaysia in 1993. The SMDS technology produces as much as possible clean diesel fuels from heavy synthetic crude from FTS. This technology can in principle be applied to CTL purposes as well.

There are quite a few other companies in the world claiming their FTS technologies. However, it seems that all are in the development stage, projecting more and more FTS technologies for the CTL plant owners to select in the future.

### 3. CTL and China

#### 3.1 Oil supply gap

The oil supply in China has been in the stage that the gap between the demands and the domestic production is expanding rapidly. According to open domain data, imported oil has reached the level of about 100 million ton in 2003. This number will certainly increase in the next decades in order to keep the economy development. Figure 2 shows the case study of China's oil demand and supply from domestic oil fields (Feng et al.).<sup>10</sup> It is predicted that the demands for the oil supply will reach the level of about 500 million tons annually by the year 2020. However, the supply from domestic oil fields will only meet less than 40% of the demand and will decline after.



**Figure 2.** Study of three cases for China's oil demands (columns) and oil supply from domestic oil fields (green line): case A: the current situation extrapolation of oil demands; case B: the limited extrapolation with consideration of a strategy for reducing oil consumption; case C: the limited extrapolation with consideration of a strategy for reducing oil consumption.

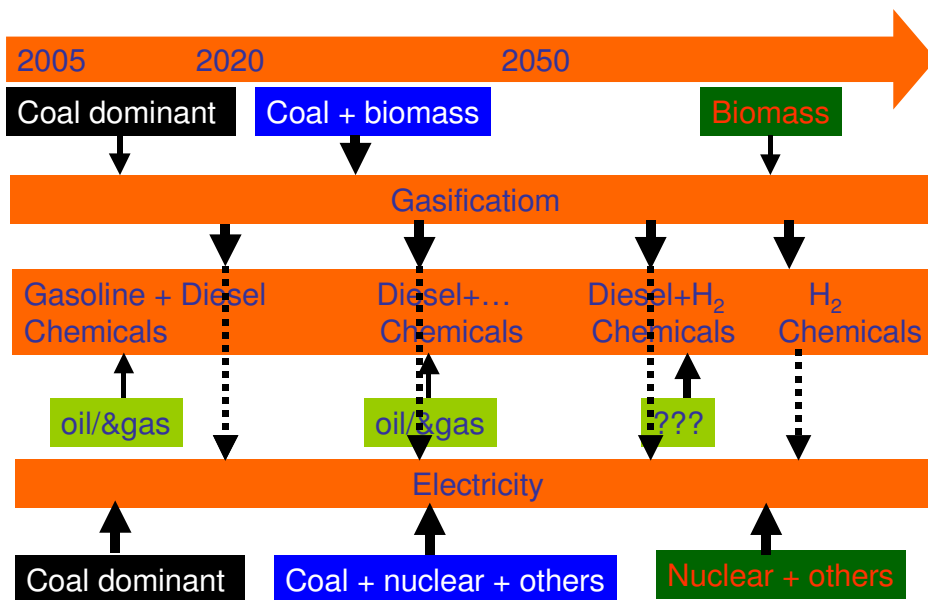
Under the pressure from the dilemma of oil supply, developing oil replacements has been a focus in China. Ethanol produced from wasted foodstuff has been used to add in gasoline in several areas of China for demonstration, for which financial support from governmental organization has been commissioned since 2001. Development of biomass derived liquid fuels has been paid much attention to. However, the technological development and energy policy system still needs to be enhanced in order to systematically forming a workable system that can notably reduce the demands for oil supply by using biomass resources.

Coal with rich reserves is the major primary energy resource in China. About 5500 billion tons of coal resources exists as estimated in the China Coal Industry Yearbook 1996, although confirmed recoverable coal reserves are 115 billion tons about 40 times as compared to oil reserves in the country.<sup>10-11</sup> It can therefore be concluded that developing oil replacements by using coal resources may constitute a feasible solution with consideration of both scale and technological factors, namely CTL will play practically dominant roles in a short

and medium term for oil replacement production.

Despite other routes in CTL options, production of clean diesel fuels from FTS is obviously an advantageous solution for China:

- (1) CTL via FTS has successfully been applied commercially at large scale;
- (2) FTS uses coal derived syngas will have seamless connection with the future biomass feed stocks via gasification;
- (3) FTS has been proved at large scale in producing high quality liquid fuels and chemical feed stocks;
- (4) The main products of FTS can be directed to super-clean diesel that can be combined with modern diesel engine technologies to formulate an energy system for transportation sector with high efficiency (30% reduction of fuel consumption compared to gasoline engine system) and high environmental standards;
- (5) FTS products will therefore provide a completely new and efficient transportation system by encouraging using diesel cars burning super-clean FTS diesel regarding to the rapid growth of the number of private cars and the population size of the country;
- (6) FTS products can be seamlessly bounded to existing infrastructures, projecting a better mines-to-wheels and life-cycle economy than any other CTL options.



**Figure 3.** Road map of China's energy resources and demanded products

For a long-term sustainable consideration, a road map regarding to resource availability and product demands is shown in Fig. 3. Apparently, the current major use of coal is in the power plants that use combustion boilers, and using coal for electricity generation will continue but will gradually transfer to using IGCC type technology in power plants. FTS will seamlessly come into the chain to convert syngas currently from large-scale gasification system into clean diesel fuels and chemicals. For a very long-term consideration, biomass derived syngas can be converted to chemicals and if necessary fuels via Fischer-Tropsch technology, implying a long span of FTS technologies.

## 3.2. Fischer-Tropsch synthesis: technology status in China

### 3.2.1 Brief history: FTS in China

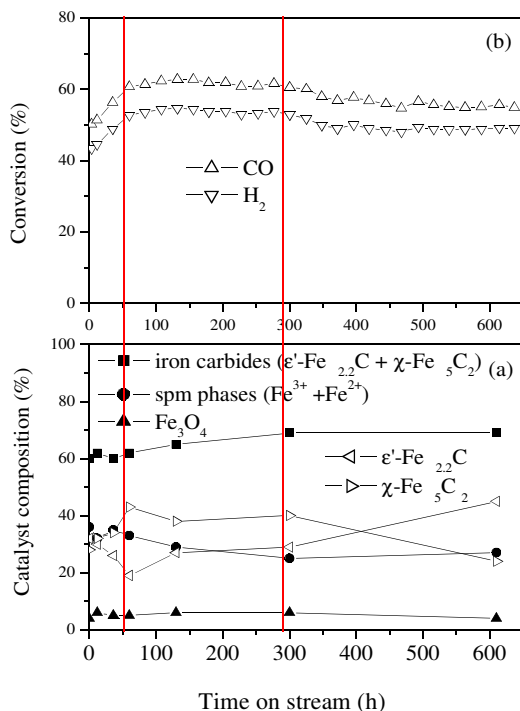
Development of FTS technology has been conducted mainly in the Institute of Coal Chemistry under Chinese Academy of Sciences. This can be divided into two different stages. Before 1997, focuses were on the iron catalyst to be used mainly in fixed bed reactors. Slurry phase FTS was studied in laboratory. In that stage tracking back to early 1980s, ICC has not systematically focused the fundamental investigation, leaving many basic questions beyond a better understanding. Only a few of international publications in fundamental studies appeared that period.<sup>12</sup> The fixed bed FTS named as the MFT (modified Fischer-Tropsch) technology using precipitated iron catalysts was scale-up to a demonstration plant of about 40 barrel/day in 1993, and that project did not run well because no support was gained due to the extremely low oil price at that time and some deficiencies in the economic aspects of the fixed bed FTS using iron catalysts.

After 1997, FTS development in ICC was assigned to go back to stress on the fundamental investigation of the FTS process technologies with focuses on the slurry phase FTS. The starting point was the reaction engineering investigation on the basis of detailed kinetics study together with catalyst development for slurry phase FTS with the view of the process technology. In 2000, two iron catalysts have been tested in laboratory scale reactors with detailed kinetics investigation. Later, modeling of reactors and processes was conducted accompanying process analyses,<sup>5-8</sup> forming the basis of current scaling-up efforts.

### 3.2.2 Laboratory investigation

FTS development in laboratory has been extensively enhanced in Synfuels China (the research & engineering center of synthetic fuels) located in ICC since 1997.

Two types of iron catalysts have been developed for slurry phase FTS (co-precipitated Fe-Cu-K catalyst and Fe-Mn catalyst).<sup>5,6</sup> Both catalysts are now scaled up accompanying the pilot plant mission. Using specific preparation procedures including shaping with spray drying techniques developed in Synfuels China, the catalysts prepared have reached the level for long-term run in severe slurry conditions. Long-term runs both in laboratory and pilot plant reactors indicate that the catalysts named as ICC-IA for the Fe-Cu-K catalyst and ICC-IIA for the Fe-Mn catalyst have excellent performances in severe slurry FTS reaction circumstance.



**Figure 4.** Correlative studies of phase transfer and activities of an ICC-IA model catalyst during FTS reaction.

For the basic understanding of these catalysts, systematic study of long-term run has been conducted in laboratory. Runs for 4200 hours for the ICC-IA catalyst and for 4800 hours for the ICC-IIA catalyst have been accomplished. Under laboratory conditions, experimental data show that these catalysts have very good stability for long-term stay in a slurry reactor. Kinetics models have been developed for these model catalysts and will be optimized for ones passing the pilot plant tests. In order to improve the catalysts further, the characterization using typically XRD, SEM, and MES is continuously performed to accumulate fundamental information on the FTS catalysis over these catalysts. One example of this type of studies conducted is continuously tracing the phase change in a model catalyst of ICC-IA by using MES. As shown in Fig. 4, the phase status of the catalyst can be correlated clearly with the formation and transfer of iron carbides. More in detail,  $\text{Fe}_5\text{C}_2$  phase plays essential roles in FTS activity, while carbide phase with a bit more carbon ( $\text{Fe}_{2.2}\text{C}$ ) in have lower FTS activity than  $\text{Fe}_5\text{C}_2$ , and  $\text{Fe}_3\text{O}_4$  phase is apparently not positive for FTS in the reaction stage. More detailed MES parameter analyses show that FTS activity is also closely correlated to the dispersion of the active phases.<sup>13</sup>

Kinetics studies are divided in two stages, laboratory stage and engineering scaling-up stage. Most works conducted in laboratory stage are focused on obtaining detailed mechanism based kinetics models, in which non-intrinsic effects normally implied in experimental data were avoided in order to get the fundamental understanding of the kinetic behaviors of the pre-assumed surface steps involved in FTS, and as many as possible mechanism possibilities are surveyed on the basis of the fundamental information available as well as the information newly obtained through quantum mechanics calculations of the reaction steps over solid catalyst surfaces.<sup>8,14</sup>

Advances in kinetics studies are going on, and improvements in established laboratory kinetics models<sup>8</sup> and expansion in the mechanism searching space are stressed. Even at this stage, it is understandable that our knowledge in the detailed FTS mechanism and the possible changes of the mechanism along the catalyst life cycle is still very limited, regarding to the complexity of both FTS reaction and catalyst phases. In addition to the extensive detailed kinetics experiments and modeling analyses covering the formation rates of hydrocarbons, and the WGS reaction rate, recent kinetic modeling has been expanded to the selectivities of oxygenates. Oxygenates are in relatively small quantities compared to hydrocarbon products, but it is essentially important to understand the kinetics of the reactions producing them in the view of further scaling-up of the process. As in the kinetics study of FTS main reactions, the kinetics modeling for the formation of oxygenates is on the basis of sets of pre-assumed mechanism typically as listed in Table 1. From Table 1, it can be seen that the surface steps listed may have totally different chemical forms in actual FTS reaction situations, keeping in mind that formation of most of the surfaces species defined in the mechanism description is lacking of experimental support. Especially for oxygenate formation over FTS catalysts (iron based), little information available in the fundamental domain. It is even true for main FTS reactions. Nevertheless, the detailed kinetics models can predicted in an ever better way the selectivities. As an example, in the recent kinetics modeling of oxygenate formation, selectivities for major oxygenates detected in FTS products are well described by the detailed kinetics model (Fig. 5).

**Table 1.** Kinetics models of oxygenate formation in FTS system

|      |  |     |
|------|--|-----|
| 1    | $\text{CO} + \text{s} \rightleftharpoons \text{CO-s}$  |     |
| 2    | $\text{H}_2 + 2\text{s} \rightleftharpoons 2\text{H-s}$  |     |
| 3    | $\text{H}_2\text{O} + 2\text{s} \rightleftharpoons \text{HO-s} + \text{H-s}$   |     |
| 4(n) | $\text{HS} + \text{COS} \rightleftharpoons \text{HCOS} + \text{S}$   | RDS |
|      | $\text{C}_n\text{H}_{2n+1}\text{s} + \text{CO-s} \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{CO-s} + \text{s}$ | RDS |
| 5(n) | $\text{HCO-s} + \text{H}_2 \rightleftharpoons \text{HCHOH-s}$  |     |
|      | $\text{C}_n\text{H}_{2n+1}\text{CO-s} + \text{H}_2 \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{CHOH-s}$        |     |

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|        |   |
|--------|---|
| 6(n)   | $\text{HCHOH-s} + \text{H}_2 \text{-----} \text{CH}_3\text{-s} + \text{H}_2\text{O}$  |
|        | $\text{C}_n\text{H}_{2n+1}\text{CHOH-s} + \text{H}_2 \text{-----} \text{C}_n\text{H}_{2n+1}\text{CH}_2\text{-s} + \text{H}_2\text{O}$ |
| 7 (n)  | $\text{HCHOH-s} + \text{H-s} \text{-----} \text{CH}_3\text{OH} + 2\text{-s} \quad \text{RDS}$   |
|        | $\text{C}_n\text{H}_{2n+1}\text{CHOH-s} + \text{H-s} \text{-----} \text{C}_n\text{H}_{2n+1}\text{CH}_2\text{OH} + 2\text{s}$          |
| 8 (n)  | $\text{HCO-s} + \text{OH-s} \text{-----} \text{HCOOH} + 2\text{s} \quad \text{RDS}$   |
|        | $\text{C}_n\text{H}_{2n+1}\text{CO-s} + \text{OH-s} \text{-----} \text{C}_n\text{H}_{2n+1}\text{COOH} + 2\text{s}$                    |
| 9 (n)  | $\text{CH}_3\text{-s} + \text{H-s} \text{-----} \text{CH}_4 + \text{s} \quad \text{RDS}$  |
|        | $\text{C}_n\text{H}_{2n+1}\text{-CH}_2\text{-s} + \text{H-s} \text{-----} \text{C}_n\text{H}_{2n+1}\text{CH}_3 + 2\text{s}$           |
| 10 (n) | $\text{C}_n\text{H}_{2n+1}\text{-CH}_2\text{-s} \text{-----} \text{C}_{n+1}\text{H}_{2n+2} + \text{H-s} \quad \text{RDS}$             |

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$$R_{\text{CH}_3\text{OH}} = k_{9,1} K_1 K_4 K_7 K_8 P_{\text{CO}} P_{\text{H}_2}^2 [s]^2$$

$$R_{\text{HCOOH}} = k_{10,1} K_1 K_7 P_{\text{CO}} P_{\text{H}_2\text{O}} [s]^2 / K_6$$

$$R_{\text{C}_n\text{H}_{2n+1}\text{OH}} = k_9 K_1 K_4 K_7 K_8 P_{\text{CO}} P_{\text{H}_2}^2 \alpha_o^{n-1} [s]^2$$

Oxygenate Kinetics Model II

$$R_{\text{C}_n\text{H}_{2n-1}\text{OH}} = k_{10} K_1 K_7 P_{\text{CO}} P_{\text{H}_2\text{O}} \alpha_o^{n-1} [s]^2 / K_6$$

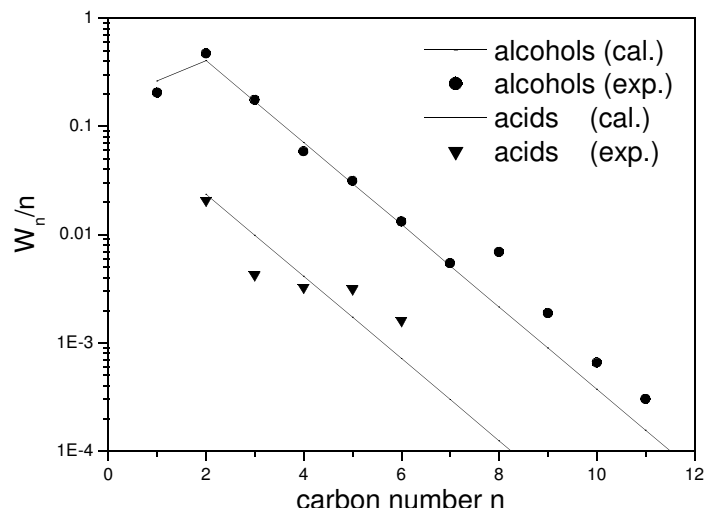
Oxygenate  
Kinetics  
Model  
II

$$\alpha_o = \frac{k_5 [\text{CH}_2 - s]}{k_5 [\text{CH}_2 - s] + k_9 K_1 K_7 K_8 P_{\text{H}_2} P_{\text{CO}} [\text{H} - s] + k_{10} K_1 K_7 P_{\text{CO}} [\text{OH} - s]}$$

$$[S] = 1 / [1 + K_1 P_{\text{CO}} + \sqrt{K_4 P_{\text{H}_2}} + K_1 K_7 P_{\text{CO}} \sqrt{K_4 P_{\text{H}_2}} + K_1 K_7 K_8 P_{\text{CO}} P_{\text{H}_2} \sqrt{K_4 P_{\text{H}_2}} + K_1 K_2 K_4 K_6 P_{\text{H}_2} P_{\text{CO}} / P_{\text{H}_2\text{O}} + K_1 K_2 K_3 K_4 K_6 P_{\text{H}_2}^2 P_{\text{CO}} / P_{\text{H}_2\text{O}} + P_{\text{H}_2\text{O}} / (K_6 \sqrt{K_4 P_{\text{H}_2}}) + \sum_{i=1}^n \alpha_o^i (1 + K_1 K_7 K_8 P_{\text{CO}} P_{\text{H}_2} \sqrt{K_4 P_{\text{H}_2}} + K_1 K_7 P_{\text{CO}} \sqrt{K_4 P_{\text{H}_2}}) \sqrt{K_4 P_{\text{H}_2}}]$$

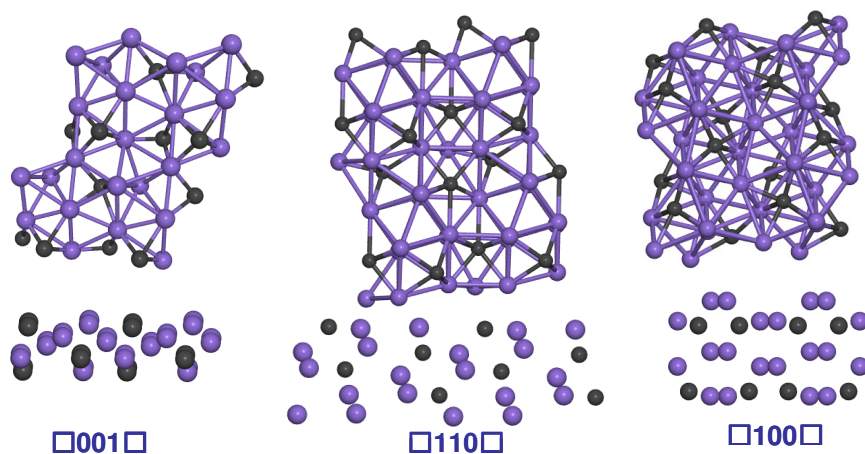

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**Figure 5.** Selectivities of oxygenates in FTS

Demands for fundamental information on catalyst surfaces under a real FTS reaction environment are obvious for establishing a solid basis for the mechanism understanding of the FTS reaction system and further the detailed kinetics modeling. However, due to the complex phase nature of iron based FTS catalysts, using various characterization tools to get information is greatly limited. Recent success in using quantum mechanics/chemistry tools to study the molecular and atomic nature of various kinds of catalytic chemical processes in Synfuels China<sup>15</sup> has encouraged us to consider the catalytic processes on the phases of iron catalysts by using these mentioned theoretical tools. The first phase chosen is naturally the  $\text{Fe}_5\text{C}_2$  having strongest correlation with FTS activity. Preliminary study was on the quantum mechanics calculations (CASTEP<sup>16</sup>) of CO adsorption on the (001), (110) and (100) surfaces of the Hägg iron carbide ( $\text{Fe}_5\text{C}_2$ ) as shown in Fig. 6. Over these surfaces, CO molecules were positioned on various kinds of sites, and the adsorption modes and energy were carefully scanned. Calculations for adsorption modes of CO over these surfaces under the coverage up to 1/2 were performed. 20 adsorption modes were identified, implying a complexity of CO adsorption on iron carbide phases.<sup>17</sup> The results from this kind of investigation are expected to be used for a comprehensive mechanism understanding of FTS reactions over iron catalysts. For this purpose, further investigation of the interaction of the surfaces of several phases with CO and  $\text{H}_2$  as well as other FTS molecules are going on.



**Figure 6.** Schematic top and front views of  $\text{Fe}_5\text{C}_2(001)$  (a), top and side views of (110) (b), and top and front

views of (100) (c) in a p(2\_2) unit cell.

Most reaction engineering studies on FTS over iron catalysts are based on detailed kinetics results along with understanding the hydrodynamics of bubble column reactors through cold mode tests and CFD calculations. For this purpose, cold mode facilities were built in 1999 for mimicking the pilot plant reactor system. These before-head investigations have been proved to be very helpful in reducing the risk in the real pilot plant operation. In addition, analyses of processes (using Aspen Plus simulation) imagined under different backgrounds have successfully assisted the implementation of the complete pilot plant that just constitutes all key parts necessary in industrial plants.

In summary, laboratory studies of the catalysis and catalysts, kinetics and reactors, and other fundamental aspects of FTS formed all the important concepts of the further scaling-up efforts. These studies with more and more enhancement are continuously playing the most important roles in the development of FTS technology initialized in ICC.

### 3.2.3 Pilot plant tests

The pilot plant for slurry phase FTS process development was founded in 2001, 5 years later from the last pilot plant operation for the fixed bed MFT technology. Construction of the new pilot plant with the capacity of 15-20 barrels/day lasted about one year. The first run was conducted in September of 2002. That was not a completely successful run, but it lasted about 25 days and did produced syncrude samples, showing a good prospect of this slurry phase FTS system. After a major equipment modification in the winter of 2002, three runs were conducted in 2003 accompanying a close feedback between the pilot plant and laboratory, leading to major improvement of several key technologies making the FTS workable. A planned two-month stable run is now going on since the beginning of June 2004. Next run will mainly test the limits of the current FTS technology, and is planned to begin on September 1, 2004.

In addition to the key technology development, Synfuels China has been cooperating with industrial partners to develop the syncrude upgrading process technologies, for which the existing technologies used in oil refineries are examined, and new specific technologies are developed to maximize the middle distillate yields from the syncrude and minimize the upgrading cost. In most cases, FTS crude has to be firstly hydrogenated to saturate the double bonds and to remove oxygenates. The hydrogenated products are separated to naphtha and diesel range fuel products, and the heavy products extracted from the bottom of distillation facilities are hydrocracked into desired fractions. The nature of FTS syncrude determines the processing strategy. Normally, hydrogenation and hydrocracking technologies used in refineries can be applied for this task. However, it is here noticed that operation conditions must be re-optimized in FTS product working up purposes in order to meet the demands in CTL plants. It is also important to think through the point that the existing oil refining technologies work under sulfur involving conditions that definitely increase the sulfur content of the final CTL plant from zero to a few ppm (<5ppm). Typical hydrocracking data by using conventional refinery technology are listed in Table 2. This can be a deficiency when the CTL products are used with higher values for lower sulfur content. Under this consideration, Synfuels China has successfully developed the sulfur-free hydrogenation and hydrocracking catalysts and process concepts at laboratory level. These technologies produce fractions with definitely zero sulfur contents (< 0.5 ppm). Some of catalysts are planned to scale up within 2005. The direct diesel fraction obtained from sulfur-free technology has been analyzed (Table 2). The sulfur free technology of CTL product working up eventually produces very pure products with extremely low smell and water-like appearance as shown in Fig. 7. The continuous optimization of the final products is arranged together with cooperation partners from both fuel specific organizations and car/engine industries.

**Table 2.** CTL diesel properties

| Indexes                              | Hydrogenated Fraction Refinery<br>Co-MoS <sub>2</sub> catalyst | Haydrocracked<br>Co-MoS <sub>2</sub> catalyst | Hydrogenated Fraction<br>S-free catalyst |
|--------------------------------------|--|---|--|
| Density kg/L                         | 0.7684   | 0.7782  | 0.7664                                   |
| Viscosity /mm <sup>2</sup> /s, 20 °C | 3.172  | 3.957   | 3.276                                    |
| Initial boiling point / °C           | 150  | 130   | 185                                      |
| Final boiling point /°C              | 370  | 385   | 330                                      |
| Disti. Range / °C                    |  |   |  |
| 5%                                   |  |   | 185-206.2                                |
| 10%                                  | 154-188  | 138-184                                       | 213.7                                    |
| 30%                                  | 257  | 231   | 232.7                                    |
| 50%                                  | 278  | 272   | 252.7                                    |
| 70%                                  | 293  | 305   | 278.2                                    |
| 90%                                  | 323  | 332   | 310.2                                    |
| 95%                                  | 330  | 341   | 322                                      |
| dried                                | 337  | 349   | 331.8                                    |
| Flash point /°C                      | 64   | 66  | 74                                       |
| Cetane number                        | 74.1   | 66  | > 74.8                                   |
| Total aromatics %                    | 0.4  | 0.7   | -  |
| Poly aromatics %                     | -  | -   | -  |
| Olefin /%                            | 0.5  | -   | -  |
| Sulfur / ppm                         | < 4  | <5  | <0.5                                     |
| CFPP / °C                            | -3   | -34   | -2                                       |
| Lubricity                            | -  | -   | -  |
| Oxidation stability                  | -  | -   | <0.3 mg/100mL                            |
| Acidity                              | 5.39   | -   | <0.2mg KOH/ 100mL                        |



**Figure 7.** CTL diesel and wax via sulfur-free working up processes

In addition to production of high quality fuels, chemicals can be produced making use of the special property

of FTS products. This aspect has been noticed and researches are also planned to increase the market opportunity of CTL plants in the future.

The economics of establishing the CTL field in China using the current FTS technology has continuously been conducted by the case study team in Synfuels China. Main conclusions formed are as follows:

- (1) Establishing large-scale CTL plants on the pitheads of several main coalfields, where long distance (> 800 km) transportation from the end users of primary energy (coal) is needed, is feasible and competitive when oil price is well above 25 \$/barrel;
- (2) Setting the critical oil price at 23 \$/barrel, the coal cost should be below 10\$/ton (raw coal with 5500-6000 kcal/kg, at the gasification feed) for CTL plant with lowest capacity of about half million tons liquid fuel products;
- (3) From the critical capacity of half million tons liquid fuel products defined for CTL plants, capacity expanding will further reduce the cost of the final products;
- (4) Coal properties are essential for successful CTL projects due to any problem in gasification section will significantly increase the cost;
- (5) The most suitable sites currently in China are the coal fields distributed over the area covering Inner Mongolia, Shaanxi, and Shanxi, where cost of coal is normally low and coal properties are good for gasification.

From intensive research and development up to pilot plant scale, the ICC's heavy fraction process technology (ICC-HFPT) is close to maturation at R&D stage. Efforts are to be put on the further scaling-up the process technology. For this purposes, extended process integration analyses are going on on the basis of closely cooperation with experienced engineering organizations and industrial partners in order to reduce the risk in the industrially demonstration stage. At the same time, scaling-up of the light fraction process technology (ICC-LFPT) based on the ICC-IIA catalyst is also enhanced, providing the flexibility in future CTL plants using ICC's technology.

### **3.3. Demonstration plant plan**

On the basis of the laboratory and pilot plant development of the CTL technology, conceptual design of a demonstration plant has been accomplished, and the detailed basic design of the plant will be accomplished by the end of this year. This demonstration plant is thus designed to validate the process integration concepts and to demonstrate the key technologies. Two year de-bottlenecking operation is planned and, then the plant is predicted to maintain a non-loss mode operation. Some profits are expected for the plant owner by policy supports. For all purposes above, the minimum capacity of this demonstration plant will be of 2500-3500 barrels/day. For meeting all the targets, Synfuels China is selecting the location and the best partners from several possible options.

Technically, gasification technology has been evaluated for this demonstration plant. The favorable choice is the entrained flow gasification technology with high syngas output from specific coal fed into the gasification reactor and at the same time with high syngas quality. In order to increase the efficiency of the single train process, flowsheeting has been severely evaluated. This plant is estimated to be well profitable at the current oil price (about 38 \$/barrel).

## **4. Summary**

Oil supply in China has reached the stage, in which a comprehensive strategy must be considered to limit the rapid increase in oil consumption under the background of rapid economy growth. Among all the possible oil

replacement options, production of liquid fuels from coal is the practically most feasible route to cope with the dilemma in oil supply. CTL solution using FTS technology can provide high quality diesel fuels meeting the stringent environment requirements with competitive economics and overall energy efficiency. These high quality products can seamlessly be combined with modern diesel engine technologies, forming a well-structured and highly efficient power train system for the transportation sector.

The development of CTL technologies using FTS from ICC has entered the stage for pursuing commercialization considerations. This includes an intensive research and development at both laboratory and pilot plant scales. Further systematic scaling-up of this technology will strongly promote the CTL applications at large scales, forming a completely new energy field in China.

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