

# SYNTHESIS OF LIQUID HYDROCARBONS BY FISCHER–TROPSCH PROCESS USING INDUSTRIAL IRON CATALYST

Hanif A. Choudhury<sup>1</sup>, Vijayanand S. Moholkar<sup>1,2</sup>

Doctoral Candidate, <sup>1</sup>Center for Energy, Indian Institute of Technology Guwahati, Assam, India

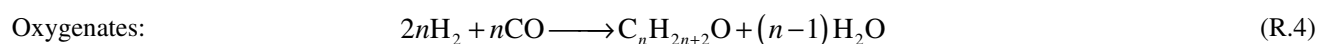
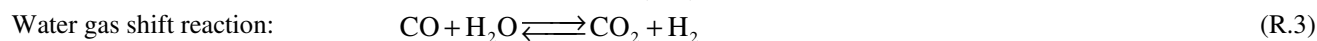
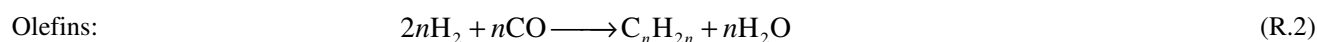
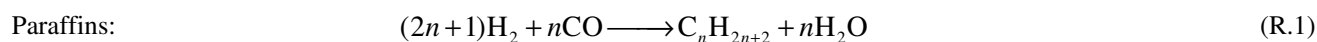
Professor and Head, <sup>2</sup>Department of Chemical Engineering, Indian Institute of Technology Guwahati,  
Guwahati – 781 039, Assam, India,

**Abstract:** Fischer–Tropsch process (F-T) is an efficient technology to synthesize liquid transportation fuel as well as other valuable chemicals. This process is associated with hydrogenation of carbon monoxide gas in presence of transition metal catalyst to valuable liquid transportation fuels and chemicals. F-T reaction is essentially a catalytic process, and most widely used catalysts are either iron or cobalt based catalysts. Iron catalysts are preferred when substoichiometric syngas (with H<sub>2</sub>/CO molar ratio is less than 2, also known as producer gas) is chosen as feed stock for F-T reaction. The deficiency of H<sub>2</sub> in substoichiometric syngas can be met by water-gas shift reaction (WGS). Normally, cobalt catalyst is WGS inactive, and hence, is chosen for F-T reaction when feed stock is synthesis gas (with H<sub>2</sub>/CO molar ratio of 2 or higher). In this work, we have studied the F-T process using an industrial iron catalyst for synthesizing liquid transportation fuels at different processing conditions or reaction parameters. A fixed bed reactor was fabricated indigenously. The physical properties of the catalyst were studied by XRD, BET and TPR study, whereas the liquid product obtained from the F-T reaction was analysed by a GC using FID detector. Carbon monoxide conversions were calculated by analysing the reactor effluent by a GC using TCD detector. The experiments reveal synthesis of liquid F-T fuel at 300°C and GHSV of 1800 h<sup>-1</sup>. The composition of synthesized liquid F-T fuel (in terms of carbon number of hydrocarbons) falls within the range of conventional diesel fuel.

**Keywords:** Industrial Iron catalyst, FT synthesis, TPR, WGS

## I. INTRODUCTION

Fischer–Tropsch reaction (F-T), which essentially is the synthesis of hydrocarbons from synthesis gas (CO + H<sub>2</sub>), was invented in Germany in 1923. At present, the large scale implementation of FT process is done by SASOL and Shell for manufacturing of transportation fuels and useful chemicals from syngas. FT synthesis is basically a catalytic reaction and the active and selective catalysts for the FT reaction are mainly based on cobalt or iron [1-2]. Main products of the FT synthesis are linear paraffins and  $\alpha$ -olefins. The general reactions of FTS are summarized as follows:



The typical molar ratio requirement of H<sub>2</sub>/CO for F-T reaction is ~ 2, which is the composition of syngas. Syngas can be derived from gasification of coal, biomass or steam reforming of natural gas. Conventional feed stock for FTS is natural gas; however,

steams reforming of methane being an endothermic process, its energy requirements are excessively high that adversely affects the process economy. Thus, producer gas from biomass gasification (with typical composition of 15% H<sub>2</sub>, 20% CO, 20% CO<sub>2</sub>, 5% CH<sub>4</sub> and balance N<sub>2</sub> [3-5] can form alternate feedstock to syngas for F-T reaction. However, utilization of biomass derived producer gas (which is also termed by biosyngas by some authors) has its own limitations for F-T reaction. Major problem with biosyngas is its sub-stoichiometric composition, in that the H<sub>2</sub>/CO molar ratio is  $\leq 1$ . Therefore, F-T reaction with conventional transition metal catalyst cannot use the biosyngas as feedstock. The deficiency of H<sub>2</sub> in the biosyngas can be met through water gas shift reaction (WGS). Iron based catalysts have received immense attention of researchers due to its water-gas shift activity as well as easy availability and low cost. The carbon number of the product hydrocarbon (either chain or branched hydrocarbon) is determined by the process conditions, viz. temperature, pressure and space velocity. Increase in temperature results in shifts towards the product with lower carbon number. Several previous authors have described the effect of these parameters on the yield and selectivity of the FT process. Dictor and Bel [6], Donnelly and Scatterfield [7], Mirzaei et al. [8] and Anderson [9] have studied the effect of temperature on FT synthesis. They observed an increase of olefin to paraffin ratio in the product with increasing reaction temperature for potassium promoted precipitated iron catalyst. Effect of total pressure on the product selectivity on alkaline promoted iron catalyst has been reported by Dry [10]. Donnelly and Scatterfield [7] found that increasing the H<sub>2</sub>/CO ratio in the reactor feed results in production of lighter hydrocarbon (with lower carbon number). The influence of the space velocity (or in other words, residence time) of the synthesis gas on the selectivity has been investigated by Bukur et al. [11]. Kuipers et al. [12] have investigated increase in the olefin to paraffin ratio with increasing space velocity (and hence, resulting in decrease of the conversion due to smaller residence time) on a poly-crystalline cobalt foil. Similar studies have also been done by Bukur et al. [11] on a commercial (Ruhrchemie) supported iron catalyst (Fe/Cu/K/SiO<sub>2</sub>), and Iglesia et al. [13] on TiO<sub>2</sub>-supported ruthenium catalysts. Bukur et al. [11] have reported no effect of the space velocity on the molecular weight (i.e. the carbon number) of the hydrocarbons, while Iglesia et al. [13] have observed an increase in the average molecular weight of the products with decrease of the space velocity. The selectivity to methane and olefins has been reported to reduce with decreasing space velocity, while the selectivity towards paraffins remains unchanged. In our earlier paper, on industrial cobalt catalyst we reported the dependence of space velocity on the product profile. With higher space velocity, the interaction between gas molecule and the catalyst particles is decreased, as a result of which higher selectivity towards short chain hydrocarbon are observed [2]. A space velocity of 1800 h<sup>-1</sup> was found to be optimum for liquid product towards diesel fraction.

In this study, we have attempted to synthesize liquid fuel by FT process using commercial iron catalyst using a fixed bed reactor. Two experimental parameters, viz. temperature and gas hour space velocity (GHSV) of the process have been kept constant, as the effect of these parameters on product distribution is well known. In this work, mainly synthesis of liquid hydrocarbons from FT reaction has been studied at three different pressure levels, so as to deduce the change in product profile of FT fuel with this parameter using an industrial iron catalyst. Such a study is also important for the best and effective use of iron catalyst for production of liquid transportation fuel from syngas and it can also become a basis for optimization of FT process for bio-syngas.

## II. MATERIALS

All gases used in experiments were procured from M/s Vadilal Gases Ltd. (Gujarat, India, purity: 99.999%). The gas cylinders of reaction mixture (H<sub>2</sub>/CO = 67%/33% v/v) were connected to gas supply lines through two-stage high pressure regulator. The analyses of the gaseous products in the reactor effluent were performed by an online gas chromatograph (Make: Thermo Fischer Ceres 800 Plus system) using Porapack-Q column provided with a thermal conductivity detector (TCD). The liquids products were analyzed by the same GC provided with a flame ionization detector (FID) using BP-10.5 column. For characterization of gas chromatograph, hydrocarbon standards in the carbon number range of C<sub>5</sub>-C<sub>24</sub> were procured from Sigma Aldrich.

## III. EXPERIMENTAL

### A. Catalyst source

Commercial grade iron based catalyst was used in experiments. It was procured from an industrial source and according to the terms and conditions of the supplier the exact elemental composition of the catalyst cannot be disclosed. However, XRD, BET and TPR study of the catalyst has been done in order to understand the active metal phase, surface and reduction property of the catalyst, which is a prerequisite for any heterogeneous catalyst employed in reaction.

### B. Catalyst Characterization

*X-Ray Diffraction (XRD)*: Powder X-ray diffraction (XRD) measurements were performed using a Bruker Axs Company, D8 Advance diffractometer (Germany). Scans were taken with a 2 $\theta$  step size of 0.02 and a counting time of 1 s using Cu-K- $\alpha$

radiation source generated at 40 kV and 30 mA. Data was collected over a  $2\theta$  range from  $20^\circ$  to  $70^\circ$ , and phases were identified by matching experimental patterns to entries in the JCPDF2.

**BET Measurement:** Brunauer–Emmett–Teller (BET) surface areas, pore volumes and average pore diameters were determined by  $N_2$  physio-sorption at 77 K using a Beckman Coulter, Model: A53878. A 0.3 g catalyst sample was degassed at  $300^\circ\text{C}$  for 2 h and then heated at  $10^\circ\text{C}/\text{min}$  to  $300^\circ\text{C}$  and held at this temperature for 2 h before analysis.

**Temperature-programmed reduction (TPR):**  $H_2$ -TPR was performed using Micromeritics TPD/TPR 2720 system to determine reducibility of the calcined iron catalysts. For  $H_2$ -TPR, the catalysts (0.5 g) were reduced in a flow of 5%  $H_2/\text{Ar}$  ( $30\text{ cm}^3/\text{min}$ ) with a ramp rate of  $10^\circ\text{C}/\text{min}$  to  $800^\circ\text{C}$ . A thermal conductivity detector (TCD) was used to measure  $H_2$  consumption. The detector output was calibrated based upon 100% reducibility of  $Ag_2O$  powder, and a  $H_2O$  trap was used to remove  $H_2O$  produced during the reduction. The degree of reduction of the catalyst was calculated as follows by using data from TPR [14].

$$(\%) \text{ reduction} = \frac{[H_2 \text{ consumption below } 450^\circ\text{C}]}{\text{Total } H_2 \text{ consumption in TPR experiment}} \times 100 \quad (1)$$

**C. Experimental set-up:** A schematic diagram of the reactor and its accessories is shown in Fig. 1. A fixed bed tubular reactor (MOC: SS 316, thickness: 2 mm, ID: 6.35 mm or  $1/4$  in.) was used for all reactions. The reactor had two gas supply lines of 6.35 mm ( $1/4$  in.) ID, each for purge gas (nitrogen) and synthesis gas (mixture of CO and  $H_2$ ). The synthesis gas supply line was preheated with wrapped thermal tapes so as to the feed gas to 423 K. The reactor effluent line (ID 6.35 mm) was also heated in a similar manner to 373 K to avoid any condensation of the product in the line prior to back-pressure regulator valve. Thereafter, no thermal wrapping was given to the product lines, thus maintaining the temperature in them at ambient condition, where higher hydrocarbon products can condense. The liquid product was collected in a trap (gas-liquid separator) kept at ambient temperature. Cold water (at 298 K) was circulated in a jacket around the trap so as to achieve maximum possible condensation of the hydrocarbon products. The lighter hydrocarbons and unreacted reactant gases are removed from the trap and purged through a gas flow meter. The flow rate of feed synthesis gas was controlled using mass flow controller (Make: Eureka MI Flow, Range: 0–500  $\text{cm}^3/\text{min}$ ). Catalyst (1 g) was placed inside the reactor enclosed between glass wool plugs. The catalyst was reduced in situ at 673 K for 12 h under a stream of 50%  $H_2$  and  $N_2$  mixture (0.1 MPa pressure, 30 ml/min). After 12 h of reduction, the temperature was reduced to 573 K under the constant flow of hydrogen. Synthesis gas was introduced at a particular space velocity (GHSV), and pressure was gradually increased and set at the desired value. The temperature inside the reactor was monitored using two thermocouples, one at the catalyst bed and other at the surface of reactor. Temperatures at these locations were maintained constant by circulating cooling water through a thermal jacket (in the form of  $1/8$  in. copper tubing) wrapped around the reactor.

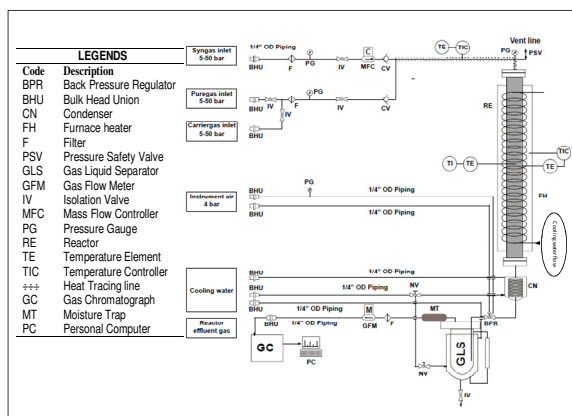


Fig. 1 Experimental setup

**D. Analysis:** The CO conversion (%) has been calculated according to the following equation:

$$\text{CO conversion} = \frac{(n_{\text{CO}})_{\text{in}} - (n_{\text{CO}})_{\text{out}}}{(n_{\text{CO}})_{\text{in}}} \times 100 \quad (2)$$

#### IV. RESULTS AND DISCUSSION

**H<sub>2</sub>-TPR and BET analysis:** Fig. 2 shows the reduction profiles of iron catalysts under the flow of H<sub>2</sub> gas. The TPR profile shows reduction profiles with (an expected) 2-step reduction process of α-Fe<sub>2</sub>O<sub>3</sub> to α-Fe. The first step is ascribed to the reduction of Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub>. The second peak can be attributed to the reduction of FeO to α-Fe. The peaks are ascribed to the two step reduction of Fe<sup>3+</sup> in α-Fe<sub>2</sub>O<sub>3</sub> to Fe<sup>2+</sup> in the mixed Fe<sup>2+/3+</sup> inverse spinel Fe<sub>3</sub>O<sub>4</sub> structure [15]. The presence of peak around 650–700°C is an indication of difficulty in reduction of FeO to α-Fe, for which high temperature is required. As an indication of the total extent of reduction of the catalysts, Fig. 1 also shows the total cumulative amount of H<sub>2</sub> uptake during the TPR experiment. The BET surface area with percent reduction (under H<sub>2</sub> gas) of the iron catalyst was ~ 20 m<sup>2</sup>/g and 20% respectively. Poor reducibility the catalyst is due to the unpromoted nature of the catalyst.

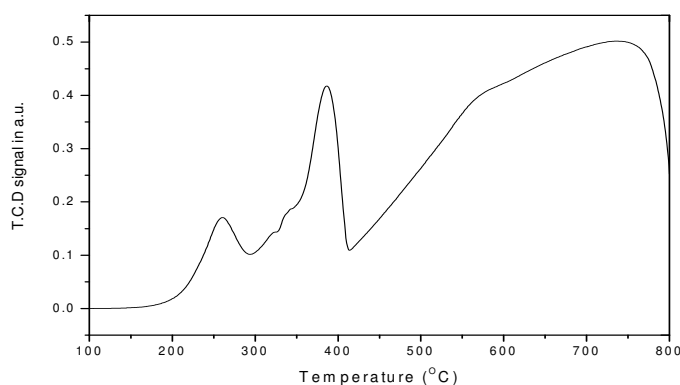


Fig. 2 H<sub>2</sub>TPR of the industrial iron catalysts

**XRD analysis:** The crystallinity and phase purity of the calcined catalyst was examined by powder X-ray diffraction (XRD). Fig. 3 shows the XRD patterns of industrial iron catalyst. The pattern of the promoted calcined catalyst matches well with the standard patterns of Iron oxide (JCPDS file no. 850987). All the peak pattern of the solid samples can be readily indexed to Fe<sub>2</sub>O<sub>3</sub>, where the diffraction peaks at 2θ values of 33.2, 54.2, 56.3 and 62.59° can be ascribed to the reflection of (1 2 1), (1 3 2), (1 2 0) and (1 3 0) planes of the hexagonal Fe<sub>2</sub>O<sub>3</sub> respectively. However, there are a number of unidentified weak intensity peaks present in between the 2θ range of 28 to 65° also present.

**E. Effect of reaction pressure:** F-T reaction is essentially a polymerization type reaction, in which the –CH<sub>2</sub>– units formed from adsorbed CO and H<sub>2</sub> reactant gases add up to form hydrocarbons of different chain length. Thus, as evident from reactions R.1, the numbers of product moles in F-T reaction are less than reactant moles resulting in positive pressure-dependence, as per Le Chatelier's principle. An obvious consequence of these effects is that increase of reaction pressure also promotes the FTS reaction, leading to an increase in the CO conversion. With increasing pressure, longer chain hydrocarbons are likely to form that could possibly condense and saturate the catalyst pores by liquid product. To assess effect of reaction pressure on product selectivity, we have carried out a series of reactions at reaction pressure range of 1 to 2 MPa using synthesis gas with molar ratio of H<sub>2</sub>/CO as 2:1 and temperature of 593 ± 10 K. At each reaction pressure, the reduced catalyst was tested for 10 h. Fig. 4 shows the GC data of the FT liquid product and the results are presented in the Fig. 5 for reaction pressures of 1, 1.5 and 2 MPa, respectively, at GHSV of 1800 h<sup>-1</sup>. The overall CO conversion for each reaction was found to be **50-70%** for pressure range of 1 - 2 MPa. It is clearly observed that with the increase in reaction pressure, there is an increase in the molar concentration of each of the carbon number of the product, and also in the CO conversion efficiency. There is no change in overall product profile, since there is no peak shift in three different pressures. The only change observed was an increase in the concentration of the each of the hydrocarbon ranging from C<sub>7</sub> - C<sub>20</sub>. However, the major selectivity was towards hydrocarbons of carbon number range C<sub>9</sub>-C<sub>16</sub>, which is the hydrocarbon fraction of conventional diesel fuel.

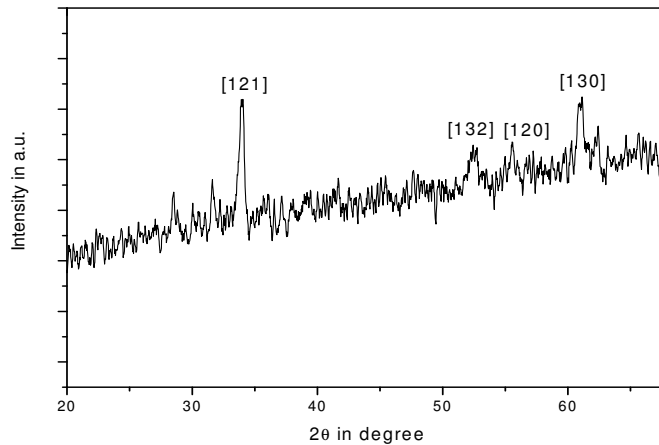


Fig. 3 XRD diffraction pattern of industrial iron catalyst

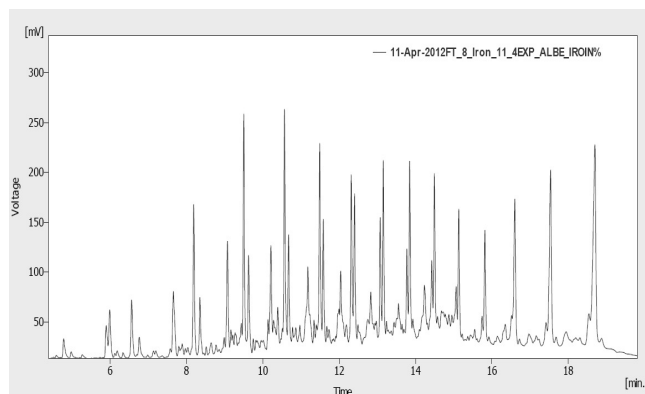


Fig. 4 GC data of FT product

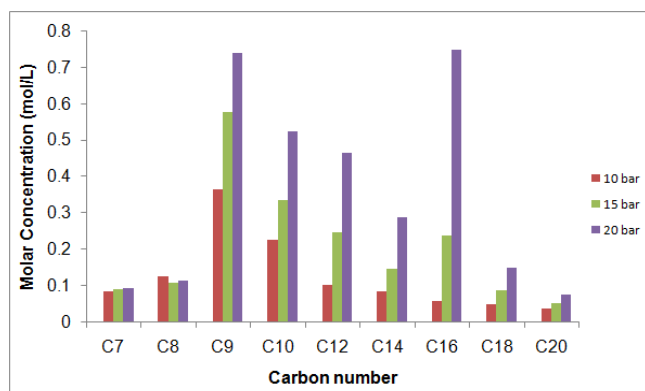


Fig. 5 Product profile and distribution in different experimental pressure

## V. CONCLUSION

Present study has attempted to synthesize liquid hydrocarbons in the range of C<sub>9</sub>-C<sub>16</sub> by FT process using commercial iron catalyst for use as transportation fuel. The major reaction parameter was chosen as reaction pressure, whereas the residence time was chosen from our earlier study of optimization of FT process using industrial cobalt catalyst. An intermediate GHSV of 1800 h<sup>-1</sup> was selected to obtain product in the desired carbon number range (corresponding to liquid fuel). Faster GHSV than this optimum value would give a gaseous product and a slower GHSV would give solid product. This will lead to additional storage and transportation problem for gaseous FT product, whereas cracking of solid FT product would be necessary for use as transportation fuel. This will severely affect the process economy. Increase in the pressure not only increases the % CO conversion, but also the concentration of liquid hydrocarbons. Main goal of our experiments was to synthesize liquid FT fuel, and hence selection of reaction or process parameters is very important. We observed that for liquid FT product temperature below 300°C is not sufficient to produce liquid hydrocarbon, whereas temperature beyond 320°C is also not favourable as this increases the selectivity of methane and other gaseous FT product at an expense of liquid product. Thus, we strictly adhered to a temperature of 300°C in order to synthesize liquid hydrocarbon that can directly be used as transportation fuel. Under the studied condition of pressure, temperature and GHSV iron catalyst did not show any severe change in the product profile. Thus, it can be suggested from this study that with this iron catalyst even at lower pressure condition of 1 MPa fuels fraction similar to that of conventional diesel can be synthesized. We believe that these results will be useful for design and optimization of a large scale FT using the same catalyst.

## ACKNOWLEDGMENT

The author wish to acknowledge Ministry of New and Renewable Energy (MNRE), Government of India for funding (vide ref.19/20/2007-R&D/BE) of the project. Mr. Hanif A. Choudhury also acknowledges MNRE for financial support during this research work through National Renewable Energy Fellowship.

## REFERENCES

- [1] S. Qin, C. Zhang, J. Xu, B. Wu, H. Xiang and Y. Li, "Effect of Mo addition on precipitated Fe catalysts for Fischer-Tropsch synthesis," *Journal of Molecular Catalysis. A: Chemical*, vol. 340, pp128-134, 2009.
- [2] H. A. Choudhury, V. S. Moholkar, "An Optimization Study of Fischer-Tropsch Synthesis Using Commercial Cobalt Catalyst," *International Journal of Scientific Engineering and Technology*. vol. 2, pp31-39, 2013.
- [3] B. Buragohain, P. Mahanta, V. S. Moholkar, "Thermodynamic optimization of biomass gasification for decentralized power generation and Fischer-Tropsch synthesis," *Energy*, Vol. 35, pp 2557-2579, 2010.
- [4] B. Buragohain, S. Chakma, P. Kumar, P. Mahanta, V. S. Moholkar, "Comparative evaluation of kinetic, equilibrium and semi-equilibrium models for biomass gasification," *International Journal of Energy and Environment*, Vol. 4, Issue 4, pp.581-614, 2013.
- [5] B. Buragohain, P. Mahanta, V. S. Moholkar, "Performance correlations for biomass gasifiers using semi-equilibrium non-stoichiometric thermodynamic models," *International Journal of Energy Research*, Vol. 36, pp 590-618, April 2012.
- [6] R. A. Dector, A. T. Bell, "Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts," *Journal of Catalysis*, Vol. 97, pp. 121-136, 1986.
- [7] T. J. Donnelly and C. N. Satterfield, "Product distributions of the Fischer-Tropsch synthesis on precipitated iron catalysts," *Applied Catalysis. A: General*, vol. 52, pp. 93-114, 1989.
- [8] A. A. Mirzaei, A. B. Babaei, M. Galavy, A. Youssefi, "A silica supported Fe-Co bimetallic catalyst prepared by the sol/gel technique: Operating conditions, catalytic properties and characterization," *Fuel Processing Technology*, vol. 91, pp. 335-347, 2010.
- [9] R. B. Anderson, "Catalysts for the Fischer-Tropsch Synthesis (Vol. 4)," New York, Van Nostrand Reinhold, 1956.
- [10] M. E. Dry, "The Fischer-Tropsch Synthesis. In: J. R. Anderson, M. Boudart. Ed. *Catalysis Science and Technology*," vol. 1, pp. 160-255. New York: Springer-Verlag, 1981.
- [11] D. B. Bukur, S. A. Patel, X. Lang "Fixed bed and slurry reactor studies of Fischer-Tropsch synthesis on precipitated iron catalyst," *Applied Catalysis. A: General*, vol. 61, pp. 329-349, 1990.
- [12] E. W. Kuipers, C. Scheper, J. H. Wilson, H. Oosterbeek (1996) "Non-ASF product distributions due to secondary reactions during Fischer-Tropsch synthesis," *Journal of Catalysis*, vol. 158, pp. 288-300, 1996.

**International Journal of Innovative Research in Science,  
Engineering and Technology**

*(ISO 3297: 2007 Certified Organization)*

**Vol. 2, Issue 8, August 2013**

- [13] E. Iglesia, S. C. Reyes, R. J. Madon “Transport-enhanced  $\alpha$ -olefin readsorption pathways Ru-catalyzed hydrocarbon synthesis,” *Journal of Catalysis*, vol. 129, pp. 238–256, 1991.
- [14] S. H. Kang, J. W. Bae, K. J. Woo, P.S. Sai Prasad, K. W. Jun, “ZSM-5 supported iron catalysts for Fischer-Tropsch production of light olefin,” *Fuel Processing Technology*, vol. 91, pp. 399–403, 2010.
- [15] E. de Smit, F. M. F. de Groot, R. Blume, M. Ha $\ddot{u}$ vecker, A. Knop-Gericke, B. M. Weckhuysen, “The role of Cu on the reduction behavior and surface properties of Fe-based Fischer-Tropsch catalysts,” *Physical Chemistry and Chemical Physics*, vol. 12, pp. 667-680, 2010.

### BIOGRAPHY



**Hanif A Choudhury** was born in Assam (India). He did his M.Sc Degree from Assam University Silchar, India and perusing Ph.D degree in the Center of Energy, Indian Institute of Technology Guwahati, India. His research interests are Fischer-Tropsch technology, Biofuel, Biodiesel, Ultrasound, Ferrite synthesis, Liquid crystal synthesis. He is a Senior Research Fellow in the Ministry of new and Renewable Energy, Govt. of India.



**V. S. Moholkar** was born in Maharashtra, India. He did his B.Chem.Engng. and M.Chem.Engng. from Institute of Chemical Technology (formerly known as UDCT Mumbai), India. He received Ph.D. from University of Twente, Netherlands. His research interests are mainly in ultrasound-assisted processes and renewable energy (biofuels). Currently, he is Professor of Chemical Engineering and also Head of Chemical Engineering Department at Indian Institute of Technology Guwahati, India. He has to his credit 68 publications in peer reviewed international journals with more than 950 citations.