

FINAL TECHNICAL REPORT
September 1, 2006, through August 31, 2007

Project Title: **MULTIFUNCTIONAL CATALYST/REACTOR DEVELOPMENT
FOR PRODUCT DEFINED FISCHER-TROPSCH SYNTHESIS**

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ABSTRACT

The aim of this research was to develop a novel bi-functional catalyst loaded on a monolithic structure to simultaneously achieve FT synthesis products from syngas along with the cracking of higher chain waxy hydrocarbons. The primary objective was to develop a bi-functional catalyst preparation methodology and to study the effect of process parameters on the product spectrum from such a reactor. It was expected that the success of this research would result in the development of a process that would eliminate the need for a hydrocracking unit and thus reduce the overall capital costs of the commercial deployment of coal to liquid fuels technology. This innovative scheme was expected to provide significant impetus to Illinois coal in finding a new market that is desperately looking for alternatives to foreign oil reserves. The basic idea of the research was to design a monolithic structure loaded with two catalysts (FT synthesis and cracking) that produce liquid hydrocarbon fuels. The end product envisioned in this process was a narrow spectrum of hydrocarbons with a maximum carbon chain length of C₁₅. The project involved the development of the bi-functional catalysts and the validation of the synthesis-cracking process along with the evaluation of the effect of process parameters on the product spectrum. Most importantly, the solids were designed such that they had the maximum selectivity to the beneficial reactions while maintaining their structure and activity.

EXECUTIVE SUMMARY

This research addresses the issue of producing liquid fuels from syngas using a novel monolithic, bi-functional catalyst.

Production of liquid transportation fuels from domestic resources is becoming increasingly attractive on both commercial and energy-security grounds. Steeply rising petroleum prices make production of synfuels more financially attractive than has been the case in the recent past, especially if technical breakthroughs further improve overall process economics. Furthermore, a significant fraction of U.S. petroleum supplies are imported from areas with geopolitical stability issues. This makes U.S. military and civilian fuel supplies vulnerable to sudden supply disruptions, with likely concomitant disruption of the U.S. economy.

One potentially attractive route for production of liquid transportation fuels from domestically available resources is Fischer-Tropsch (FT) conversion of coal derived syngas. The Illinois basin is a strong potential candidate for large scale development of FT liquid fuel production due to the abundance (and characteristics) of Illinois coal, the availability of abundant water resources, and the availability of relevant infrastructure and technical expertise.

This research deals with one area of FT synthesis where significant technical breakthroughs, with potentially significant impacts on the overall economics, may be achievable – use of multifunctional catalysis for optimization of the characteristics of raw FT product. FT chemistry produces primarily linear hydrocarbons across a broad molecular weight range. This product can be refined into useful fuels, but significant down stream processing is typically required, especially to break down high molecular weight components of the primary product. High molecular weight waxes are also difficult to separate from FT catalysts. Potentially, these challenges can be overcome by the use of monolith multifunctional catalysts that both catalyze syngas conversion and preferentially crack high molecular weight materials to products with a more useful boiling point range. This effort involved preparation of novel bifunctional catalysts that incorporate both Fe-based (Zn/K modified) FT catalyst and zeolite cracking catalyst in a single monolithic catalyst body. Monolithic catalysts have potentially significant advantages over conventional catalysts due to their mass transfer and diffusion characteristics. These catalysts were tested under a range of FT reaction conditions to evaluate catalyst performance and to optimize reaction conditions to maximize yields of the desired product range.

This effort included catalyst preparation and characterization, reactor design, fabrication and operation, and product analysis and evaluation. Underlying kinetic and thermodynamic considerations of the process, (especially at elevated pressures), were also investigated. An engineering analysis to optimize process parameters and guide process scale up and evaluation efforts was also conducted.

The underlying concept (the reactions involved) are well known and widely published in the literature. The concept is innovative, utilizing the knowledge of washcoating technique to develop a bi-functional catalyst that will eliminate a unit process entirely, and thereby make the coal to liquid fuels technology more attractive commercially. The ideal catalysts were identified along with the best coating method that provided a good distribution of the catalysts on the monoliths. The catalysts were thoroughly characterized to understand the effect of their physical and chemical properties on the final product distribution and the selectivity of the overall process towards certain chain lengths. The properties of the products of FT liquids employing our specially formulated bi-functional catalysts were evaluated. The investigation also included lab- scale experimental studies to demonstrate the above described scheme. The process parameters were optimized based on these studies and the technical feasibility of the process is demonstrated.

Task 1. Multi-functional Monolithic Catalysts Preparation - Washcoating

Bare cordierite cylindrical monoliths (height = 1", Φ = 1", and 200 channels per square inch) and 1 cm³ monoliths were obtained from Applied Ceramics (Atlanta, GA). The required washcoating chemicals such as AlOOH Catapal[®] B Alumina "bohemite" (Sasol, Houston, TX), urea (Sigma-Aldrich, St. Louis, MO), NaOH, and HCl (Fischer Scientific, Fair Lawn, NJ) were also acquired.

Washcoating of monoliths is conducted to increase the surface area of catalysis on the monolithic structure. It also helps in a uniform distribution of the catalyst in addition to helping the catalyst adhere to the surface of the monolith. A "sol-gel coating" method was used to washcoat both the monoliths. After washcoating, the monoliths were analyzed for uniformity of the coating and the increase in surface area. The surface area of the washcoated monoliths was measured using a BET Quantachrome Nova 2200e analyzer and nitrogen as an adsorbate. Additionally, the SEM analysis was carried out for the surface characterization of the washcoated layers, especially the washcoated layer thickness of the samples.

Task 2. Multi-functional Monolithic Catalysts Preparation – Impregnation with Fe-Zn-K

The materials obtained for impregnation were Fe(NO₃)₃, Zn(NO₃)₂, and K₂CO₃ (Sigma-Aldrich, St. Louis, MO). The washcoated monoliths (as described in Task 1), 1/8" γ -alumina pellets, and γ -alumina granules (Alfa Aesar, Ward Hill, MA) were impregnated. In addition, Fe-Zn-K powder catalysts for FT synthesis were also produced.

- Monoliths – Both Fe-Zn-K and Fe-Co catalysts were impregnated on to the cordierite monoliths.
- γ -alumina pellets – Four samples were prepared, namely –Fe on alumina, Fe-Zn on alumina, Fe-Zn-K on alumina, and Fe-Co on alumina.
- γ -alumina granules – Both Fe-Zn-K and Fe-Co catalysts were impregnated on to the alumina granules.

- Powders - Six powders were formed namely γ -ZnO, Fe, Fe on ZnO, ZnO on Fe, co-precipitated Fe-Zn and co-precipitated Fe-Zn-K.

Particle size analyses were performed on the alumina granules before and after impregnation. BET pore size distribution and surface area analyses were conducted for the powders, monoliths, and the catalysts supported on alumina. TPR studies of the *as-produced* catalysts were performed which indicated that the catalysts have to be reduced at the temperatures above 350°C prior to run the FT reaction. In addition, the literature review indicated that pretreatment of the catalysts in syngas is beneficial by forming Fe_xC phase sites. This was confirmed by our initial set of experiments.

Task 3. Multi-functional Monolithic Catalysts Preparation – Impregnation with ZSM-5 zeolite

Two cracking catalysts were used in the FT experiments. Calcium Bentonite powder was obtained from American Colloid Company (Arlington Heights, IL) and zeolite monoliths (height = 1", dia. = 1") were donated by the Applied Ceramics, Atlanta, GA. For ease of preparation and experimentation, the catalysts in these forms were used instead of impregnating zeolites on to the same monolith as the FT catalysts. However, this should not have a significant impact on the results as both the FT catalysts and cracking catalysts were still placed consecutively in the same reaction zone.

Task 4. Fischer-Tropsch Synthesis Experiments Using Laboratory Scale Monolith Reactor

The FT and cracking catalysts, prepared as described above and chosen for each specific experiment, were placed in a 6" tall by 1" Φ Inconel reactor. Void space around the monolith(s) was sealed to ensure that gas flows through the catalyst channels instead of around the monolith. FT synthesis reactions were carried out over a range of temperatures, pressures, syngas flows, and compositions to establish optimal conditions for generation of the desired product distribution. A mass flow controller and meter determined the inlet and outlet gas flows, respectively. Nominally, temperatures were between 200 and 450°C, total pressures between 0 and 15 bar and feed compositions ($H_2:CO$) from 1:1 to 2:1.

Product and reactants analysis was carried out by gas chromatography (Buck Scientific) using a ten-port sampling valve. The analysis of H_2 , N_2 , CH_4 , CO , and CO_2 was performed using a thermal conductivity detector (TCD). All hydrocarbons up to C_8 were analyzed using a flame ionization detector (FID). A molecular sieve column and a silica gel column preceded both detectors for separation of the gases. CO and H_2 conversions, CH_4 and CO_2 selectivities, and carbon number distribution were obtained from the GC data.

Task 5. Technical Feasibility Analysis

Mass and energy balances were carried out for estimating the system efficiency. A study was also made of the reactors and the impacts of various reactor configurations on pressure drop, heat loss, reactor size and efficiency.

OBJECTIVES

The research addressed a novel approach for the development of the bi-functional catalyst that will catalyze simultaneously both the FT process and crack the long-chain hydrocarbons in the same reactor. Implementation of this technology will result in (a) reduction of the capital cost of the FT process, (b) simplification of the coal to liquid fuel production technology, (c) allow operations at higher temperatures, therefore will increase the conversion of the syngas without increasing the formation of the long chain hydrocarbons.

The specific objectives included development of catalysts that simultaneously achieve the FT synthesis and crack the waxes being formed in the process. The catalysts were characterized in order to understand the physical and chemical properties and their activities in the process. The optimal operating conditions (temperature, pressure, flowrates) were identified to produce liquid fuels with the narrow distribution of the carbon chain links no longer than C₁₅.

The effort consisted of two major activities: (a) development of the wash coating procedures to prepare the bi-functional catalyst and (b) the study of the effect of process parameters on the performance of this bi-functional catalyst in the production of a narrow spectrum of FT synthesis products. This involved engineering development and demonstration of the overall process. After completion of the initial study of the first activity, activities (a) and (b) were conducted in a coordinated fashion such that the information was fed back and forth to fine tune the key issues. The task structure of the research with a summary of the outline of each task activities is presented below.

Task 1. Multi-functional Monolithic Catalysts Preparation – Washcoating

The aim of this task was to washcoat monoliths of various sizes to optimize the surface characteristics for impregnation with active Fischer-Tropsch catalysts.

Task 2. Multi-functional Monolithic Catalysts Preparation – Impregnation with Fe-Zn-K

The purpose of Task 2 was to prepare several different combinations of active FT catalysts on varying supports.

Task 3. Multi-functional Monolithic Catalysts Preparation – Impregnation with ZSM-5 zeolite

The objective of this portion of the research was to prepare the hydrocarbon-cracking portion of the multi-functional catalyst.

Task 4. Fischer-Tropsch Synthesis Experiments Using Laboratory Scale Monolith Reactor

The aim of Task 4 was to run several FT catalyst / cracking catalyst combinations and experimental conditions to optimize the process.

Task 5. Technical Feasibility Analysis

The aim of this task was to summarize the data in order to evaluate the technical feasibility of the process.

INTRODUCTION AND BACKGROUND

This research is concerned with the development of a novel technology that will enable the production of liquid transportation fuels from coal derived syngas. Fixed-bed and slurry reactors have been so far the reactors of choice for low temperature Fischer-Tropsch (FT) synthesis. However, the large particles in fixed-bed reactors result in poor intra-particle mass transfer characteristics and the space time yield is limited by heat transfer in the catalyst bed. The slurry reactor shows a great improvement of mass transfer within the catalyst particles, however, the separation of the catalyst from the products can be troublesome. Additionally, the back-mixing makes the slurry reactor less efficient in terms of the reactor volume than the plug flow reactors. In addition, formation of hydrocarbons heavier than the diesel cut, i.e. waxes, in the FT process requires installation of additional cracking (hydrocracking) systems for waxes decomposition. This work incorporates a monolithic, bi-functional catalyst to achieve the primary objective. The use of this monolithic, bi-functional catalyst enables the synthesis of FT liquid products while simultaneously hydrocracking long chain hydrocarbons. The two primary advantages of this process are the reduction in the number of unit processes (due to the use of a single reactor) and the narrow distribution of the product as defined by the market needs.

The process is schematically shown in Figure 1. The feed to the reactor was syngas with the desired CO/H₂ ratio for simultaneous synthesis and cracking. The synthesis catalysts (Fe-Zn-K based) produced the liquid fuels from the syngas. The produced long chain carbons and excess hydrogen then passed through the cracking section where the zeolite cracking catalyst broke the carbon chains greater than C₂₀ to produce the resulting distribution.

Having an adequate amount of liquid fossil fuels is currently becoming very important and may become imperative in the future. There are many possible reasons for an inadequate amount of liquid fossil fuels in the future, with some of them being political conflicts, natural disasters, decreased supply, and increased demand. Because the future of natural liquid fossil fuels is uncertain due to some of the reasons listed above, it is important to investigate the production of synthetic liquid fuels. Synthetic liquid fuels were produced in Germany from 1938 to 1944, during WWII, using thoria and magnesia-promoted cobalt catalysts¹. They were also produced in South Africa from the mid 1950's at Sasol plants in fixed and fluidized-bed reactors utilizing potassium-promoted iron catalysts; and the facilities there are still in operation¹. Synthetic liquid fuels are most commonly made catalytically in the Fischer-Tropsch (FT) reaction. This proposal will

review previous work that has occurred and propose to design, fabricate, and test devices that produce synthetic liquid fuels from simulated syngas that ultimately would be formed from the gasification of Illinois coal.

Much research has been conducted and reported about activating the catalyst used in F-T synthesis. Rao *et al.*² studied iron FT catalysts during activation and synthesis. They found that catalysts activated with CO had a much higher activity than catalysts activated with syngas. Luo and Davis³ also studied the activation of iron-based catalysts and similarly found that catalysts that were activated with CO had the best hydrocarbon production rate and yielded the lowest selectivity to CH₄. Bukur *et al.*⁴ studied the effect of the gas used (CO, H₂, or H₂/CO = 0.68), activation temperature (250, 280, or 310°C), duration (8 or 24 h), and pressure (0.1, or 1.48 MPa) on the activity, selectivity, and stability of an iron based FT catalyst. They found that activation at 280°C, 0.1 MPa, and 24 h was the most desirable for overall catalyst activity, selectivity, and stability. Burkur *et al.*⁵ further researched catalyst activation and found that the catalyst activated with H₂ instead of CO showed lower activity initially but increased with time-on-stream, whereas catalysts activated with CO or syngas decreased in activity due to conversion to less active iron oxide. However, they also found the catalyst activated with H₂ produced more CH₄ and other gaseous hydrocarbons compared to catalysts activated with CO or syngas. O'Brien *et al.*⁶ studied the long term (> 500 h) activation of iron catalysts used for FT synthesis using CO or simulated syngas with different amounts of H₂. Pretreatment of FT catalysts with a high partial pressure of H₂ formed Fe₃O₄ that is relatively inactive in FT synthesis. Sault and Datye⁷ determined that the material of the catalyst and the activation procedure affects the final activity of the catalyst. For example, the conversion of a catalyst with Fe, Cu, and K varied by a factor of 3 depending on the activation treatment, whereas, conversion of a catalyst with Fe, Cu, K, and SiO₂ had little dependence on the activation treatment.

Other research has been done to determine the effect of catalytic activity by adding different materials to the iron FT catalysts. O'Brien and Davis⁸ determined the effects of copper on the activity of FT iron catalysts and selectivity of water-gas shift. They reported the effects of copper at the same conversion extent to determine the true impact of the copper and performed tests over a wide range of syngas conversions. Luo *et al.*⁹ determined the effect of using palladium in iron Fisher-Tropsch synthesis catalysts. Palladium enhanced the FT activity to a small extent and changed the selectivity of CO₂ and CH₄. Raje *et al.*¹⁰ determined the effect of potassium on iron FT catalysts. They found the potassium affected the catalyst activity differently depending on the hydrogen formed during the water-gas shift reaction. Dlamini *et al.*¹¹ determined the effect of adding SiO₂ to FT catalysts during precipitation or after heat treatment. Adding SiO₂ during precipitation strongly interacted with Fe resulting in crystallites that are resistant to reduction and carburization. However, they determined adding SiO₂ after heat treatment, as a binder, resulted in segregated SiO₂-rich and Fe-rich phases. Xu *et al.*¹² added platinum to silica-supported iron catalysts and determined that methane and hydrocarbon selectivities at a specified operating condition was 7-9%, and 91-93%, respectively. These results and others show it is feasible for an active, selective, stable, and attrition-resistant supported iron catalyst for FT synthesis.

Duvenhage and Coville¹³ determined the effect of potassium, chromium, and manganese on hydrogenation of CO during FT synthesis. They found that K and Cr modestly improved activity, decreased formation of methane, and increased the C₅ and greater fraction of the FT product, while Mn-promoted catalysts decreased activity and reduced selectivity. Li *et al.*¹⁴ determined the effects of Zn, K, and Cu on the structure and surface area, and on the reduction, carburization, and catalytic behavior of Fe-Zn and Fe oxides used as precursors to FT synthesis. Zn, present as ZnFe₂O₄, increased the surface area and therefore led to higher rates than ZnO-free precursors. K and Cu both increased the FT rates of catalysts formed from Fe-Zn oxide precursors; Cu increased methane formation but the additional presence of K inhibited this effect. Saglam¹⁵ determined the effect of vanadium and zinc, separately or together, on selectivity of FT catalysts. The finding was that the addition of V, separately or together with Zn, greatly increased the selectivity of the iron FT catalyst, while only adding Zn was less effective in the selectivity of the catalyst. Boskovic *et al.*¹⁶ determined the effect of K- and Al-promoted Fe/MgO FT catalysts. They determined that Al results in suppression of adsorption of both CO and H₂.

Li *et al.*¹⁷ used promoters (K, Ru, Cu) with iron-based FT catalysts. They found that Fe-Zn-Cu-K catalysts gave much lower CH₄ selectivities than Co-based catalysts and they also shown much weaker effects of temperature on CH₄ and C₅₊ selectivities. Gallegos *et al.*¹⁸ covered SiO₂ with MgO to use as a support of iron catalyst in FT reaction. They found the activity to total hydrocarbons produced increases with MgO added and 4% by weight was found to have the highest selectivity to olefins. Wu *et al.*¹⁹ prepared an iron catalyst that contained sulfur for FT synthesis. Fixed bed and slurry reactors were used to test the activity of the catalyst after a long time-on-stream. They found that the catalyst had a high CO conversion and C₅₊ selectivity in the slurry reactor. They also proposed that sulfur, existing as SO₄, may promote the catalyst by increasing activity and improving the selectivity of heavier hydrocarbons. Tihay *et al.*²⁰ studied the properties and reactivity of Fe-Co FT synthesis catalysts. They proposed the properties were due to the formation of a Fe-Co alloy rather than the sum of their respective properties.

Other researchers have characterized the material of the catalyst. Mansker *et al.*²¹ used X-ray diffraction to determine the form and composition of the iron. They pointed out that iron catalysts can undergo oxidation during their removal from the reactor and before analysis, which makes it very difficult to determine the actual phase composition of the catalyst during operation. Also it was stated to not expose hot wax to the ambient temperature as this may cause transformations in the catalytically active components of it.

Jin and Datye²² used X-ray diffraction to follow the phase transformations of iron FT catalysts during temperature-programmed reduction. The results showed that three stages of phase transformation of the iron could be seen, namely: hematite to magnetite, magnetite to iron carbide, and finally significant carbon deposition and further carburization. Li *et al.*²³ used *in situ* X-ray absorption spectroscopy to determine the local structure starting with Fe₂O₃ being reduced to Fe₃O₄, followed by carburization to form

FeC_x . The reaction rates increased during the initial stages of carburization suggesting that conversion of the near surface layers to FeC_x is sufficient for formation of the required active sites.

Fischer Tropsch based coal to liquid fuels process involves three broad steps a) syngas production b) syngas conversion and c) hydrotreatment. Syngas production is achieved by gasification of coal followed by the water gas shift reaction to increase the proportion of hydrogen in the syngas. An additional gas conditioning step is required to alter the CO/H_2 ratio for optimal performance in the syngas conversion step and to remove toxic impurities that are hazardous both to the environment and to the catalyst for FT synthesis. In the syngas conversion step, the FT synthesis reactions occur that convert the CO and H_2 to long chain hydrocarbons. This step produces a wide spectrum of compounds with varied carbon chain lengths. FT reactions can be carried out at both high and the low temperatures. The FT process is used for the production of gasoline and chemicals like alpha olefins. However, the formation of compounds with a high number of carbon atoms is unavoidable. These compounds are waxy in nature and need to be hydrotreated to form liquid fuels necessitating the cracking step which cracks these waxes. Each of the processes, namely gasification, FT synthesis and hydrocracking has been widely studied. However, their combined use has not been widely used. The two primary reasons for problems with deployment is the preparation of optimal feed conditions and capital and operating cost issues. The authors have already developed a technology that effectively alters the syngas composition for use in FT processes as well as complete removal of sulfur compounds from syngas. Several researchers are attempting to control the product spectrum of the FT process by manipulating the operating conditions (e.g. temperature, pressure and gas composition) and thereby reducing the size of the hydrocracker. However, due to the variation of temperatures within the reactor and the exothermic nature of the FT process precise control of the product spectrum is ineffective by just controlling these parameters. The authors propose to eliminate the need of the hydrocracker by developing a bi-functional catalyst that can simultaneously achieve synthesis as well as crack the long chain hydrocarbons in the same reactor. The technology will have a significant impact on the progression of the Fischer-Tropsch reaction. It will significantly improve the economics of the reaction because it eliminates one large piece of the equipment, namely the hydro-cracker. This reduces the initial cost of the equipment. It also reduces the total footprint for the FT reaction thereby reducing the amount of land and size of the building needed; both which reduce the initial cost of the facility. Recognizing the increase in energy prices and the reduction in cost with the improvements in the FT reaction, it will greatly assist in making the FT reaction economical, which will significantly improve the use of Illinois coal.

Figure 1 shows the schematic of the process to produce liquid fuels with a narrow C-chain spectrum. The monolithic reactor, loaded with the catalyst, was produced by washcoating methods described in the tasks. Fe-Zn-K has been identified as the synthesis catalyst while ZSM-5 has been selected for cracking purposes. The two catalysts will be washcoated on the same monolithic support. In the first section of the reactor the syngas will be converted into long chain hydrocarbons while in the latter section, the hydrocarbons with more than 20 carbon atoms per molecule will be cracked selectively.

Since the two processes will be carried out in the same reactor, the need for an additional unit and associated logistics will be eliminated. In addition, proper manipulation of the operating conditions will eliminate the need for additional energy requirements.

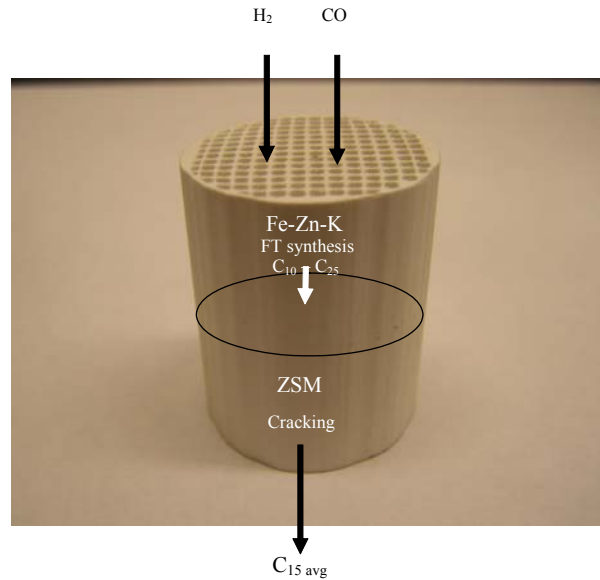


Figure 1. Schematic of the Concept

The political instability in the oil producing nations and the rapid depletion of crude oil reserves have resulted in a rapidly increasing crude oil prices (and hence, gasoline and diesel prices). As a result, alternative technologies (such as bio-diesel, gas-to liquid technologies, etc) to produce competing transportation fuels have gained importance. The technology described in this proposal aims at improving FT technology for the conversion coal-derived syngas to liquid fuels. This will be achieved by a novel design of the reactor and catalyst. One of the main drawbacks of the currently available technologies that exploit the Fischer-Tropsch reaction is the wide distribution of the products formed (including very long chain hydrocarbons appearing as waxes). To overcome this drawback, researchers have proposed an additional unit process (namely hydrocracking) that would not only increase the cost of production (both from an operational and capital costs point of view) but would also increase the complexity of the operation and requires diversion of hydrogen from the FT reaction to supply hydrocracking demand. The research aims at developing a novel reactor/catalyst design that would enable FT synthesis and cracking reactions to be accomplished in a single reactor. This would reduce the above mentioned costs as well as provide a narrow range of product distribution designed to better meet the end user specifications. This technology combined with advanced gasification technology (with regards to conditioning of coal gasification products) will overcome a number of problems currently faced by the industry. The gas conditioning technology developed by the authors is able to effectively alter the CO/H_2 ratio amenable for narrow product distribution while removing impurities such as H_2S and CO_2 in a single reactor. Thus, the combination of

these two technologies is especially crucial to the market for FT liquid fuels production utilizing the high sulfur Illinois Coal.

Illinois coal is high in sulfur and chlorine. However, it is significantly low in mercury. This particular distribution of the toxics will be useful in the reduction of mercury after the gasification stage. However, the high sulfur issue has plagued Illinois coal in the energy production sector (via combustion processes). The emergence of the need for domestically produced liquid transportation fuels at costs comparable to that obtained from the refineries dependent on foreign sources will help develop new markets for Illinois.. This technology will boost the acceptance of Illinois coal in the FT liquid fuels market primarily due to comparable costs with the added benefit of lower toxic impurities.

Additional Benefits

End user defined product: The improved FT process will produce liquid fuels with a narrow product distribution closer to end user needs, in a single reactor.

Operating costs: the technology will reduce both capital and operating costs for FT production of liquid fuels by eliminating the need for down-stream hydrocracking of crude FT.

Likelihood of obtaining patent: We believe the concept of multifunctional catalyst design is a patentable idea. The successful demonstration of the technology will result in additional patent rights.

EXPERIMENTAL PROCEDURES

Task 1. Multi-functional Monolithic Catalysts Preparation – Washcoating

Bare cordierite cylindrical monoliths (height = 1", Φ = 1", and 200 channels per square inch) and 1 cm³ monoliths (200 channels per square inch) were used. The bare cordierite supports were first washed in 1 M NaOH solution for 30 minutes, then washed in distilled water for 5 minutes, followed by washing in HCl for 30 minutes and then again in distilled water for 15 minutes. The method call "sol-gel coating" was used for washcoating. A sol was prepared from AlOOH Catapal[®] B Alumina "bohemite", urea, and 0.3M nitric acid in a weight ratio of 2:1:5. These components were vigorously mixed. The acid made the alumina form positively charged agglomerates, which repelled each other, and prevented the formation of large three-dimensional alumina networks. The addition of the polar urea helped keep a low-viscosity sol by preventing the gelating of the AlOOH from proceeding too far. The given ratio for pseudo-bohemite, acid and urea resulted in the formation of a stable sol with a typical viscosity of 20 mPa s⁻¹. The supports were dipped in the sol and stirred for 3 hrs. . The monolith supports were then emptied by shaking and by passing pressurized air. The wash coated supports were then dried for 10 hrs at 110 °C, followed by calcination at 500 °C for 5 hrs. In the calcination step, the carbon dioxide and nitric oxide produced from the oxidation of the urea helped

in the formation of micropores in the alumina coat layer. Only one coating was used initially. After washcoating, the monoliths were analyzed for uniformity of the coating and the increase in surface area. The surface area of the washcoated monoliths was measured using a BET Quantachrome Nova 2200e analyzer and nitrogen as an adsorbate. Additionally, SEM analysis was carried out for the surface characterization of the washcoated layers, especially the washcoated layer thickness of the samples. The results of the BET and SEM analyses indicated a need for washcoating to be carried out twice on each monolith. Thus, the above method was performed twice before the impregnation step.

Task 2. Multi-functional Monolithic Catalysts Preparation – Impregnation with Fe-Zn-K

Monoliths – Both Fe-Zn-K and Fe-Co catalysts were impregnated on to the cordierite monoliths. The active phase (Fe-Zn-K) of the FT catalyst was applied by homogeneous deposition precipitation at 70 °C from the aqueous solution of Fe and Zn nitrates. Solution containing 3.0 M $\text{Fe}(\text{NO}_3)_3$, 1.4 M $\text{Zn}(\text{NO}_3)_2$ and urea were mixed such that the Zn/Fe atomic ratio was 0.1. The monolith was then dipped into the resulting solution. As the urea decomposition is a slow process, the Fe and Zn hydroxides are deposited uniformly over the thickness of the washcoat. The impregnation was carried out for 60 minutes. The impregnated monolith was then dried at 100 °C for 12 hrs and then calcined at 350 °C for 16 hrs. The calcined product was then dipped for 15 minutes into an aqueous solution of 0.16 M K_2CO_3 , thereby doping the catalyst with potassium by the incipient wetness impregnation method. These samples were dried at 100 °C in ambient air for 15 hrs and then calcined at 400 °C for 4 hrs.

Alumina pellets – Four samples were prepared, namely – Fe on alumina, Fe-Zn on alumina, Fe-Zn-K on alumina, and Fe-Co on alumina. 1 M solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and K_2CO_3 were prepared in distilled water. The solutions were mixed such that the Fe: Zn ratio was 1:0.4 and Fe: K ratio was 1:0.02. Approximately 5 g of alumina pellets was immersed in 100 mL of the respective solutions and stirred slowly for 10 hrs. The pellets were then filtered, washed once with distilled water and dried at 110 °C for 3 hrs and then calcined for 16 hrs.

Alumina granules – Fe-Zn-K, Fe-Co-Zn-K, and Co-Zn-K catalysts were impregnated on to the alumina granules. 1 M solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_4 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and K_2CO_3 were prepared in distilled water. The solutions were mixed such that the Fe: Zn ratio was 1:0.4 and Fe: K ratio was 1:0.02. In the case of Fe-Co-Zn-K, Fe/Co ratio was maintained to be 1:1. Approximately 20 g of alumina granules were immersed into 100 mL of the respective solutions and stirred slowly for 10 hrs. The granules were then filtered, washed once with distilled water, dried at 110 °C for 3 hrs, and then calcined for 16 hrs.

Powders - The powders were prepared by precipitation from the precursor solutions by reduction with sodium borohydride. Six powders were formed namely –ZnO, Fe, Fe on ZnO, ZnO on Fe, co-precipitated Fe-Zn and co-precipitated Fe-Zn-K. 1 M solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and K_2CO_3 were prepared in denatured ethyl alcohol.

The solutions were mixed such that the Fe:Zn ratio was 1:0.4 and Fe:K ratio was 1:0.02. 1 % NaBH₄ solution in water was then added dropwise to the respective solutions to obtain the required powders till sufficient amount of powder for analysis was formed. The solution containing the powder was then centrifuged (Marathon model) at 3500 rpm. The supernatant liquid was decanted and the solids were washed with ethyl alcohol. The solids were then filtered and stored under nitrogen. In the cases of ZnO on Fe and Fe on ZnO powders, the Fe and ZnO particles were first precipitated, centrifuged, washed and then filtered. The filtered Fe and ZnO particles were then soaked with the precursor solutions containing Zn and Fe, respectively. 1 % NaBH₄ solution was then added dropwise to precipitate the second component onto the existing solid.

Particle size analyses were performed on the alumina granules before and after impregnation. BET pore size distribution and surface area analyses were conducted for the powders, monoliths, and the catalysts on the alumina supports. TPR studies of the as-produced catalysts were performed which exhibited the need for catalyst pretreatment in hydrogen. In addition, initial FT experiments indicated that pretreatment of the catalysts in syngas is beneficial by forming Fe_xC phase sites.

Task 3. Multi-functional Monolithic Catalysts Preparation – Impregnation with ZSM-5 zeolite

Two cracking catalysts were used in the FT experiments. Calcium Bentonite powder was obtained from American Colloid Company (Arlington Heights, IL) and zeolite monoliths (height = 1", Φ = 1") were donated by Applied Ceramics, Atlanta, GA. For ease of preparation and experimentation, the catalysts in these forms were used instead of impregnating zeolites on to the same monolith as the FT catalysts. However, this should not have had a significant impact on the results as both the FT catalysts and cracking catalysts were still placed consecutively in the same reaction zone.

Task 4. Fischer-Tropsch Synthesis Experiments Using Laboratory Scale Monolith Reactor

The catalytic monoliths, powders, granules, and cracking catalysts, prepared as described above and chosen for each specific experiment, were placed in a 6" tall by 1" Φ Inconel reactor. FT synthesis reactions were carried out over a range of temperatures (200-450 °C), pressures (0-15 bar) and syngas compositions (H₂:CO ranging from 1:1 to 2:1) to establish optimal conditions for generation of the desired product distribution. A mass flow controller and meter determined the inlet and outlet gas flows, respectively.

Leak tests were conducted before each experiment using nitrogen under ambient conditions, followed by further leak tests at elevated temperatures and pressures. After making sure no leaks were present, the catalyst was reduced under hydrogen for 12 hours at 450 °C and atmospheric pressure. As discussed in Task 2, the reduction step was then followed by the Fe_xC formation step. This step consisted of passing syngas through the reactor at 400 °C for one hour. Upon completion of both the reduction and Fe_xC

formation steps, the reactor was purged with nitrogen and the desired reaction temperature and pressure were set.

A heated trap (at 200 °C and reactor pressure) was placed immediately below the reactor in order to collect heavy hydrocarbons $>C_{20}$ and a cold trap (ambient temperature/pressure) was placed after the back pressure regulator in order to collect water, oxygenates and $C_8 <$ hydrocarbons $< C_{20}$. Product and reactants analysis was carried out by gas chromatography (Buck Scientific) using a ten-port sampling valve. The analysis of H_2 , N_2 , CH_4 , CO , and CO_2 was performed using a thermal conductivity detector (TCD). All hydrocarbons up to C_8 were analyzed using a flame ionization detector (FID). A molecular sieve column and a silica gel column preceded both detectors for separation of the gases. CO and H_2 conversions, CH_4 and CO_2 selectivities, and carbon number distribution were obtained from the GC data.

Task 5. Technical Feasibility Analysis

Mass balance was carried out for estimating the system efficiency. Impact of the reactor configurations on the FT synthesis was evaluated.

RESULTS AND DISCUSSION

Task 1. Multi-functional Monolithic Catalysts Preparation – Washcoating

The washcoating technique was optimized in order to produce the uniform layer of the γ -alumina washcoat. Two consecutive processes of washcoating were performed to produce the desired surface of the monolith for impregnation with the active components of the catalysts.

Task 2. Multi-functional Monolithic Catalysts Preparation – Impregnation with Fe-Zn-K

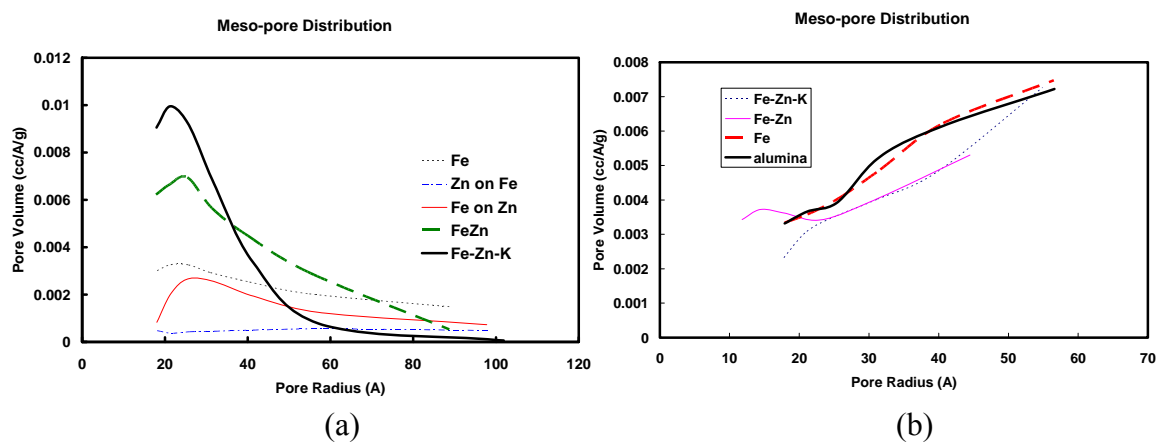
TEM photomicrographs of the powders show that they were well below 100 nm. In fact most of the particles were below 20 nm. BET pore size distribution and surface area analysis were conducted for the powders and the catalysts on the alumina supports. Figures 1 a and b show the meso pore distribution of the powders and the catalysts on the alumina supports while Figures 2 a and b show the micropore distribution of the powders and catalysts on alumina supports. Tables 1 and 2 summarize the maximum pore size, surface area and the specific pore volume for the various samples.

Table 1 BET Summary of precipitated powder catalysts

	Surface Area m ² /g	Pore Radius Å	Pore Volume cc/g
Fe	42.2	18.13	0.16
Zn	14.3	92.4	0.03
Fe on Zn	50.3	78.14	0.11
Zn on Fe	30.2	57.89	0.06
Fe-Zn	101.92	21.12	0.21
Fe-Zn-K	228.35	18.12	0.26

Table 2 BET Summary of catalysts on γ -alumina

	Wt of support %	Surface Area m ² /g	Pore Radius Å	Pore Volume cc/g
Alumina	100	170.63	56.6	0.3
Fe/Alumina	111.9	146.92	56.51	0.3
FeZn/Alumina	116.24	120.4	44.48	0.19
FeZnK/Alumina	120.3	143.84	54.9	0.26

Figure 1 Pore size distribution of (a) precipitated powder catalysts and (b) catalysts on γ -alumina

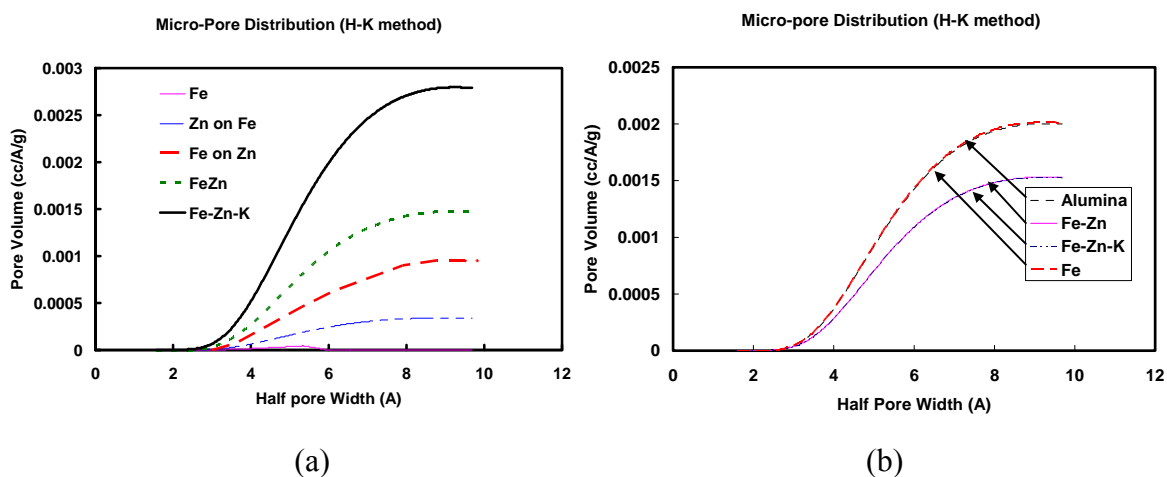


Figure 2 Pore size distribution of (a) precipitated powder catalysts and (b) catalysts on γ -alumina

BET pore size distribution and surface area analysis are being conducted for the bare catalyst support, wash coated monoliths and impregnated washcoated monoliths. The pore size distribution changed drastically from the bare monolith to the washcoated monolith. No further change in the shape of the distribution was observed during impregnation although the pore volume distribution was drastically affected. Employing the current method of washcoating, the surface area was increased modestly by around 2 times from an initial specific surface area of $6.37 \text{ m}^2/\text{g}$ to $14.64 \text{ m}^2/\text{g}$. Impregnation with the catalyst further increased the specific surface area to $33.28 \text{ m}^2/\text{g}$. In order to increase the surface area further, the dipping and calcination procedure has to be repeated several more times. Table 3 and Figure 3 show the BET data on the bare, washcoated and impregnated monolith.

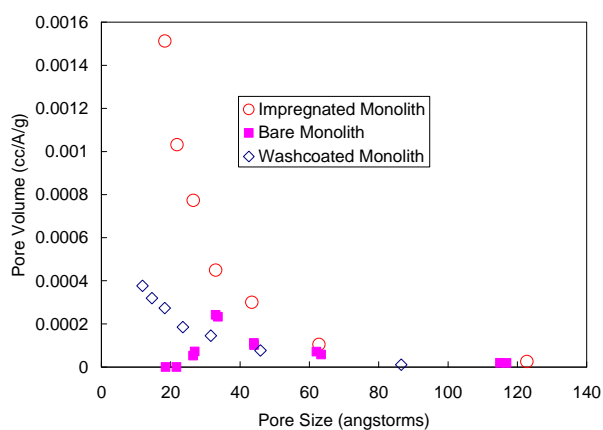


Figure 3 Pore size distribution of bare, washcoated and impregnated monoliths

Table 3 BET Summary of catalysts on monoliths

	Surface Area m ² /g	Pore Radius Å	Pore Volume cc/g
Bare Monolith	6.37	32.97	0.01
Washcoated Monolith	14.64	11.86	0.03
Impregnated Washcoat	33.28	18.31	0.03

Task 3. Multi-functional Monolithic Catalysts Preparation – Impregnation with ZSM-5 zeolite

The ZSM-5 catalysts in the form of the monolith and powder were used as received. Originally, we proposed to washcoat the monolith with thin layer of ZSM-5. However, we were able to receive the samples of the ZSM-5 monolith from the commercial source and it was used as received. Moreover, the powder of ASM-5 was also used with both pellets and powder FT catalysts.

Task 4. Fischer-Tropsch Synthesis Experiments Using Laboratory Scale Monolith Reactor

Experiments for analyzing the residence time distribution for a step input of the reactive gases were conducted and evaluated. Figure 4 shows the residence time distributions at the different syngas content and flowrate at 200°C and 200 mL/min.

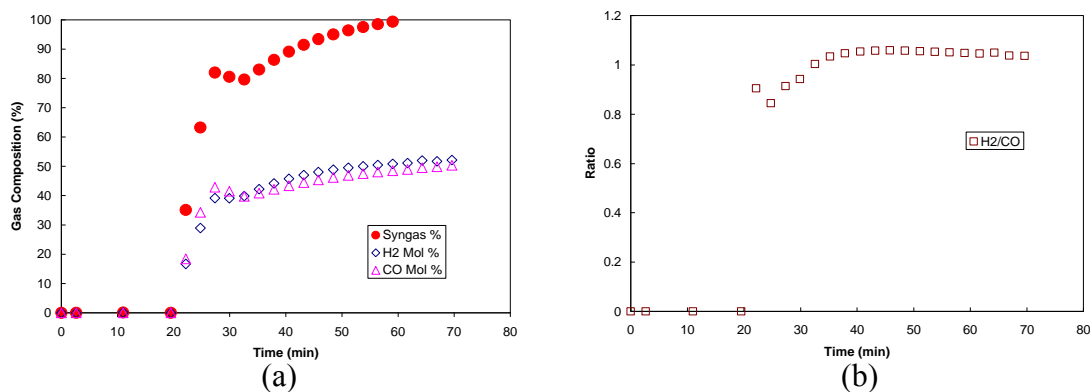


Figure 4 RTD experiments 250°C, 200 mL/min syngas flow rate, 10 bar: (a) syngas % and gas composition vs time, (b) H₂:CO ratio

Preliminary FT synthesis experiment at 10 bars and 200 and 250°C were conducted at flow rates of 50, 100 and 200 mL/minute of syngas in the ratio of 48 % H₂ and 52 % CO. Figure 5 presents the FT synthesis results (CO, CO₂, H₂) for the preliminary runs. No significant reaction was observed. The only product of the experiments was found to be CO₂. Several TPR experiments were then conducted to evaluate the catalyst which requires in situ reduction of iron oxide to the FT active catalyst. However, the TPR experiments (Figure 6) indicated that the reduction of the impregnated iron oxide

occurred at in the range of 400 – 600°C. It has thus been concluded that the catalyst should first be reduced at a high temperature of 600°C and upon completion of the reduction, the temperature would be lowered for FT synthesis.

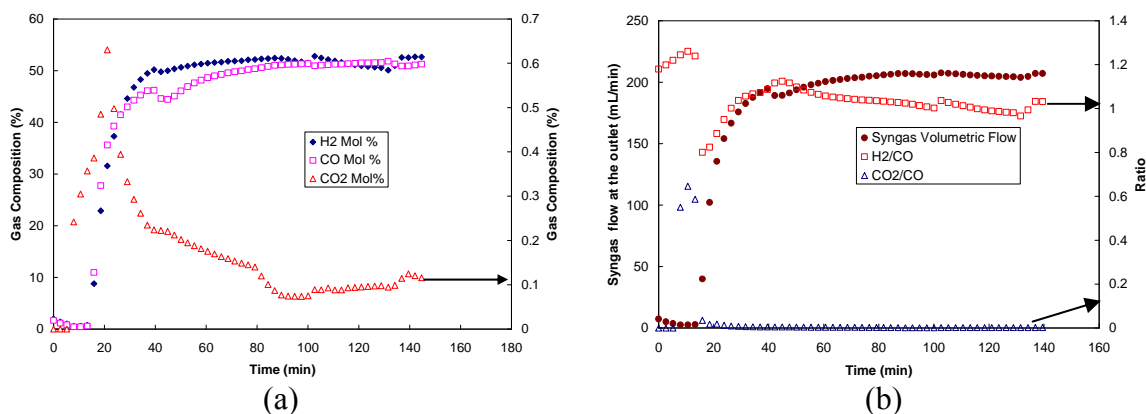


Figure 5 FT synthesis experiments 250°C, 200 mL/min syngas flow rate, 10 bar: (a) gas composition vs time, (b) syngas flow at the outlet, H₂:CO and CO₂:CO ratios

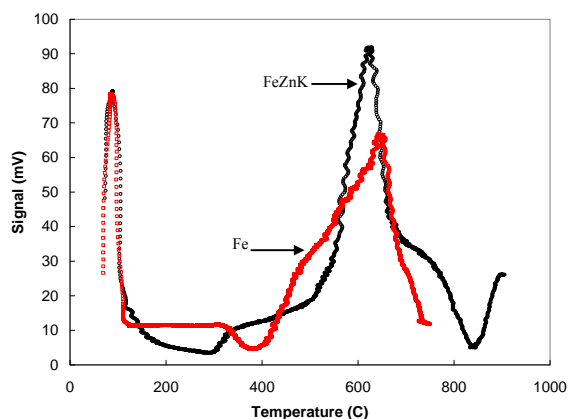


Figure 6 TPR profiles of Fe and Fe-Zn-K catalysts in 5% hydrogen (5°C/min)

In the next series of experiments, the catalyst was first reduced in hydrogen atmosphere for 1 hr at 500°C (Figure 7). The Fe-Zn-K catalyst supported on alumina was used for these experiments. Approximately 5 gms of the catalysts on support were used. The catalyst loading on these supports were around 20% of the total weight. Subsequently, FT synthesis experiment was conducted at 10 bars and 250°C. Very little synthesis was observed. It has been reported in literature that the active catalyst in FT synthesis when iron is used as a catalyst is the Fe_xC phase. Thus, in the next series of experiments, after the reduction in hydrogen, the catalyst was then pretreated at 400 and 450°C (for two different tests) with syngas to form the active Fe_xC phase and then the FT synthesis experiments were conducted at 10 bars and 250°C (Figure 8). At the elevated temperatures, the GC showed the presence of carbon dioxide, methane and some higher hydrocarbons which were not seen at 250°C. The syngas flow rate in all the experiments

were 100 mL/min. 100 % syngas was used for all the experiments. Approximately 50 ml of liquid was formed. However, the GC did not show the presence of hydrocarbons during the FT synthesis phase. It is assumed that the use of pure syngas combined with the low catalysts loading (~1g) may not show the small changes in concentration in the outlet gases. However, the presence of significant amount of liquid was testament of successful reactions.

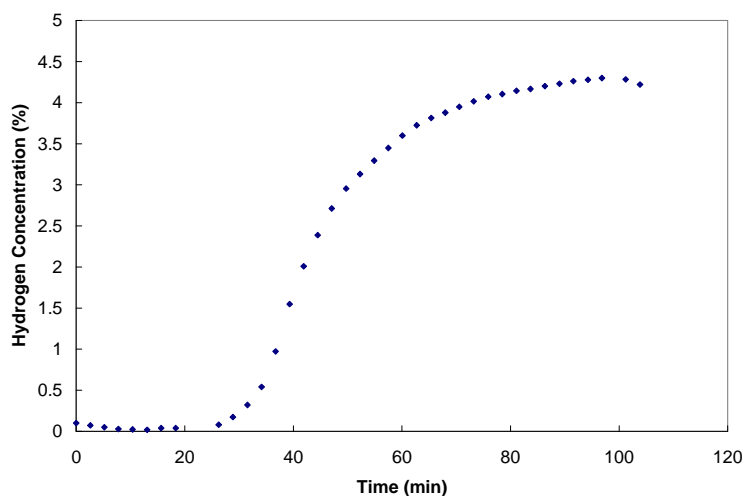


Figure 7 Catalyst reduction with hydrogen at 500°C

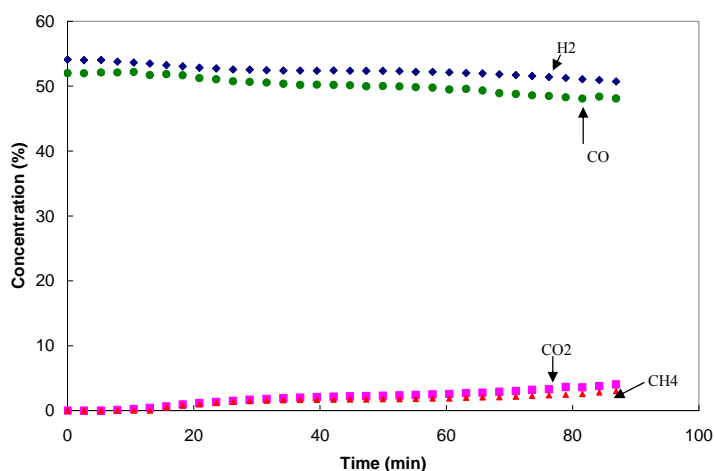


Figure 8 Catalyst pretreatment at 450°C in syngas atmosphere

FT synthesis experiments ranging from atmospheric pressures to 150 psig and 200-400°C were conducted at flow rates of 6 and 25 mL/minute of syngas in the ratio of 48 % H₂ and 52 % CO as well as with syngas in the ratio of 66 % H₂ and 33 % CO. The catalyst was first reduced in hydrogen atmosphere for 1 hr at 500°C. Subsequently, FT synthesis experiment was also conducted at atmospheric and elevated pressures of 50, 100 and 150 psig pressures and temperatures of 250 280, 300 and 350°C. 100 % syngas was used for all the experiments. Figure 9, 10, and 11 present the data on CO and H₂

conversions of the experiments with low volumetric flowrates. . It can be seen from these Figures that CO conversion > 90% is achievable at the temperatures greater than 290°C and pressures greater than 100 psig. Generally, increasing both temperature and pressure yields the higher syngas conversion. On the hand, increasing the flowrate (decreasing contact time) yields the lower conversions (Figure 11).

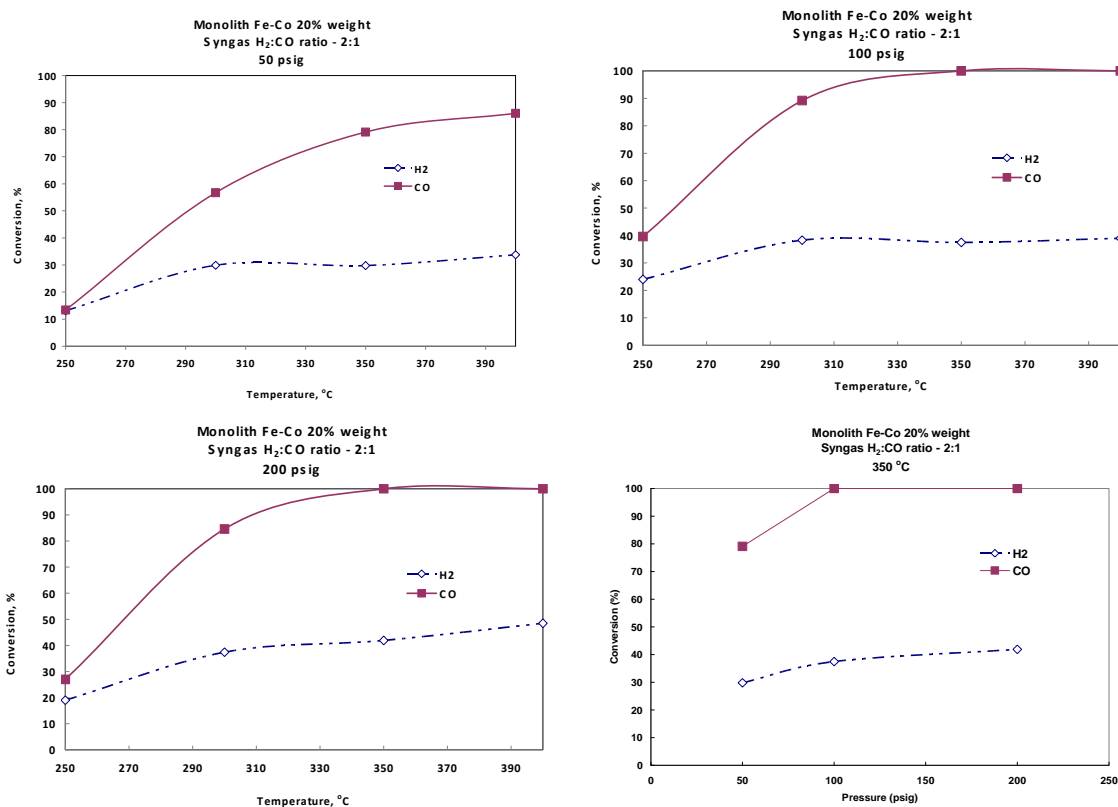


Figure 9 CO conversion during FT synthesis on monolithic catalysts at low volumetric feed flow rates - CO:H₂ = 2:1

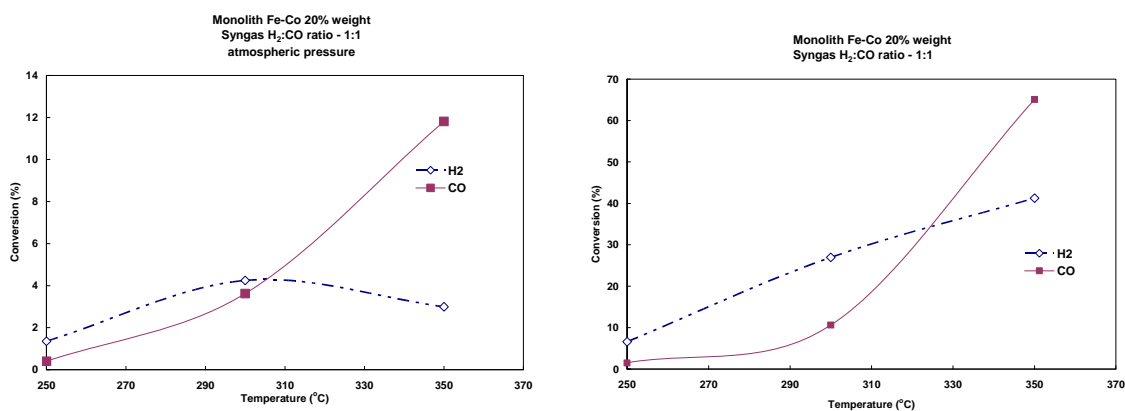


Figure 10 CO conversion during FT synthesis on monolithic catalysts at low volumetric feed flow rates, CO:H₂ = 1:1

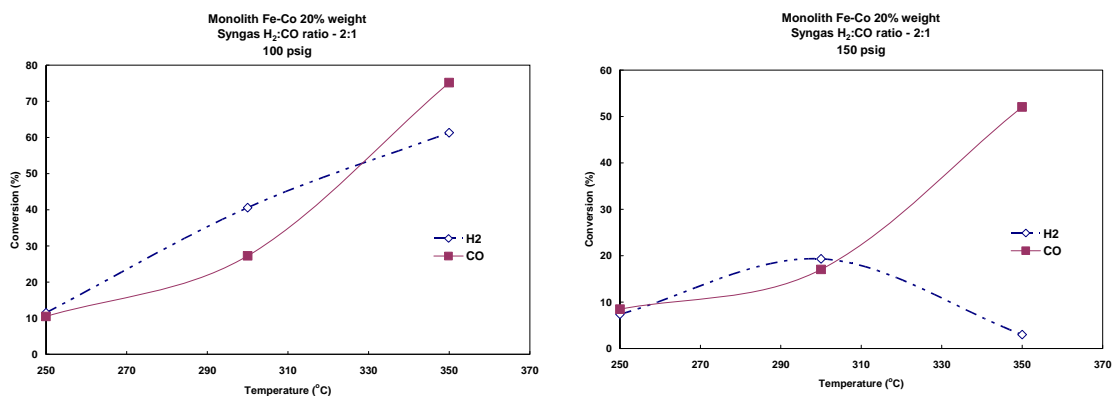


Figure 11 CO conversion during FT synthesis on monolithic catalysts at high volumetric feed flow rates - CO:H₂ = 2:1

Similar experiments were also conducted with monolithic FT catalysts. Figure 12, 13 and 14 present the data on CO and H₂ conversions of some the experiments. In general, it was found that the conversions were lower when compared with those supported on the pellets. This can be attributed to both lower loading and contact time. The 90% Co conversions were achieved at the temperatures around 350°C.

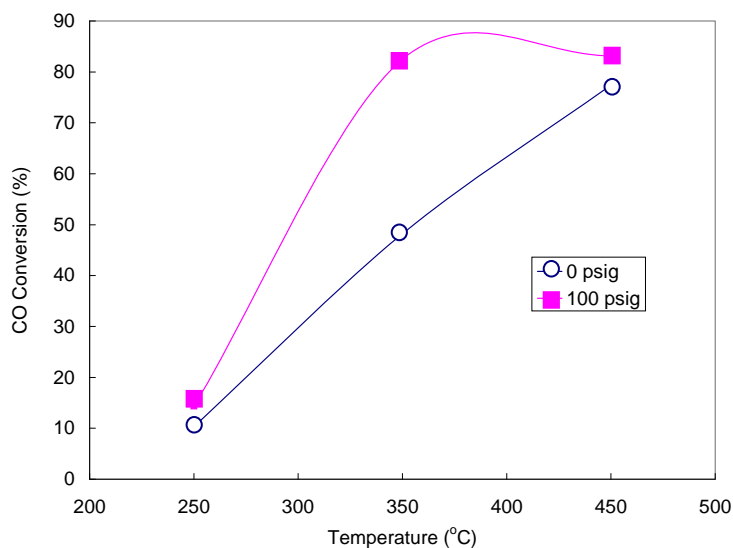


Figure 12 CO conversion during FT synthesis on monolithic catalysts - CO:H₂ = 2:1

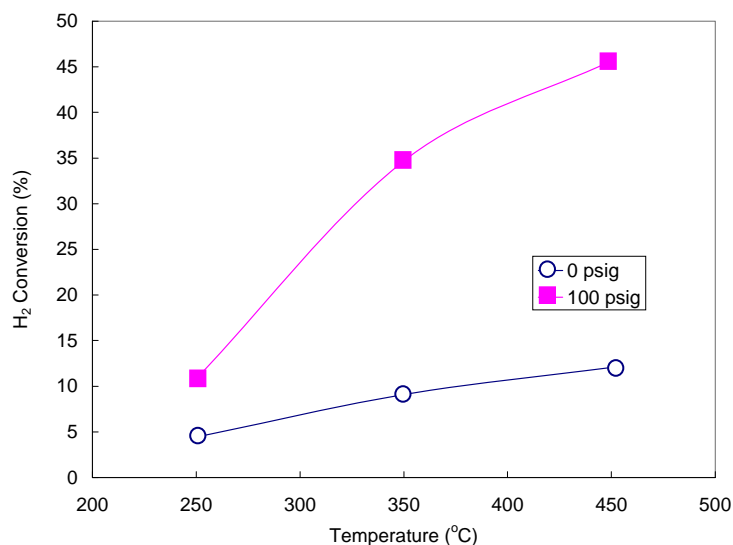


Figure 13 H₂ conversion during FT synthesis on monolithic catalysts, CO:H₂ = 2:1

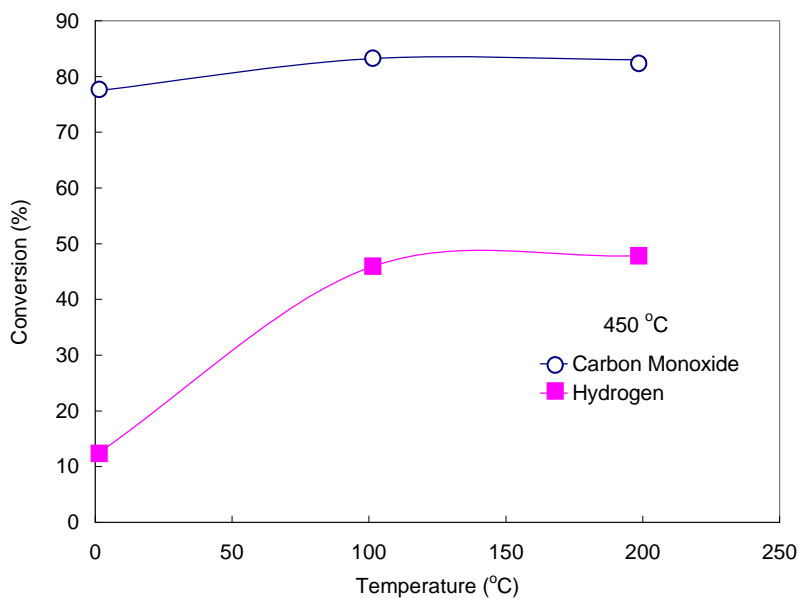


Figure 14 CO conversion during FT synthesis on monolithic catalysts as a function of pressure - CO:H₂ = 2:1, 450°C

Figures 15 and 16 show the plots of the relative product distribution as a function of the carbon chain length in the temperature range 200°C – 300°C and pressures of 100 and 150 psig. The data show that the product distribution is independent on the temperatures except the highest one (300°C).

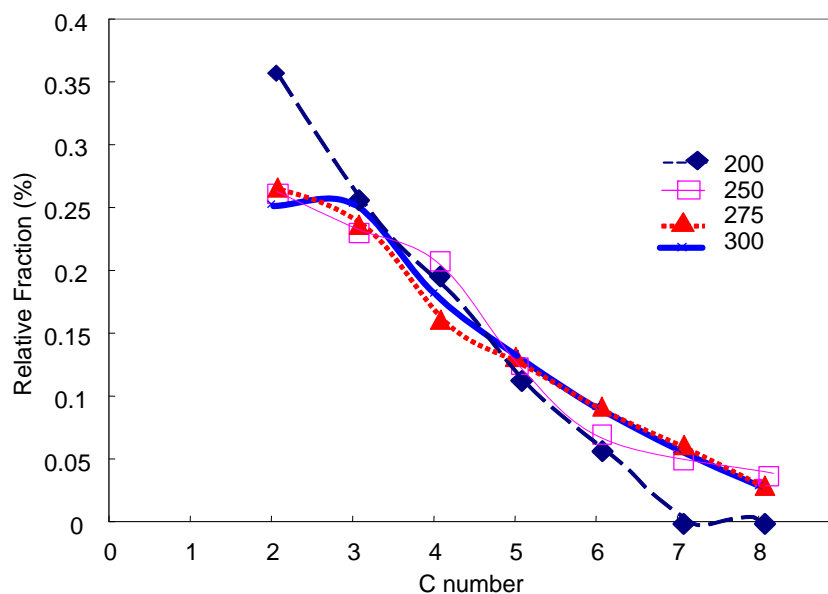


Figure 15 Relative product distribution – 100 psi

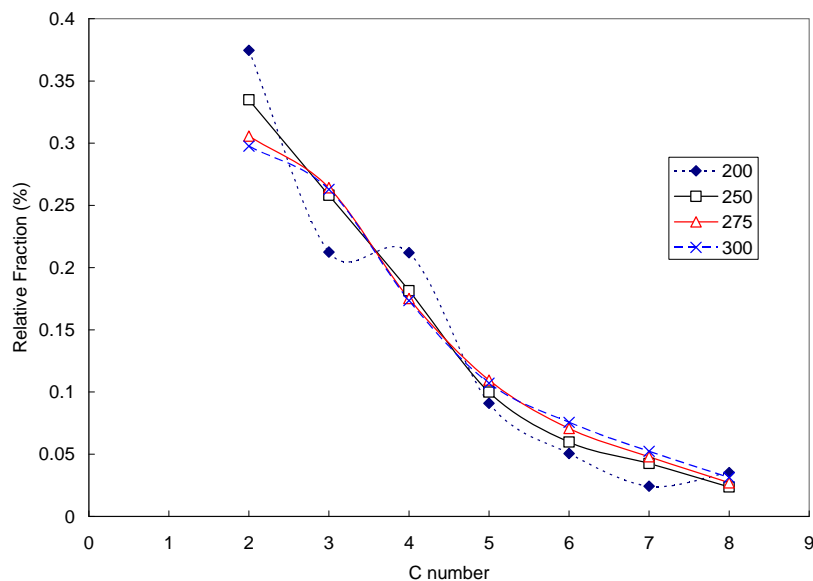


Figure 16 Relative product distribution up to C_8 – 150 psi

The effect of pressure on the product distribution is shown in Figure 17. It may be concluded that C_3 hydrocarbons content in the product is the highest amount observed within the range of C_1 - C_8 .

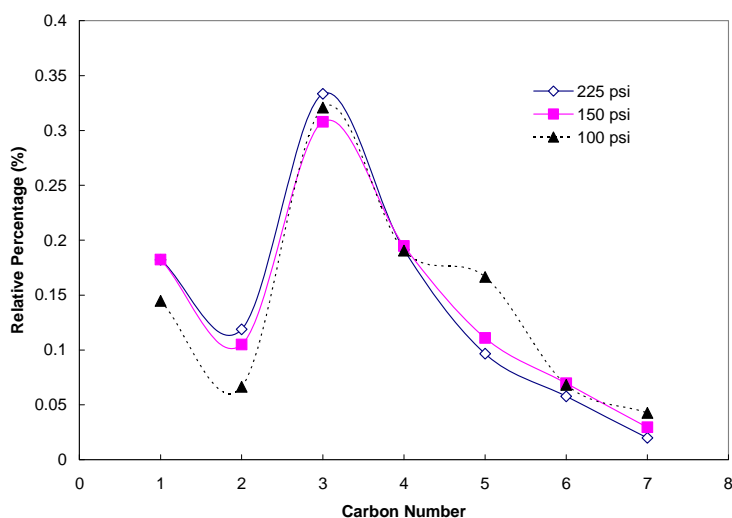


Figure 17 Relative product distribution by pressure – FT catalyst only

Figures 18 through 22 show the comparison of the relative product distribution and CO conversion when FT catalyst was used and when both FT and cracking catalyst was used. Comparing Figures 18 and 20 it is observed that the product distribution changes due to the presence of cracking catalyst shifting the products line toward the shorter carbon chain compounds. At the same we have observed that when cracking catalyst is present, the observed CO conversion decreases. It can be explained that this catalyst probably has dual activity – (a) cracking and (b) dry reforming. High CO_2 selectivity was observed when only FT catalyst was used and the presence of cracking catalyst lower CO_2 formation. It is possible that CO_2 produced in the FT synthesis zone in the reactor was used to reform the hydrocarbons produced (both reversed FT and Boudouard reactions).

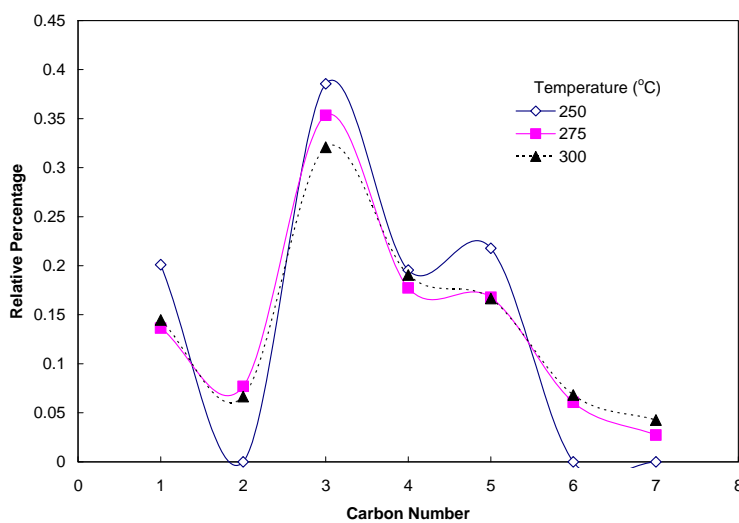


Figure 18 Relative product distribution by temperature – FT catalyst only

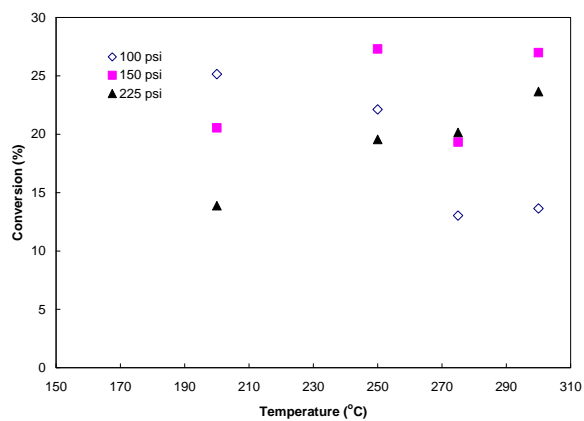


Figure 19 CO conversion – FT catalyst only

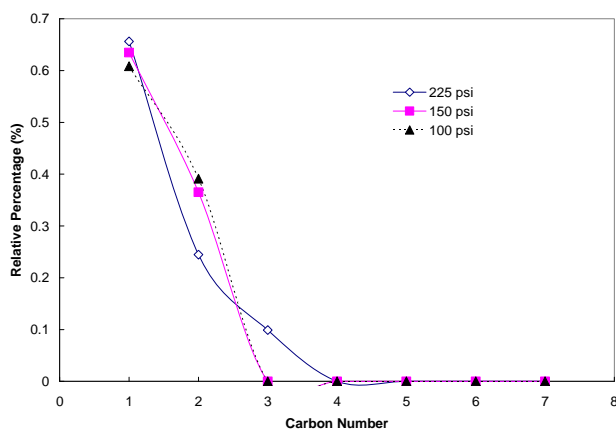


Figure 20 Relative product distribution upto C₈ by pressure – FT + Cracking Catalyst

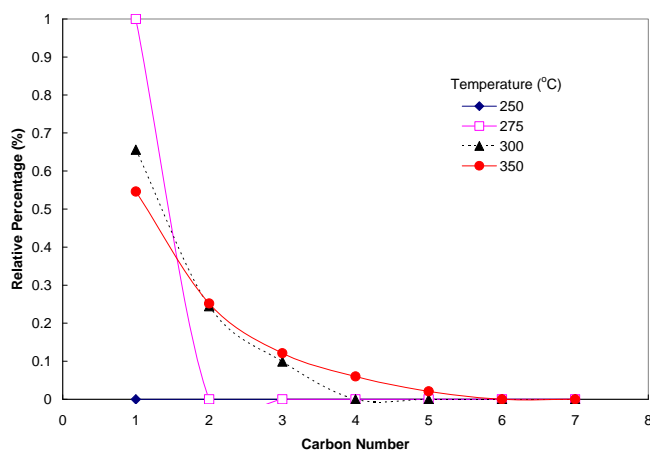


Figure 21 Relative product distribution upto C₈ by temperature – FT + Cracking Catalyst

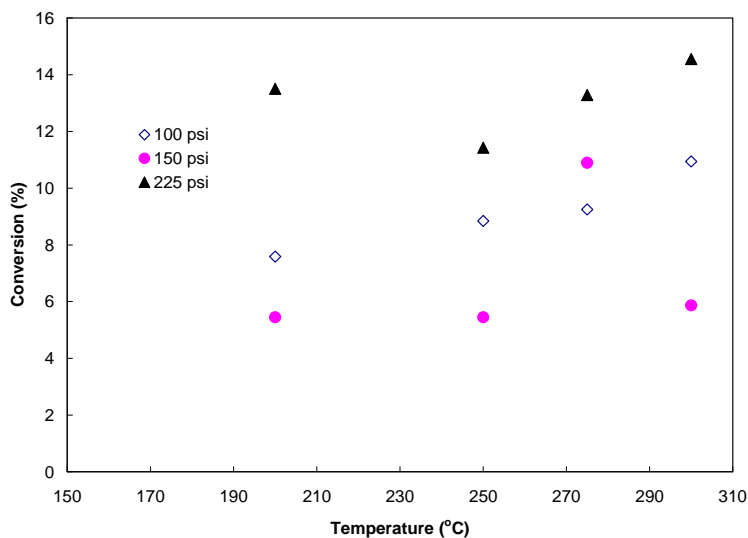


Figure 22 CO conversion – FT + Cracking Catalyst

Task 5. Technical Feasibility Analysis

From the results presented above, it can be seen that it is technically visible to have both FT synthesis and longer chain hydrocarbons cracking in the same reactor. The mass balance calculation conform the conversion levels.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were made from the results obtained in this research:

1. It is possible to conduct the FT synthesis in the gas phase.
2. FT synthesis was successfully carried out in a monolithic reactor.
3. The active catalysts used for FT synthesis showed high selectivity for CO₂ and CH₄.
4. Increasing the temperature and the pressure resulted in higher syngas conversions.
5. Increasing the contact time increased the yield of hydrocarbon products.
6. Both, FT synthesis and hydrocarbon cracking can occur simultaneously in the same reactor.
7. A monolithic reactor containing both the FT synthesis and cracking catalyst was successfully demonstrated for converting syngas to lower hydrocarbons.
8. When both synthesis and cracking occurred in the same reactor, the hydrocarbon product distribution was shifted towards shorter carbon chain hydrocarbons.
9. It is necessary to increase the contact time to achieve the complete conversion at high flowrates. This can be done by increasing the size of the reactor.

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