

Thrust Area 3: Biomass (Thermo-Chemical Conversion)

Production of Liquid Fuels Biomass via Thermo-Chemical Conversion Processes

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Description: The objective of this project is to develop technology for the economical thermo-chemical conversion of lignocellulosic biomass (non-food grade biomass such as agricultural waste, bagasse from sugar mills, citrus peels, switch grass, municipal green waste, etc.) to clean burning liquid fuels. Five of the major advantages of this process over a biochemical route to production of ethanol are: (i) it does not utilize food-grade feed stocks and therefore complements and does not compete with the agricultural food production in the state, (ii) the fuel produced is similar to those derived from petroleum unlike ethanol derived fuels which have at least a 25% lower energy content, (iii) the conversion is accomplished in using fast chemical reactions unlike the slow biological reactions for fermenting alcohol, (iv) the process does not require large amounts of water and associated energy costs of separating the water from the fuel as in bioethanol processes, (v) it can utilize a wide variety of biomass sources unlike the biochemical route which cannot work with high lignin containing biomass.

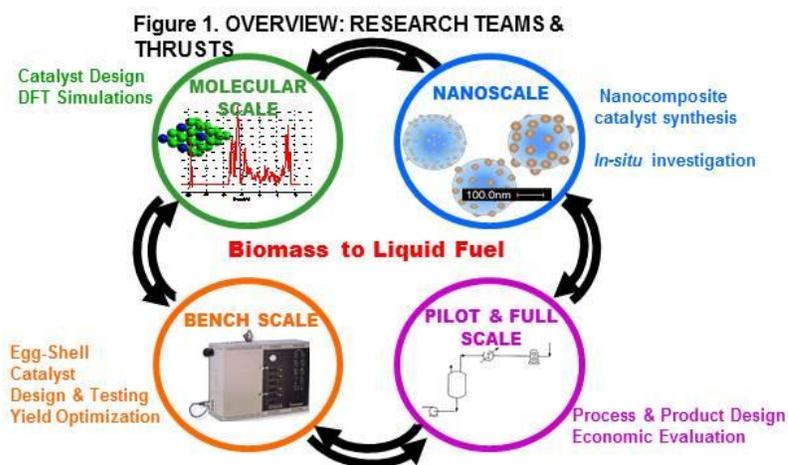
Budget: \$554,447

Universities: USF

External Collaborators: Prado & Associates

Progress Summary

During the past year, we made progress on four fronts: catalyst design using density functional theory (DFT) simulations in the molecular scale, nanocomposite catalyst synthesis in the nano-level, bench scale reactor testing for the synthesis of liquid fuels from bio gas and biomass conversion process design in the pilot and full scale.



Our research focus is primarily based on cobalt catalysts since they represent the optimal choice for low temperature FTS processes because of higher stability, higher conversion (up to 60–70%), higher productivity, and relatively smaller negative effect of water on conversion. However, fundamental knowledge on reaction mechanisms and development of an economic technology to convert biomass to liquid fuels via FTS process is still not known. Our approach is to study FTS processes at these four different levels to achieve our objective.

In the past year, at the molecular level, we have performed DFT simulations to understand the role of promoters in the reduction of cobalt oxide which is one of the key steps required in this process for a cobalt catalyst. In the nanoscale level, we have prepared novel composite colloids such as silica supports surface decorated with cobalt nanoparticles as a model FT catalyst. This method allows control over the Co size and its aggregation on the support material. Our bench scale testing of egg-shell catalysts using our fixed bed reactor setup was successful. We were able to produce high grade liquid fuels from both mixtures of CO and H₂ as well as Biosyngas produced from poplar wood. In the area of process design, we have been evaluating alternative strategies to combine the energy intensive biomass gasification step with the energy producing Fisher-Tropsch synthesis of clean liquid fuels from syngas produced in the gasification step.

Funds leveraged/partnerships: We have started discussion with QNRF to continue the research in collaboration with Texas A & M University in Qatar. A proposal is under preparation for submission in Jan, 2012. We continue discussions with local industry as well as venture capitalists regarding the construction of a pilot plant using biomass feedstocks. Negotiations are underway between USF and a company regarding the licensing of our egg shell catalyst.

DFT studies: The main objective of this research is to study the effect of promoters on the catalyst performance using Density Functional Theory (DFT). Understanding the effect of promoters in the molecular scale would help in tailoring catalysts with higher activity and desired selectivity. Promoters have different functions such as increasing the reducibility, dispersion, activity or extending the life of a catalyst by reducing the deactivation rate. Catalysts are often modified by adding promoters to obtain these desirable properties. The commonly used promoters are transition metals (Zr, Mn, Re, Ru, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au), and alkali metals (e.g. Li, K, Na, Cs).

The effect of Pt promoter on the reduction of cobalt oxides to metallic cobalt was studied on both flat and stepped surfaces using surface alloy models where the promoter metal was dispersed on the top surface of the catalyst. We found that the activation barrier on promoted catalyst was reduced compared to that on the unpromoted catalyst by about 0.3 eV. We also found that on the promoted catalyst CO dissociation was difficult. A kinetic model was developed and the reaction rate for the promoted catalyst was higher than that for the unpromoted catalyst.

Determining the chain-growth pathway is very important to understand the FTS mechanism. Different mechanisms were proposed for FTS but still there is no clear consensus on the actual mechanism. FTS consists of the following steps: CO activation, hydrogenation and O removal, chain growth and termination. Activation barriers for various primary reactions will be found on Pt promoted and unpromoted Co catalyst to determine the CO initiation pathway that a promoted Co catalyst would follow. The calculations show that the reaction barriers are reduced for most of the reactions in the pathway.

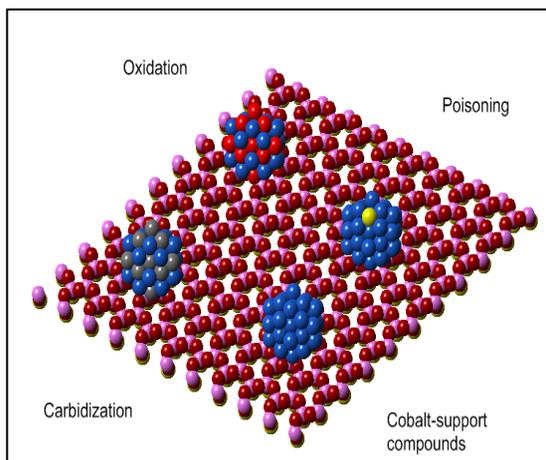


Figure 2 : Schematic of deactivation of catalyst

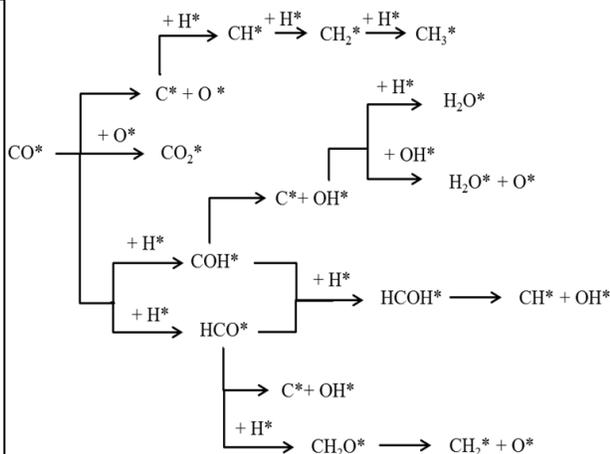


Figure 3: Reaction pathways considered

Eggshell Catalyst Performance Assessment in Biomass Derived Syngas: The biomass gas derived from pine chips was supplied from Pearson and Associates. Its constituents were analyzed using an Agilent 5975C Mass Spectrometer hooked up with a 6890 N GC. HP-5 MS (5% phenyl)-methylpolysiloxane column provided the initial separation before injection into MS. The results shown in Figure 4 indicate the presence of syngas mixture (H_2 and CO), hydrocarbons and tar components (benzene, toluene). It was not possible to detect the moisture with mass spectrometer. For moisture detection, the biomass derived syngas was analyzed in a BIO-RAD Excalibur FTS 3000 FTIR equipped with an aligned gas cell. Figure 5 represents the FTIR spectra; the presence of moisture is evident at around 3400 cm^{-1} . Both the tar constituents and moisture presents problems for downstream unit process (reactor). The presence of higher H_2O content has been shown to favor CO_2 formation in a fixed bed reactor operation, downgrading one of the advantages of cobalt as Fischer Tropsch catalyst. Additionally, under the normal FTS process conditions i.e. 473-483 K and 20 bar, the system is very close to the saturation temperature of water (i.e. 486 K). Increment in temperature for activity improvement will result in the steam formation accompanied with thermal expansion. This expansion can damage spherical pellet resulting in dust formation inside the reactor. On the other hand, tar can condense in the downstream piping or can accumulate on the catalyst. Although our research group has not come across any literature dealing with the effect of aromatic and poly-aromatic compounds on FTS catalysts, our research experience has shown that the presence of these ring compounds lead to the loss of catalytic activity. However, this needs further investigation which is in progress.

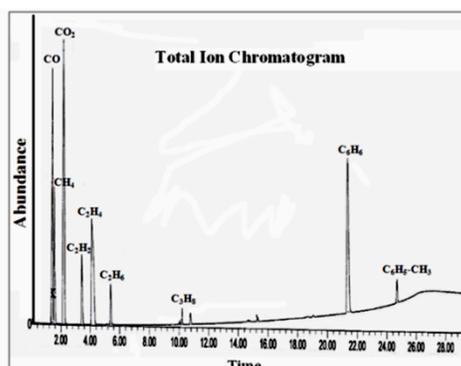


Figure 4: Total ion chromatogram of biomass derived syngas.

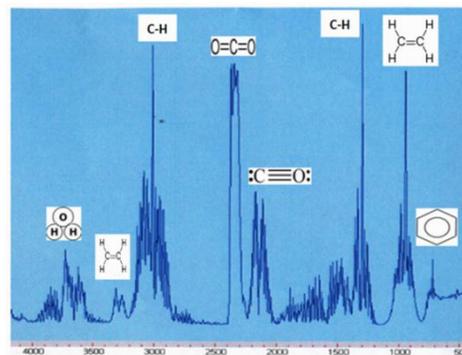


Figure 5: FTIR gas cell analysis of biomass derived syngas.

Cleansing of Syngas to Remove Moisture and Tar: Conditioning of biomass derived syngas is a challenging aspect as it needs to be continuous and multistep for successful integration with the downstream operation. As stated earlier, removal of both moisture and aromatics is essential as they can be detrimental for catalyst performance. For this purpose, two inline filters have been installed, consisting of a combination of silica gel beads (Sobead orange, Sorbead WS), molecular sieve for moisture removal and GC C-40 activated carbon pellets for physical adsorption of aromatics. An inline shaw “Moisture meter” is used for to monitor the moisture level going to the reactor. This setup (shown in Figure 6) has successfully cleansed the gas as can be seen by the MS analysis of the gas at the outlet of the filtration system as can be seen in the attached mass spectrometer analysis.

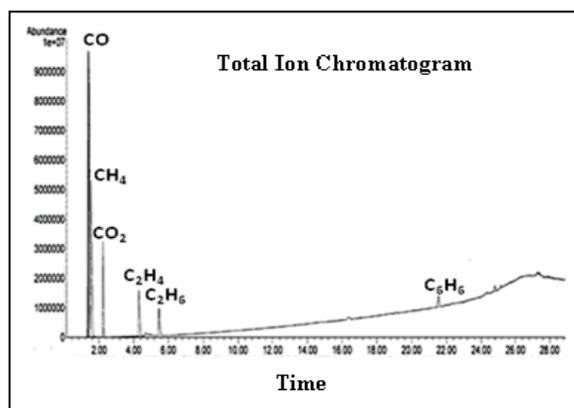


Figure 6: (left) Multistep filtrations setup (right) Total ion chromatogram of biomass derived syngas after cleansing.

Preliminary Performance Assessment Using Biomass Syngas: The optimized eggshell catalyst was tested in a fixed bed reactor using cleansed biomass syngas under conventional FTS conditions. The overall material balance shown in Figure revealed a CO conversion of around 52%. This

conversion was relatively lower than that reported in previous literatures (for cobalt catalyst) and in comparison to the performance (of same catalyst) on pure gaseous feed (reported earlier). Some of the possible reasons include, transitional nature of the FTS run, the process had to be stopped after 48 hours, due to filtration issues resulting in benzene breakthrough. Later investigations revealed that the activated carbon being used for aromatics removal was surface impregnated with phosphoric acid resulting in pore blockage and diminished physic-sorption activity and regenerability. This filter has thus been replaced. Similarly, the presence of other components lowers partial pressure of carbon monoxide causing the reduced activity. We are planning to perform the next run above 20 bar to bring the partial pressures to the desired level. Other contaminants e.g. CO₂ can be removed from the system using appropriate traps. All these strategies will be implemented to enhance the performance of the liquefaction process.

- **Co/SiO₂ Nanocomposite analysis using *in situ* FTIR:** In the previous reports, we have shown that we synthesized cobalt based FTS catalysts with precise cobalt nanoparticle size control (1-14nm). The nanocomposite catalysts were prepared by self-assembly of cobalt

nanoparticles on SiO₂ colloids. The immobilization of cobalt nanoparticles on SiO₂ was achieved by surface modification of SiO₂ surface. The nanocomposites thus prepared were next analyzed using an *in situ* AABSPEC FTIR reactor to study the dependency of Co nanoparticle size on catalytic activity. CO gas is one of the primary reactants in FTS. Therefore, we studied the interaction of CO on cobalt surface to understand the effect of cobalt nanoparticle size on CO reaction kinetics. From X-ray diffraction spectroscopy as shown in Figure 7, we identified the cobalt crystal structure as CoO. Then, AABSPEC reactor was used to study an elementary reaction such as CO oxidation on Co-oxide nanoparticle surface to study the dynamics of CO adsorption and CO₂ formation by using infrared spectroscopy. A schematic of CO oxidation on CoO is shown in Figure 8. Based on CO adsorption peak and CO₂ peak profiles obtained from IR, activation energies for step 1 and step 2 were estimated.

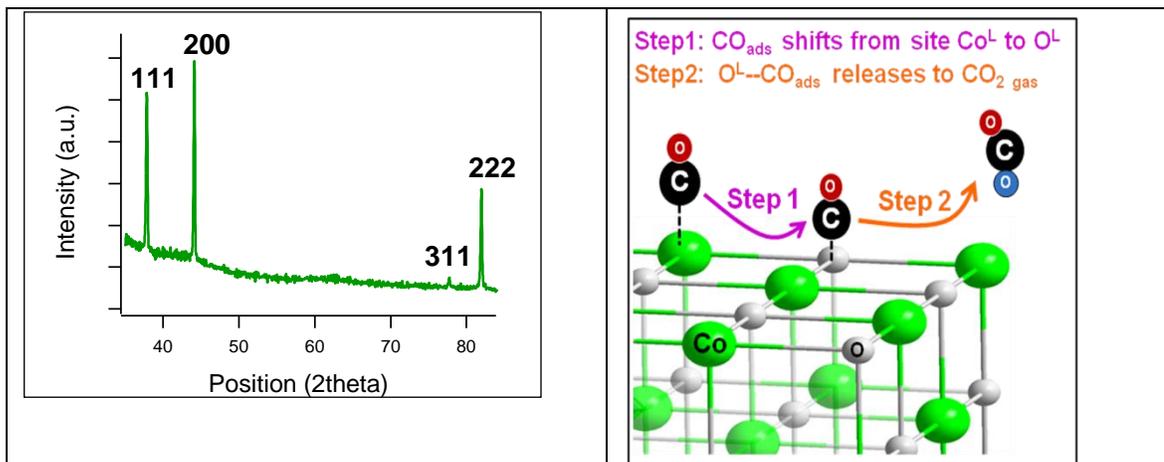


Figure 7: XRD of CoO nanoparticles

Figure 8: Schematic of CO oxidation reaction

- Process & Plant Design:** We are now developing a dynamic model of the FTS fixed bed reactor. This model would be useful for plant design and scale up. We are also developing a full process design for the combined gasification/liquefaction process starting with biomass and ending with liquid fuels. This model would be used for economic analysis of such processes.

Publications resulting from the work so far:

- S. A. Gardezi, L. Landrigan, B. Joseph. J. T. Wolan, "Synthesis of Tailored Eggshell Cobalt Catalysts for Fischer-Tropsch Synthesis Using Wet Chemistry Techniques", *Submitted to Industrial & Engineering Chemistry* (2011).
- S. A. Gardezi, B. Joseph, Y. D. Goswami, J. T. Wolan, "Modeling the Start up Phase of Fischer Tropsch Synthesis in a Fixed Bed Reactor: Effect of Pore Filling and Heat Transfer Through the Catalyst Bed", AICHE 2011 Spring Meeting & 7th Global Congress on Process Safety, Mar-2011

3. B. D. Mankidy, C. A. Coutinho, and V. K. Gupta*, “Probing the Interplay of Size, Shape, and Solution Environment on Macromolecular Diffusion using a Simple Refraction Experiment”, *Journal of Chemical Education* 87(5), 515-518 (2010)
4. C. A. Coutinho, B. D. Mankidy, and V. K. Gupta*, “A Simple Refraction Experiment for Probing Diffusion in Ternary Mixtures”, *Chemical Engineering Education* 44(2), 134 (2010).
5. A.H. Kababji, B. Joseph, J.T. Wolan; “*Silica-Supported Cobalt Catalysts for Fischer–Tropsch Synthesis: Effects of Calcination Temperature and Support Surface Area on Cobalt Silicate Formation;*” *Catal. Lett* (2009) 130: 72-78
6. S. A.Z. Gardezi, J. T. Wolan, B. Joseph, *An Integrated Approach to the preparation of effective catalyst for Biomass-to-liquid (BTL) process*, 33rd Annual AIChE Clearwater conference, June-2009
7. S.A. Z. Gardezi, B. Joseph, J. T. Wolan, *Metal support interaction effects in Fischer Tropsch synthesis: significance of catalyst preparation*, AIChE annual meeting Nov-2009.
8. C. A. Coutinho and V. K. Gupta*, “Photocatalytic Degradation of Methyl Orange Using Polymer-Titania Microcomposites”, *J Colloid and Interface Science* 333(2), 457-464 (2009).
9. Balakrishnan, N.; Bhethanabotla, V. R.; Joseph, B. In *Effect of Cluster Size on CO Adsorption and Dissociation on Cobalt Catalysts: DFT Studies Using Cluster Models*, Accepted for presentation in AIChE Annual Meeting, Conference Proceedings, Nashville, TN, United States, 2009.
10. Balakrishnan, N.; Bhethanabotla, V. R.; Joseph, B. In *Effect of Cluster Size on CO Adsorption and Dissociation on Cobalt Catalysts: DFT Studies Using Cluster Models*, presented in FESC summit, USF, Tampa, United States, 2009.
11. Choudhury, P.; Balakrishnan, N.; Bhethanabotla, V. R.; Stefanakos, E. In *Complex Borohydride for Reversible Hydrogen Storage* Accepted for presentation in AIChE Annual Meeting, Conference Proceedings, Nashville, TN, United States, 2009.
12. Balakrishnan, N.; Choudhury, P.; Bhethanabotla, V. R.; Joseph, B. In *Density Functional Theory Studies on a Reversible Hydrogen Storage "Li-Mg-B-N-H" System*, Annual Meeting, Conference Proceedings, Philadelphia, PA, United States, 2008.
13. Bijith D. Mankidy and Vinay K. Gupta, "Novel Composite Particles for Catalysis: Cobalt Nanoparticles on Silica Colloids", The Southeastern Regional Meeting of American Chemical Society, Nashville (TN), November, 2008.
14. Bijith Mankidy and Vinay K. Gupta, “Cobalt Nanoparticles on Surface Modified SiO₂ Colloids for Fischer Tropsch Synthesis”, Florida Energy Systems Consortium Summit, University of South Florida, Tampa (FL), September 29-30, 2009.

15. Babu Joseph, Y. Goswami, V. Bhethanabotla, J. Wolan and V. Gupta, Production of Biomass via Thermochemical Process, FESC Summit, Tampa, Florida, Sept 2009.
16. Babu Joseph, SURA Workshop on Energy: A brief update and summary, FESC Summit, Tampa, FL, Sept 2009.
17. Balakrishnan, N.; Bhethanabotla, V. R.; Joseph, B. In *DFT studies on the promotional effect of platinum for the reduction of CoPt bimetallic catalyst in Fischer Tropsch Synthesis*, AIChE Annual Meeting, Conference Proceedings, Salt Lake City, UT, United States, November 2010.
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19. Balakrishnan, N.; Joseph, B; Bhethanabotla, V. R. In *Influence of Pt Promoter On Fischer-Tropsch Initiation Pathways Over Cobalt Catalysts*, Accepted for presentation in AIChE Annual Meeting, Conference Proceedings, Minneapolis, MN, United States, 2011.
20. Balakrishnan, N.; Bhethanabotla, V. R.; Joseph, B. In *The Role of Added Promoters In Reducing the Deactivation of Co Catalyst Used In Fischer Tropsch Synthesis*, Accepted for presentation in AIChE Annual Meeting, Conference Proceedings, Minneapolis, MN, United States, 2011.
21. Balakrishnan, N.; Bhethanabotla, V. R.; Goswami, Y.; Joseph, B. In *Influence of platinum promoter on CO activation pathway of cobalt catalyst in Fischer Tropsch Synthesis*, Poster presented in FESC summit, USF, Tampa, United States, 2009.