

Technology Development for Fischer-Tropsch Synthesis: Efficient Conversion of Biomass to Liquid Hydrocarbons

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Abstract:

Originating in Germany in 1920's, Fischer Tropsch Synthesis (FTS) is a process for converting syngas (a mixture of carbon monoxide and hydrogen) into clean liquid fuel e.g. gasoline, diesel and aviation fuel. With the gradual rise in global energy requirements (60 % between 2002-2030 **source: world energy handbook 2004**) there is an urgent need for alternate renewable energy resources. Following the current energy trends and future predictions (expected fourfold rise in the use of biomass for transportation fuel **source: world energy handbook 2004**) we have designed a tunable catalyst for efficient conversion of synthesis gas produced from biomass (coal or natural gas may also be used) into liquid fuels. An egg shell catalyst consisting of a silica support impregnated to a tailored depth with cobalt nanoparticles has been designed and synthesized in our laboratory for this purpose.

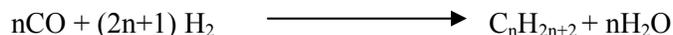
Egg shell catalyst design is an exceedingly innovative concept that overcomes mass transfer limitations inherent with conventional reactor catalyst systems. Production of long chain hydrocarbons in FT synthesis is rate limited due to the accessibility of active catalytic sites for diffusion of carbon monoxide. The tunable thickness of the active catalytic surface area ensures that enough active sites are available for desired, highly selective hydrocarbon chain growth. In this way the required petroleum cut is obtained thus eliminating the need for expensive separation processes. Such a design has not been explored or exploited commercially as yet. Conventional reactors provide waxy product and additional unit operations are required to obtain the desired fractions. Additionally, the specific reactor design that we offer eliminates current heat transfer issues. FT synthesis is a highly exothermic process, if the evolved heat is not removed; catalytic sintering, decay and attrition are the net result. This problem has been a major stumbling block for commercial reactors that must be operated far below full capacity as a result. By mixing an inert heat sink and catalyst along with inter-compartmentalization effective heat removal in the absence of cooling jacket has been realized. Thus reactor can be operated at optimal conditions giving higher conversion. Indications are that linear scaling up of this reactor will preserve the optimized bench-scale results.

An attractive market for the developed technology is the Department of Defense. The US Air Force has a goal to obtain half of its fuel used in the continental US from renewable sources by the year 2016 (**DOD Energy Security Task Force 2008**). This technology is one means to provide a clean, continuous, reliable and domestic supply of NATO JP-8 (Jet Propellant-8)

grade, the highest of its kind. Liquid fuel is a strategic resource that has significant security, economic and geo-strategic implications. DOD's fuel consumption varies from year to year in response to changes in missions and the tempo of operations. In FY 2000, fuel costs represented 1.2% of the total DOD spending, but by FY 2008 fuel costs had risen to 3% (**DESC Fact Books 2008**). The Defense Energy Support Center (DESC), under the command of Defense Logistics Agency (DLA), has the mission of purchasing fuel for all DOD services and agencies, both in continental US and outside US. The Air Force and the Army represent the primary consumers of JP-8 fuel whereas the Navy consumes JP-5. The majority of DESC's bulk fuel purchases are for JP-8 jet fuel, which has ranged from 60 to 74 million barrels annually. A September 2009 report published by the Congressional Research Services indicated that in FY 2008 the DOD's purchases for JP-8 fuel totaled 62.5 million barrels at \$3.13 per gallon (Congressional Research Service, Department of Defense Fuel Spending, Supply, Acquisition and Policy- Sept 2009). According to the same report, the DOD spent almost \$18 billion on acquiring fuels in FY 2008. With the ongoing operations in Iraq and Afghanistan to support the ground operations, the DOD's demand for JP-8 jet fuel will continue to go up and will only put upward pressure on reaching the target of obtaining 50 % of its fuel supply from renewable sources by 2016.

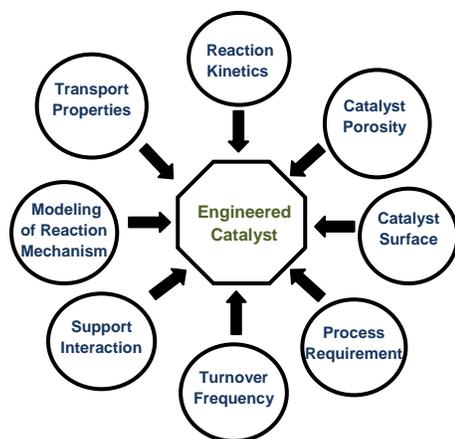
Introduction:

Fischer Tropsch synthesis is a catalytic reaction which converts mixture of hydrogen and carbon monoxide (also called syngas) into liquid hydrocarbons and water:



FT synthesis is an integral part of Gas to Liquid (GTL), Biomass to Liquid (BTL) and Coal to liquid (CTL) technologies. In these technologies syngas is generated respectively from natural gas, biomass and coal which then react on a cobalt or iron catalyst to yield a wide range of gaseous, liquid and solid hydrocarbons. Several industrial projects involving FT synthesis have been realized recently (Bintulu in Malaysia, Oryx in Qatar) or are currently under construction (Pearl in Qatar, Escravos in Nigeria). The world consumption of crude oil in 2015 can be estimated as 20 million barrels per day. If all GTL must be realized by that time, total GTL capacity might reach about 600,000 bpd they only 3 % of crude oil consumption [1]. Following the current and future energy trends there is expected fourfold rise in the use of biomass for transportation fuel which present great promise for FTS.

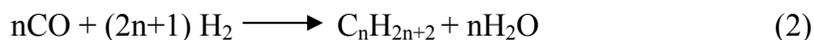
Many factors are involved in Fischer Tropsch synthesis process. These include the catalytic material and its support, their synthesis procedure, choice of desired and undesired reactions, the choice of reactor and the process conditions (e.g. reactor design, syngas composition, and residence time of feed in the reactor). These in turn control the syngas conversion, hydrocarbon selectivity and product distribution. In our last paper submitted to this forum [2] we defined an integrated approach which takes into consideration many variables as well as timed application, the result is an "Engineered" catalyst.



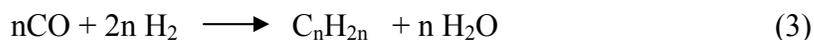
As far as the optimization of reaction chemistry is concerned, a number of desired (paraffin, olefin, alcohol) and undesired products (aldehyde, ketones, acids, esters, carbon etc) are possible.

Desired reactions

Paraffin



Olefins



Alcohol



Undesired reactions

Water-gas shift reaction



Carbonaceous materials



Boudard reaction



Bulk carbide formation



It is possible to retard the unfavorable chemistry by choosing the appropriate catalyst design and reactor technology. Product selectivity depends on the choice of active metal e.g. cobalt gives paraffinic product while iron has high selectivity of olefins. The extent of water gas shift reaction is more on iron than that on cobalt. Precise control of reactor temperature avoids catalyst plugging due to carbon deposition either by cracking or Boudard reaction. Apart from reaction chemistry there are other unfavorable conditions that need to be addressed such as blockage of pores by waxes, catalyst poisoning and coking; hydrogen treatment can restore lost activity, sintering resulting in crystal growth; fine temperature control (240°C for cobalt and 270 °C for iron) avoids this issue. Thus an integrated approach aimed at improving Fischer Tropsch synthesis technology not only produces the desired product, but also improves the overall economic feasibility of process by being specific to the reactor design.

The first is to develop the catalyst having the right morphology and properties. This task is not a simple one as it involves blending science, engineering and artful skill. Following discussion depicts our approach towards this challenging area of alchemy.

Catalyst Fabrication:

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 [3]:



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 (reversible dissociation) of carbon monoxide represented as [4]:



Dissociative energies calculated from DFT (density functional theory) are used to identify the most active material (higher turnover frequency, TOF) [4]. Shown below is an experimentally developed volcano curve based on DFT modeling and CO conversion on different surfaces.

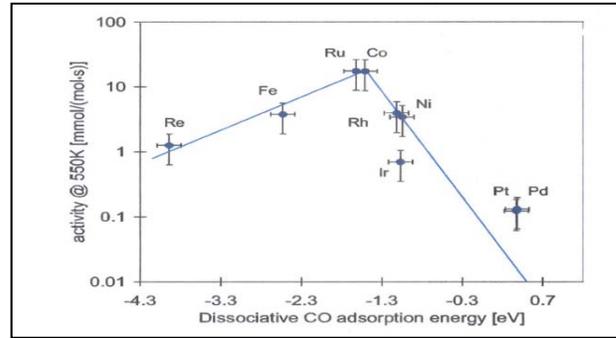


Figure 2: Calculated turn over frequencies (activity) for CO₂ dissociation on different atomically stepped metal surfaces. Reproduced from reference [4].

Clearly cobalt is the most active material. Other advantages of cobalt catalyst are, environment friendliness (H₂O is the byproduct), resistance to water produced in the reaction, and more paraffinic products.

Catalyst profile:

The optimal catalyst profile; activity, selectivity and other characteristics of the chemical reaction mechanism greatly influence the design path [5]. On the molecular level CO is the diffusion limited reactant (when a 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 (bond length of 0.074 nm) is much smaller than CO (bond length 0.1128 nm) and has a much higher diffusion coefficient.

It has been identified that pellets smaller than about 0.2mm diameter are required to avoid mass transfer restriction [6]. 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 [6]. 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.

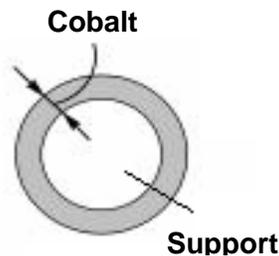


Figure 3: Eggshell catalyst

Thickness of the eggshell (χ) is the controlling parameter for selectivity of the diffusion limited catalyst. The 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 in fig 4 [6]

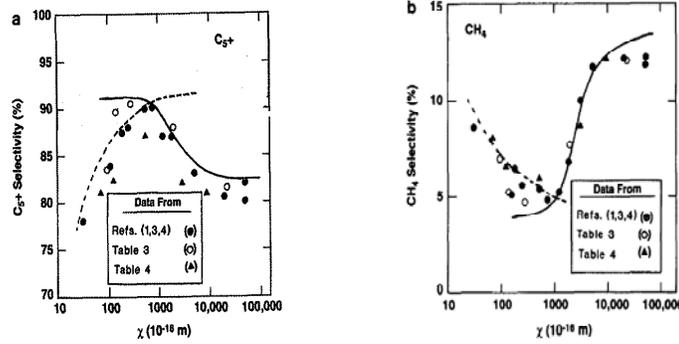


Fig 4: Methane & higher hydrocarbon selectivity dependence on χ value.
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χ is related to eggshell thickness as follows [6]:

$$\chi = (R_o - R_c)^2 \Theta_M / r_p \quad (13)$$

Where 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). Based on the favorable limits of χ , effective thickness of the 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 [5]. On the other hand alumina support leads to lower crystal size and higher dispersion. Higher surface area of catalyst (200-250 m^2/g) is 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 to a certain limiting value and then it decreases. Higher hydrocarbon (C_{5+}) selectivity shows a similar trend. 6-10 nm range is the most optimal based on conversion and selectivity [5].

Catalyst Preparation:

The purpose of any heterogeneous catalytic metals 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/SiO₂, activity and chain growth probability has been investigated. Activity has been shown to follow the order; Co₂(CO)₈ > Co(NO₃)₂ > Co(CH₃COO)₂ while chain growth probability followed the sequence Co(NO₃)₂ > Co₂(CO)₈ > Co(CH₃COO)₂ [7]. Based on these findings Co(NO₃)₂ is a preferred precursor salt.

In this study an 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 an eggshell catalyst preparation include:

1. Time controlled deposition to limit precursor presence in the given thickness (χ).
2. Exploiting physical interaction between different hydrophobicities of molecular species.
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 and most effective technique for egg shell formation. The main disadvantage is non- uniform deposition, occasionally the base metal precursor form oxide in the aqueous solution and these oxide have strong interaction with the alumina or silica support and are difficult to reduce. On the other hand precipitation is used to deposit the precursor in the form of a hydroxide or carbonate. Uniform finely divided deposition can be obtained by controlling the precipitation procedure (avoiding bulk nucleation) and selecting the appropriate base (e.g. urea rather than a conventional base or alkali).

Catalyst Characterization:

All the catalyst samples prepared have been characterized by Optical microscopy, X-ray photoelectron spectroscopy, and hydrogen chemisorption.

XPS:

XPS (X-ray photoelectron spectroscopy) has been carried out in Perkin Elmer PHI 560 UHV XPS/ SAM system. Sample degassing was performed for 24hrs under 10⁻⁶ Torr vacuum. XPS elemental analysis was done using both Al K α and Mg K α radiation based on binding energy range and resolution requirement. A “Gaussian Curve Fit” was used to identify the chemical-state and relative concentration of elemental species. Reference for the binding energies was taken from the Handbook of Photoelectron Spectroscopy (published by Physical Electronics Inc) and past research papers. Note that XPS is a surface analysis technique limited to 10⁻¹ monolayer fractions and is not representative of bulk composition.

XPS (X-ray photoelectron spectroscopy) was primarily used for the identification of different cobalt phases (Co₃O₄, CoO, metallic cobalt and mixed oxide) [5] in the near surface region. Atomic percentages (depth 2-4 nm, monolayer fraction = 10⁻¹) [8] were also obtained. The presence of the oxides, more specifically “Co₃O₄” spinel is represented as the Co2p core

electron. Spin-orbital splitting is around 15.0 eV with the main feature center around 780 eV [5]. The spectrum shown in figure 5 below indicates the presence of Co^{3+} and Co^{2+} based on Gaussian curve fitting with a reference binding energy of 779.5 eV and 781.5eV respectively as shown in figure 5.

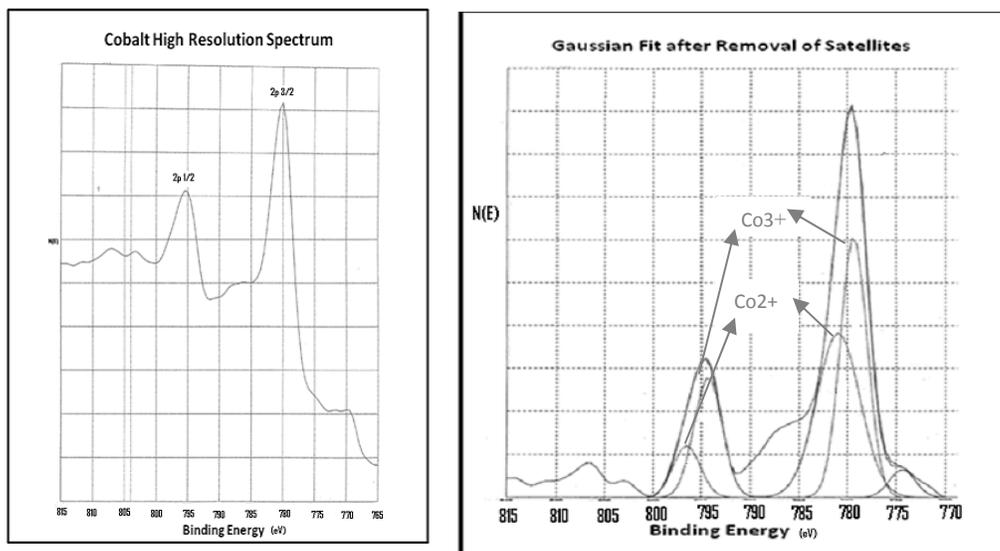


Fig 5: (Left) XPS high resolution spectrum for cobalt showing 2p_{1/2} and 2p_{3/2} peaks. (Right) Gaussian fit confirming the presence of cobalt spinel (i.e. Co^{2+} and Co^{3+} ions).

Optical Microscopy:

The presence of eggshell formation and thickness (χ) was verified by optical microscopy on randomly chosen samples. Based on the degree of magnification (which must be held uniform), the thickness of shell is measured and compared with the calculated value from χ . The Θ_M values were obtained from hydrogen chemisorptions results. Shown below is an optical microscopic image with results obtained using the same magnification ratio. The experiment results fit the model within satisfactory limits.

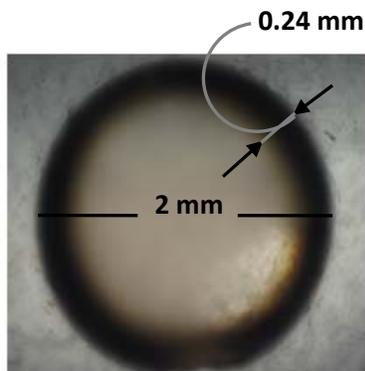


Fig 6: Magnified optical microscopic image of a typical catalyst along with the thickness measurement result.

Hydrogen Chemisorption:

A Hydrogen adsorption isotherm was recorded using Quantachrome Autosorb gas sorption unit at 373K. The sample was reduced in hydrogen at 673 K; the flow of hydrogen was maintained at level to swiftly remove water formed during reduction. Following reduction, the sample was evacuated at 673K and then cooled to 373 K. An adsorption isotherm was recorded from 80-560 mmHg. The amount of chemisorbed hydrogen was determined by extrapolating the straight-line portion of the isotherm to zero pressure. For calculating dispersion, it was assumed that two cobalt sites will be covered by one hydrogen molecule. Hydrogen chemisorption provides strong insight into metal support interactions and dispersion.

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	7	9 (promoted with Pt)	53	92	18
12%Co/SiO₂ catalyst	14	13 (promoted with Pt)	100	100	9
20%Co/SiO₂ catalyst	10	10	80	100	11.2

The results indicate that the engineered catalyst exhibits properties consistent with the best found in literature. High dispersion translates into a high density of active sites, while the extent of reducibility indicates the availability of active metal sites. These results show that under Fischer Tropsch conditions, the catalyst is expected to yield high conversion and superior selectivity.

Reactor System

FTS is highly exothermic process; therefore, it is imperative to maintain isothermal condition within the bed. For this purpose, research was carried out in integral fixed bed isothermal reactor designed by Autoclave Engineers as shown in figure 7.

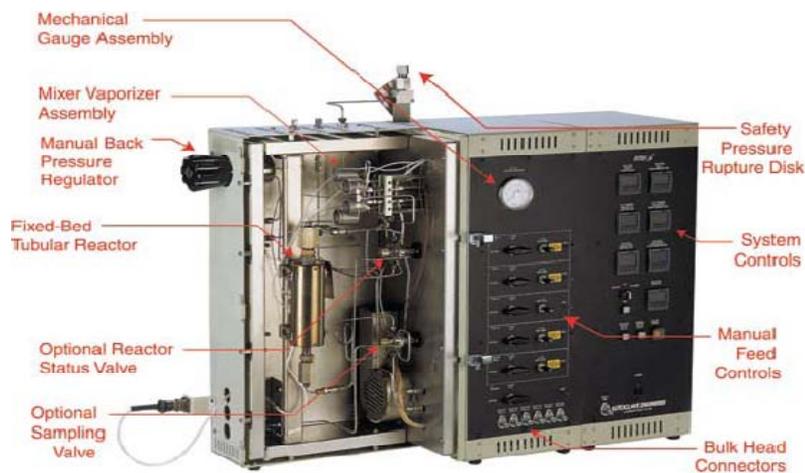


Fig 7: BTRS-Jr reactor, labels showing various electrical and mechanical components. With permission from Autocalve

Performance Evaluation:

A detailed understanding of catalyst and reactor design has led to the development of a “state of the art” process. Although, all catalyst properties are important, dispersion has the most significant impact. The engineered egg-shell profile was shown to enable precise control of selectivity. The engineered catalyst is tunable, customer specific and inexpensive. The choice of a reactor is based on desired application and reaction thermodynamics.

Based on the catalyst design, a narrow liquid hydrocarbon distribution has been obtained; mainly in the diesel and aviation fuel range. A photograph of the resulting product as well as the gas chromatograph analysis is shown in figure 10.

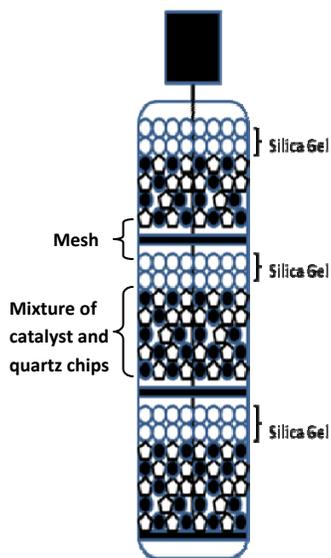


Fig 8: Innovative strategy to avoid heat spots.

Conversion = 72%

Fig 9: Reactor performance under FTS conditions.
Temp= 220 °C, Press= 20 bar, Space velocity= 17.1 ml
g⁻¹ min⁻¹



Biomass Derived

Product Selectivity

Naphtha:	10%
Middle Distillate:	85 %
(Diesel & JP-8)	
Soft waxes	5%

Fig 10: Analysis of condensable hydrocarbon using GC

Conclusion:

Basic understanding of catalyst development and reactor design has led to the development of “state of the art” process. Although, all catalyst properties are important, dispersion has the most significant impact. Egg shell profile enables the precise control of selectivity. This catalyst is tunable, customer specific and inexpensive. Choice of reactor is based on the desired application and reaction thermodynamics. Technical understanding is important to develop a technology, but its success mainly depends on its market potential. If there is a demand then will there be a supply, otherwise it will be impossible to mature a developed technology.

I acknowledge the strong insight of my advisors Dr Babu Joseph, Dr John Wolan, and Tino Prado of Prado and Associates for turning this idea into a reality.

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