Technical Presentation:

An Integrated Approach to the preparation of effective Catalyst for Biomass-to-Liquid (BTL) process

Syed Ali Zeeshan Gardezi, John T Wolan, Babu Joseph.

Department of Chemical & Biomedical Engineering, USF, Tampa, FL 33620

Abstract:

The depletion of fossil energy reserves and the need for reduction of greenhouse gas emissions make renewable/sustainable energy sources very attractive. Biomass represents an important renewable energy source that will play a vital role. For these reasons, interest in GTL (gas to liquid) and BTL (biomass to liquid) technologies has increased dramatically. The economics of such a process are critically dependent on "suitable" catalysts. A suitable catalyst is defined as being active (high degree of conversion, long life), selective (minimum side reactions) cost effective (abundantly available) and is integrated with reactor design.

Catalyst design and preparation has a strong bearing on the above mentioned properties. Each step used in catalyst preparation must be carefully considered and verified with proper characterization techniques. Some of the challenges include selection of the active material phase, support choice, effective active phase deposition and pretreatment. An integrated understanding of the physical phenomenon that affects the physical properties of the catalyst can significantly reduce the cost of the catalyst and reactor design. In this presentation we will discuss some of the issues that are important in the design and development of catalysts for the BTL process.

1. Introduction:

The rise in global energy requirements and the upcoming shortages in petroleum-derived fuels have placed a premium on alternate energy sources. Designing an efficient overall integrated process based on BTL is not an easy task. Different approaches have been adopted by researchers; the usual method consists of identifying the limiting factors (specific unit operations, reaction requirements), debottlenecking the limitations by analytical research, process design, and modeling, performing test run (on bench scale), and finally scaling up the process.

Fischer Tropsch (FT) synthesis is a process that utilizes syngas (a mixture of carbon monoxide and hydrogen) and coverts it into liquid petroleum. Syngas can be obtained from a variety of raw materials e.g. coal, natural gas and most biomass. As far as the bench scale research (that covers a size range from 10^{-9}m to 1 m) [1] is concerned reactor limitations (mass transfer, heat transfer) are the main bottlenecks. To ensure Optimum results (desired hydrocarbon chains) with little effort an integrated approach is the smart choice. This integrated approach as shown below takes into consideration all the aspects and apply them at the right stage of the research, the result is an

"Engineered" catalyst [1]. This catalyst not only produces the desired product, but also improves the overall economical feasibility of process by being specific to reactor design.
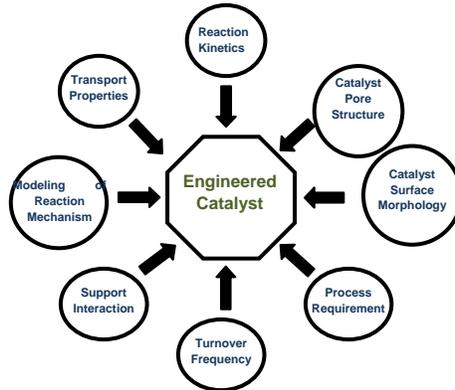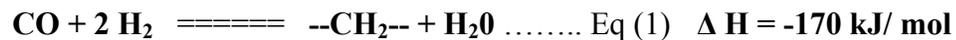

Figure 1: Integrated approach for designing the catalyst

2. Identification of active material:

The first step is the identification of the most active metal surface for the desired reaction. Fischer Tropsch (FT) synthesis is generally represented by following reaction [2]:

$$CO + 2 H_2 ====== --CH_2-- + H_2O$$ …….. Eq (1) $\Delta H = -170$ kJ/ mol

From the reaction it is evident that in case of heterogeneous catalysis, dissociative adsorption of gaseous species is the **limiting** step. Fischer Tropsch synthesis involves activation (dissociation) of carbon monoxide represented as [3]:

$$A_2 + 2S ====== 2A-S$$ ………Eq (2)

$$A-S + B ====== AB+ S$$ …….. Eq (3)   **B = H_2 in gaseous phase.**
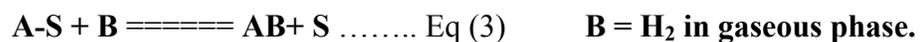
Dissociative energies calculated from the DFT (density functional theory) is used to identify the most active material (higher TOF) [3]. Shown below is an experimentally developed volcano curve based on DFT modeling and CO conversion on different surfaces.
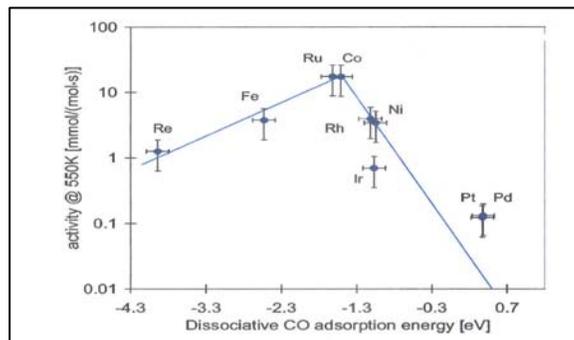

Figure 2: Calculated turn over frequencies (activity) for CO_2 dissociation on different atomically stepped metal surfaces. Reproduced from reference [3].

Clearly cobalt is the most active material. Other advantages of cobalt catalyst are, environment friendliness (H_2O is the byproduct), resistance to water produced in the reaction, and more paraffinic products.

3. Catalyst profile:

Next, one needs to decide on the optimal catalyst profile; activity, selectivity and other characteristics of chemical reaction greatly influence the choice [4]. On molecular level CO is the diffusion limited reactant (when porous catalyst is in use) because of two reasons, firstly, it is present in smaller amount than hydrogen based on the stoichiometric ratios, secondly, hydrogen is the smallest molecule in the nature and diffuse easily, on the other hand carbon monoxide bond length (0.1128 nm) is higher than hydrogen.

It has been identified that pellets smaller than about 0.2mm diameter are required to avoid mass transfer restriction [5]. However, in the commercial fixed bed reactor and even at the bench scale such small particles would lead to significant pressure drop. We propose that "egg shell" engineered spherical support pellets of approximately 2mm in diameter present design flexibility to avoid diffusion restrictions in FT synthesis [5]. This design ensures an improvement in activity and selectivity by restricting the active material to the zone easily accessible to diffusion limited reactant. This results in decoupling diffusion restriction from pressure drop and other reactor parameter. Shown below is the cutaway profile of a typical egg shell catalyst.
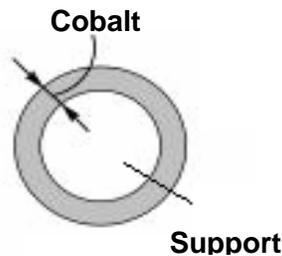

Figure 3: Eggshell catalyst

Thickness of the eggshell is the controlling parameter for selectivity of the diffusion limited catalyst. χ parameter is a well known index for the performance evaluation of egg shell catalyst . The variation of higher hydrocarbons selectivity with χ is shown as [5]
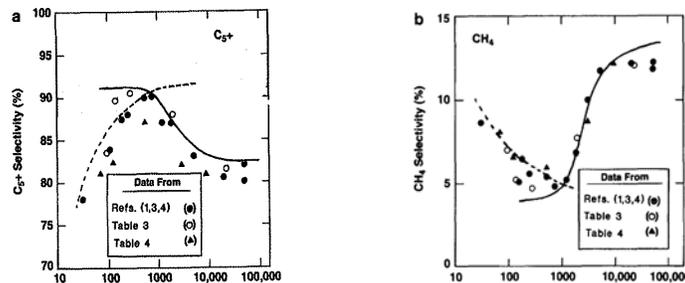

Fig 4: Methane & higher hydrocarbon selectivity dependence on χ value.
Reproduced from reference [5], Copyright 1995, with permission from Springer.

χ is related to eggshell thickness as follows [5]:

$$\chi = (R_o - R_c)^2 \; \Theta_M / r_p \quad ………..Eq(4)$$

r_p is the average pore radius, R_c is the radius of internal non impregnated core, R_o-R_c is the shell thickness, and Θ_M is the density of available sites (obtained from hydrogen chemisorption data) . So based on the favorable limits of χ, effective thickness of egg shell can be identified.

Selection of support material is based on the desired reducibility and degree of metal support interaction. Between the two common support materials, alumina or silica, silica gives better reducibility but at the same time dispersion (fraction of active metal sites present on surface) is much less. The reason is lower metal support interaction [4]. On the other hand alumina support leads to lower crystal size and higher dispersion. Higher surface area of catalyst is always desired, BET analysis used to verify surface area and pore size distribution. In diffusion limited reactions pore size distribution greatly influence the molecular weight of product hydrocarbons. It has been observed that carbon monoxide conversion increases by increasing the pore size upto a certain limiting value and then it decreases. Higher hydrocarbon (C5+) selectivity shows a similar trend. 6-10 nm range is the most optimal based on conversion and selectivity [4].

4. Catalyst Preparation:

The purpose of any catalytic metal deposition method is to evenly "spread" the metal precursor onto or into the support. Different techniques have been suggested including impregnation, precipitation and sol-gel techniques. Selection of the precursor salt is also important. For Co/SiO_2, activity and chain growth probability has been investigated. Activity followed the order; $Co_2(CO)_8 > Co(NO3)_2 > Co(CH_3COO)_2$ while chain growth probability followed the sequence $Co(NO_3)_2 > Co_2(CO)_8 > Co(CH_3COO)_2$ [6]. Based on these findings $Co(NO_3)_2$ is a preferred precursor salt.

As eggshell catalyst is the preferred choice based on diffusion limitation, incipient wetness impregnation has been widely used but the precipitation technique is also viable. Important parameters for eggshell catalyst preparation include:

1. Time controlled deposition to limit precursor presence in the given thickness.
2. Exploiting physical interaction between different kind of molecules e.g. hydrophobic / hydrophilic.
3. Drying rate, i.e. at low rate deposition is mostly at the core, while too fast drying a temperature gradient is setup and evaporation takes place at the deep pores resulting in precursor deposition at pore entrance.

Incipient wetness impregnation is the simplest technique. Main disadvantage is non- uniform deposition, sometime base metal precursor form oxide in the aqueous solution and these oxide have strong interaction with the alumina or silica and are difficult to reduce. On the other hand precipitation is used to deposit the precursor in the form of hydroxide or carbonate. Uniform finely divided deposit can be obtained by controlling the precipitation procedure (avoiding bulk nucleation) and selecting the "right" base (e.g. urea rather the conventional base or alkali).

5. Catalyst Characterization:

Verification of Cobalt and Its Phases:

XPS

XPS (X-ray photoelectron spectroscopy) is primarily used for the identification of different cobalt phases (Co_3O_4, CoO, metallic cobalt and mixed oxide)[4]. Atomic percentages of top layer (depth 2-4 nm, monolayer fraction = 10^{-1})[7] is also obtained but this result is highly superficial and cannot be considered a representation of bulk atomic distribution. The presence of the oxides, more specifically "Co_3O_4" spinal is represented as Co2p. Spin-orbital splitting is around 15.0 eV and the main peak usually center at 780 eV [4]. The spectrum shown below indicate the presence of Co^{3+} and Co^{2+} based on Gaussian curve fit with the binding energy of 779.5 eV and 781.5eV respectively .
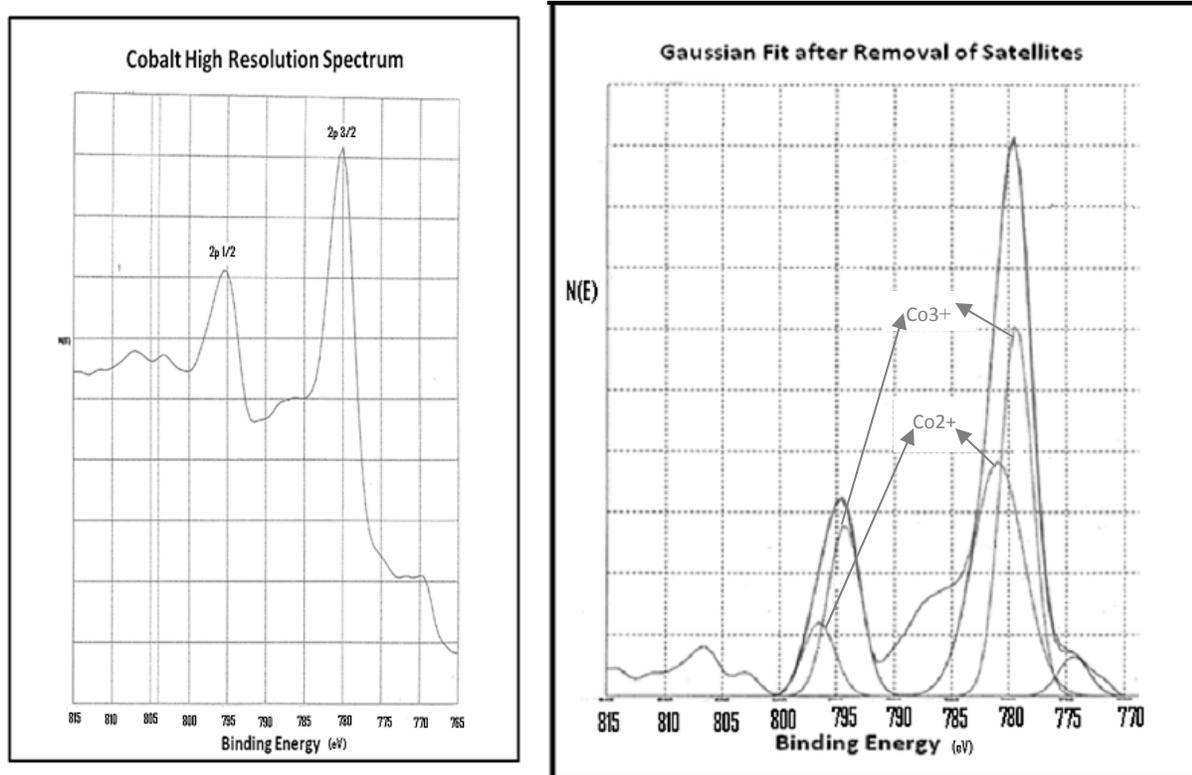

Fig 5: (Left) XPS high resolution spectrum for cobalt showing $2p_{1/2}$ and $2p_{3/2}$ peaks.
(Right) Gaussian fit confirming the presence of cobalt spinal (i.e. Co^{2+} and Co^{3+} ions).

XRD

X ray diffraction (XRD) is a method used for long range characterization of solid and heterogeneous catalysts. In situ technique leads to valuable information about dispersion and reducibility during different phases of pretreatments and FT reaction condition. Ex-Situ

characterization can show well defined XRD pattern for Co_3O_4 and CoO, in some cases cobalt support oxides patterns can be observed but usually these mixed oxides are amorphous and do not produce any distinct line. XRD is commonly used to calculate the crystal size using Scherrer equation. Its has been shown that angular breadth of the diffraction peak β is [4]

$$\beta = \{C\ \lambda\}/\ \{L\ cos\Theta\} \quad \ldots\ldots\ldots\ldots Eq(5)$$

C is a constant, λ is X-ray wavelength, L is the volume average crystal size and Θ is the Bragg angle. Peak breadth is either identified FWHM (full-width half-max) or integral width (area under diffraction peak divided by peak maximum).

Powder diffraction method can be applied. The spectrum shown below has a small peak indicative of the presence of metal-support oxide (Co_2SiO_4). This interaction is required to improve dispersion. Co_3O_4 had well defined peak, the presence of this spinal was also confirmed by XPS high resolution. Silica support peak is also observed.
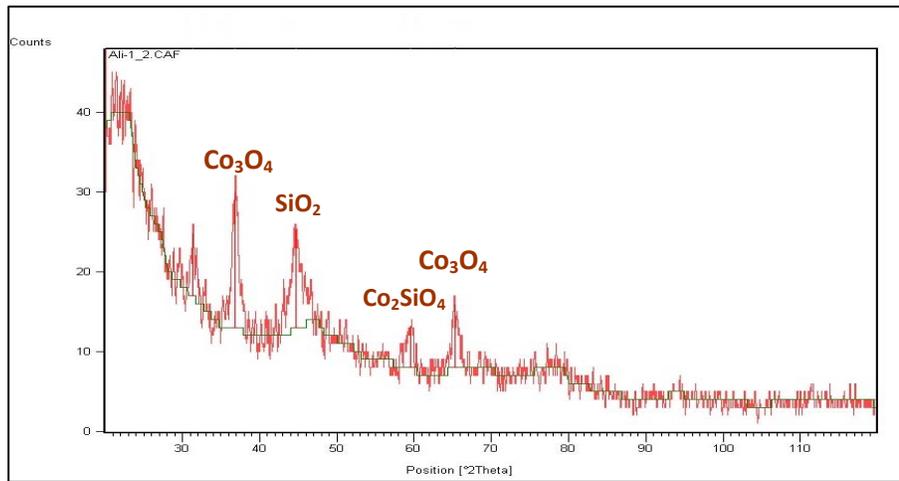

Fig 6: Powder XRD analysis of the eggshell catalyst. A small peak confirms the presence of weak metal support interaction (Co_2SiO_4).

Identification of Surface Morphology

Physisorption (BET analysis)

High surface area support is always desired to improve the performance of the catalyst. As far as the pore size is considered, the desired limit is between 6-10nm. A Commercially available silica support provides both optimal surface area and required pore diameter.

Physical adsorption is performed to confirm the surface area and pore size distribution for original support and unreduced catalyst. Shown below is the trend for calcined catalyst, and surface areas and pore size distribution (calculated using BET isotherm) during different phases

of catalyst preparation. Such BET results form the basis of further investigation since they confirm the fundamental properties of support and catalyst.
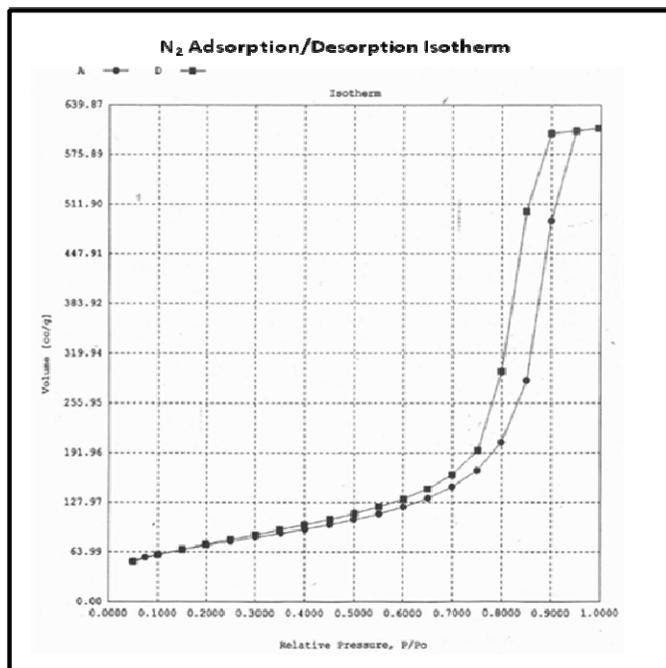

Table 1. Results from BET Isotherm

	BET Surface Area (m^2/g)	Avg Pore Diameter (nm)
Original Silica Support	321.7	8
Pre-calcination sample	317.5	8
Calcined sample	281.3	10

Fig 7: N_2 adsorption /desorption isotherm (measurements done at 80°C).

Chemisorption

Hydrogen chemisorption coupled with TPR (Temperature program reduction) is imperative for the successful operation of catalyst. Only chemisorption techniques provide information about the number of active sites. Information about the number of cobalt surface sites is essential for description of catalytic performance. Dissociative hydrogen uptake at static condition (373 K) [4] is taken into consideration.

Average crystal size of metallic cobalt is also measured through hydrogen uptake. When compared with XRD, this data can provide information about directional change in cobalt crystal size during the reduction. Dispersion results are direct indicators of the extent of metal-support interaction. High dispersion is always desired with minimal impact on the reducibility. Our goal is to reach 9-10% dispersion at 20% Co/SiO$_2$ catalyst. Dispersion can significantly improve by using alumina support but the reducibility decreases significantly. Based on our own literature review, a comparison is given for our hydrogen chemisorption results and the best reported figures. An isotherm plot at 100 °C for the 14% Co/SiO$_2$ is also shown.

We have focused our attention to underlying physical principles instead of using expensive promoters. With this integrated approach and strong characterization techniques we are sure that we will improve upon the results reported in the table below.

Table 2. Results from Hydrogen Chemisorption Experiments (using Langmuir Isotherm)

Catalyst	% age Dispersion		Extent of Reduction (Based on Hydrogen Uptake)		Crystal Size (nm)
	Our Eggshell Catalyst	Highest Reported	Our Eggshell Catalyst	Highest Reported	Our Eggshell Catalyst
8% Co/SiO2 catalyst	5	9 (promoted with Pt)	53	92	18
14%Co/SiO2 catalyst	6	13 (promoted with Pt)	59	100	17
20%Co/SiO2 catalyst	Under Investigation	10	–	100	–

This isotherm is developed by measuring total hydrogen uptake at a temperature of maximum hydrogen chemisorption (for a defined pressure range). Other available approach included measuring the amount of irreversibly chemisorbed hydrogen using improved flow method [4]. 373 K has been identified (in previous research works) as the temperature that will provide maximum reversible and irreversible chemisorption.
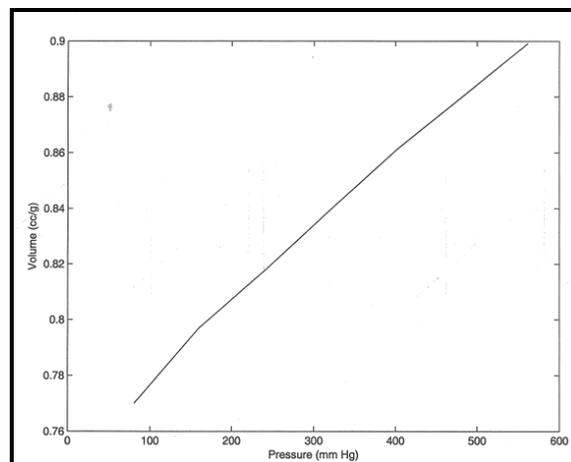

Fig 8: H_2 adsorption isotherm of reduced cobalt catalyst (measurements done at 373K).

Optical Microscopy

Presence of eggshell and its thickness can be verified by performing optical microscopy on randomly chosen samples. Based on the magnitude of magnification (which has to be uniform), the thickness of shell is measured and compared with the calculated value from χ. Θ_M values are obtained from hydrogen chemisorptions results. Shown below is an optical microscopic image and results obtained using the same magnification ratio. Our results fit the model within satisfactory limits.

Table 3. Results from Optical Microscopy

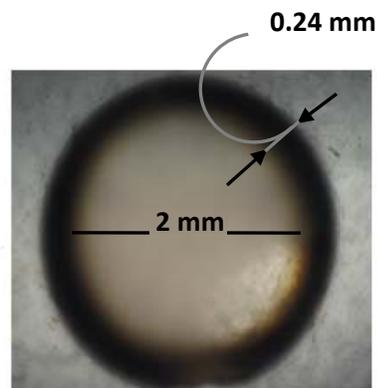|	
Actual Diameter of Particle	2 mm
Magnified Diameter	23 inches
Shell Magnified Thickness	2.8 inch
Actual Thickness (based on magnification)	0.24 mm

Fig 9: Magnified optical microscopic image of a typical catalyst along with the thickness measurement result.

TPR

TPR is a valuable technique to obtain information about the reduction process. According to various sources the reduction of supported and unsupported catalyst proceed in the two steps [8].

$$Co_3O_4 + H_2 \longrightarrow 3\,CoO + H_2O \quad \ldots\ldots\ldots.Eq(6)$$

$$3CoO + 3\,H_2 \longrightarrow 3Co + 3H_2O \quad \ldots\ldots\ldots.Eq(7)$$

It is usually observed that bulk Co_3O_4 exhibit two peaks [9]. Based on the above equations the ratio of two peaks has to be 1:3. So the area under two peaks can indicate the extent of interaction between metal and support material, i.e. if the ratio is substantially higher than 3 there is a significant interaction present. Given below is the TPR profile of 14% Co/SiO_2 catalyst.

It has been observed that initial reduction step is independent of the particle size, pore size and surface, so the first peak always occurs at same temperature interval. However it is the second peak which shifts towards higher temperature side due to metal-support interaction. The stabilization of the oxide phase due to interaction is also responsible for the broadening of the second peak [8]. Some catalyst studies have also shown only one peak indicative of possible simultaneous reduction of the cobalt oxide species.
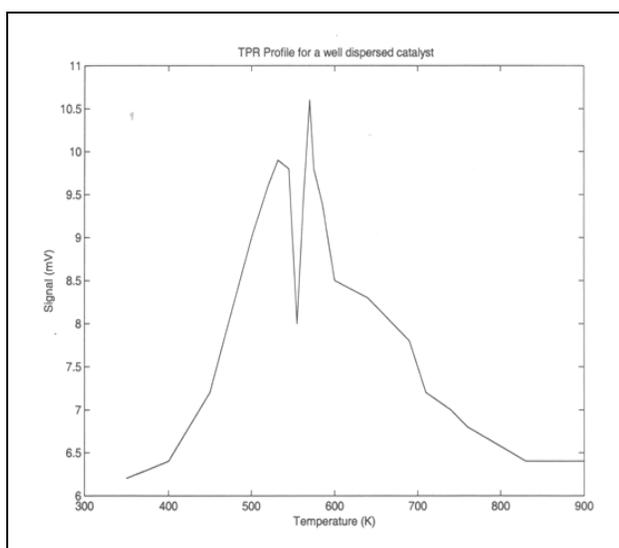

Fig 10: TPR profile of catalyst showing highest dispersion. Location of second peak at around 570K shows very little impact of metal-support interaction. 9

We are planning to develop different samples of catalyst under different conditions (e.g. changing solvents, changing pre-drying procedure) to observe the directional shift and broadening of the peaks. This study will provide us conclusive results about presence of metal support interactions. At present the ratio between two peaks and the broadening of second peak indicate the presence of metal support interaction but to a nominal degree.

6. Reactor Design and Performance of Catalyst:

The choice of the reactor is one the most important decision in the research of FT synthesis. Heat transfer limitations and pressure drop issues greatly limits the choice of reactor. It has been reported that for small FT plants (500-2000 bbl/day) compact fixed bed reactors are more cost effective. However, because of their excellent heat transfer and relative low cost, slurry reactor are the clear choice of the for large Fischer Tropsch plants [10].

For our bench scale arrangement, we are using Autoclave Engineers BTRS-jr fixed bed reactor with a maximum capacity of 40-45 cm^3 for 2mm catalyst. Some advantages of such a reactor are little attrition of the catalyst, and an economically practical reactor at high pressure. Disadvantages of using this design is poor heat transfer causing thermal catalyst degradation, non uniform flow pattern, and plugging due to high pressure drop.
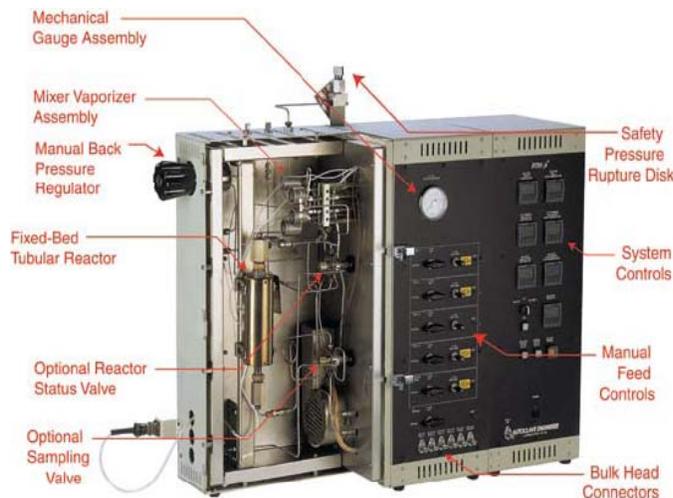

Following steps are taken to overcome the heat transfer and flow problem.

1. Staging of the reactor.

2. Use of diluents

The performance of the reactor has improved significantly which has increased both the selectivity and activity of catalyst.

Fig 11: BTRS-Jr reactor, labels showing various electrical and mechanical components.

The selection of reaction condition requires careful consideration. Catalyst is first reduced at around 400°C (673K). The choice of this temperature is a direct consequence of TPR studies (which ensures the complete reduction). FT synthesis can take place around 200-300°C, higher temperature can lead to higher conversion rates, but increases methane production. High water production (due to high temperature) can also degrade the catalyst.

Pressure range selection is also important. Industrial Fischer Tropsch cobalt catalyst operates at a total pressure of 2-3 MPa. However this high pressure increases risk of condensation of hydrocarbon at the catalyst pore which results in clogging and severely affects heat transfer,

mass transfer and chemical kinetics [4]. Restructuring of the cobalt particles in the presence of FT products is possible, high pressure may influence the concentration of liquid and gaseous water in contact with cobalt particle and thus increase catalyst deactivation.

Based on the above mentioned reasons Fischer Tropsch catalyst was subjected to the following reaction conditions.

Temperature = 230 ^{o}C
Pressure   = 1-1.5 bar
Space Velocity = 17.1 ml g^{-1} min^{-1}

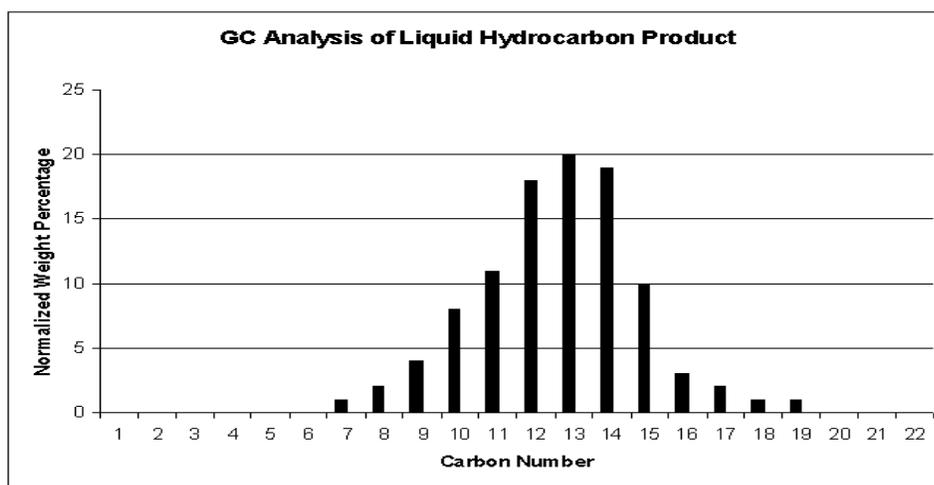Following GC product distribution was obtained.

Fig 12: Result showing carbon chain distribution. Evidently most of the product lies in range of diesel fractions.

Presence of higher hydrocarbon clearly indicates the validity of concepts being applied for towards the development of this catalyst.

7. Conclusion:

The integrated approach being used for the development of Co/SiO2 catalyst has produced promising results for an economically feasible catalyst. With continued integrated optimization e a highly dispersed, easily reducible, very active, and economically feasible catalyst will allow the realization of an economically feasible and scalable biomass-based FT process.

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