

SUPPORT MODIFICATION OF COBALT BASED SLURRY PHASE

FISCHER-TROPSCH CATALYSTS

J. van de Loosdrecht, S. Barradas, E.A. Caricato, P.J. van Berge, and J.L. Visagie

Sasol Technology (Pty) Ltd, PO Box 1, Sasolburg 9570, South Africa

Tel: +27-16-9603075; Fax: +27-16-9602053

KEYWORDS: Fischer-Tropsch synthesis; cobalt catalyst; support modification

INTRODUCTION

Gas-To-Liquids (GTL) processes have received widespread attention as an economically viable route to convert natural gas to liquid transport fuels^(1,2). The GTL process consists of three main steps, i.e. (i) the reforming of natural gas, (ii) the production of hydrocarbons from synthesis gas (i.e. the Fischer-Tropsch synthesis), and (iii) the optimisation to middle distillates. The Fischer-Tropsch synthesis step is preferably performed in a slurry phase bubble column reactor with a suspended cobalt Fischer-Tropsch catalyst of high intrinsic activity^(3,4). For optimum cobalt utilisation, a supported catalyst is selected. The commercial supports of choice are alumina, titania, and silica. In addition to a specification with respect to the mechanical strength of the eventual slurry phase catalyst, it is important to ensure proper cobalt anchoring during the impregnation step of the pre-shaped support material. Insufficient anchoring could result in the washing out of cobalt-rich ultra-fine particulates from the porous support material during commercial slurry phase Fischer-Tropsch synthesis.

Support modification has been reported earlier in the open literature⁽⁵⁻⁹⁾. Zirconia modification of silica supports was used to prevent the formation of unreducible cobalt-silicates⁽⁵⁾. Zr, Ce, Hf, or U modification of titania supports was reported to prevent the formation of cobalt-titanates during regeneration⁽⁶⁾. To increase the porosity of titania supports, they were modified with small amounts of binders, e.g. silica, alumina or zirconia⁽⁷⁾. Lanthanum oxide promotion of alumina was reported to be beneficial for improved production of products with higher boiling points⁽⁸⁾, and zirconia modification of alumina supports was carried out to decrease the interaction of cobalt with alumina⁽⁹⁾. All these modified supports were either used for fixed bed cobalt based Fischer-Tropsch catalysts or they were used for slurry bed cobalt catalysts, but not tested under realistic Fischer-Tropsch synthesis conditions in large scale slurry bed reactors.

This paper will deal with the modification of alumina and titania supports for cobalt based slurry phase Fischer-Tropsch catalysts to ensure the successful operation of slurry phase bubble column reactors on commercial scale.

EXPERIMENTAL

Two alumina-supported catalysts were prepared by means of a two-step slurry phase impregnation method, using an aqueous cobalt nitrate solution⁽¹⁰⁻¹³⁾. After impregnation and vacuum drying, the dried intermediate was calcined in air at 250°C for 6 hours. The calcined catalyst was reduced at 380°C in pure hydrogen using a heating rate of 1°C/min. Platinum was incorporated as a reduction promoter. The catalyst compositions were: catalyst A: 30gCo/0.075gPt/100gAl₂O₃, and catalyst B: 30gCo/0.075gPt/1.5gSi/100gAl₂O₃.

Silicon support modification was performed, prior to the catalyst preparation, in the case of catalyst B, by means of a non-aqueous slurry phase impregnation step using Tetra Ethoxy Ortho Silicate (TEOS) as precursor. TEOS dissolved in dry ethanol was used as impregnation solution. After impregnation, the slurry was dried at 60°C under vacuum for 6 hours. The dried modified support was calcined in air at 500°C for 2 hours⁽¹¹⁾.

The dissolution behaviour of the supports were characterised by monitoring the conductivity of a support in a model acidic aqueous slurry. The support was added to an acidic aqueous medium with a pH of 2 at 25°C. The conductivity was measured continuously for 30 hours under stirring at 25°C. As the dissolution of the support will increase the pH, continuous and automatic titration with a 10% HNO₃ solution was required to fix the pH at 2.0 during the 30 hours dissolution experiment.

Laboratory Fischer-Tropsch synthesis tests were performed in a slurry phase CSTR. The pre-reduced catalyst (20-30 g) was suspended in ca 300 ml molten Fischer-Tropsch wax. Realistic Fischer-Tropsch conditions were employed, i.e.: 220 °C; 20 bar; commercial syngas feed: 50 vol% H₂, 25 vol% CO and 25 vol% inerts; syngas conversion levels in excess of 50%. Use was made of the ampoule-sampling-technique as the selected on-line synthesis performance monitoring method⁽¹⁴⁾.

Larger scale Fischer-Tropsch synthesis runs were performed in a pilot plant slug-flow slurry reactor using 3-8kg catalyst as well as in a slurry phase bubble column demonstration unit using 500-1500kg catalyst. The reaction conditions were similar to those in the laboratory CSTR runs. The reactor wax production varied between 5 and 30kg per day for the pilot plant runs and up to 60bbl/day for the demonstration unit. On-line catalyst samples were taken for particle size distribution measurements and SEM analyses.

RESULTS AND DISCUSSION

The intrinsic Fischer-Tropsch activity as well as the selectivity of the supported cobalt catalysts studied in this paper (i.e. catalyst A and B) is such that these catalysts are economically viable for the GTL process (table 1). Low level silica modification of alumina supports did neither influence the acidity of the support and nor the Fischer-Tropsch synthesis behaviour of the catalysts (table 1).

Table 1: Fischer-Tropsch synthesis data for catalysts A and B, as tested under realistic reactor conditions (refer: Experimental).

	Catalyst A 30gCo/0.075gPt/100gAl ₂ O ₃	Catalyst B 30gCo/0.075gPt/1.5gSi/100gAl ₂ O ₃
Run number	175\$	98F
Time on line (h)	15	20
Syngas conversion (%)	75	76
FT reaction rate (mol/s)	6.8×10^{-6}	7.1×10^{-6}
Productivity (gHC/gcat/h)	0.34	0.36
CH ₄ selectivity (%C-atom)	4	7

Important for slurry phase Fischer-Tropsch catalysts is the mechanical strength, as catalyst break-up will result in (i) loss of catalyst, (ii) difficulties with the catalyst/wax separation, and (iii) undesired contamination of the wax product with cobalt. During extensive Fischer-Tropsch synthesis runs in both pilot plant scale reactors as well as the demonstration unit, the mechanical integrity of the catalyst was monitored by means of Particle Size Distribution (PSD) measurements as well as SEM analyses on extracted catalyst samples. The average particle size did not change even after 8 months of operation, which strongly indicates that catalyst break-up did not occur. This was in agreement with SEM analyses (figure 1).

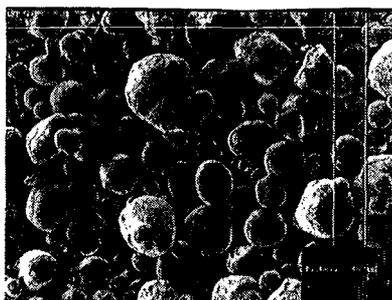


Figure 1: SEM image of alumina-supported cobalt catalyst A after Fischer-Tropsch synthesis test run in the demonstration unit.

The unmodified alumina-supported cobalt catalyst (catalyst A) was tested in the pilot plant slug-flow reactor under realistic Fischer-Tropsch conditions. The produced wax was secondary filtered over a 2 micron filter and analysed for cobalt content. Initially, clean white wax was produced without any cobalt contaminants present. After about 10 days on stream, however, the secondary filtered wax started discolouring and high levels of cobalt containing particulates were

observed (figure 2). This is very undesired, as cobalt contamination of wax may poison the downstream hydroprocessing catalysts. These cobalt containing particulates did not originate from catalyst break up.

The presence of high levels of cobalt-containing particulates in secondary filtered wax was correlated with the dissolution behaviour of the alumina support during the slurry phase impregnation steps of the catalyst preparation procedure. It was reported earlier that alumina supports could (partially) dissolve in aqueous solutions⁽¹⁵⁾, even at pH values close to the isoelectric point⁽¹⁶⁾. Partial dissolution of the alumina used during the preparation of catalysts A and B was experimentally confirmed during the aforesaid model dissolution test (figure 3).

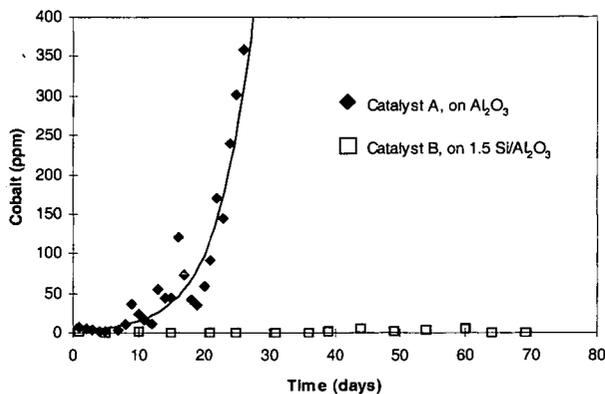


Figure 2: Cobalt content in secondary filtered wax during pilot plant scale Fischer-Tropsch synthesis runs, using catalyst A: 30gCo/0.075gPt/100gAl₂O₃ (run F102), and catalyst B: 30gCo/0.075gPt/1.5gSi/100gAl₂O₃ (run F117).

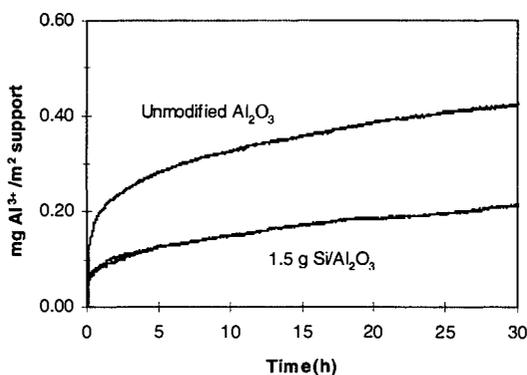
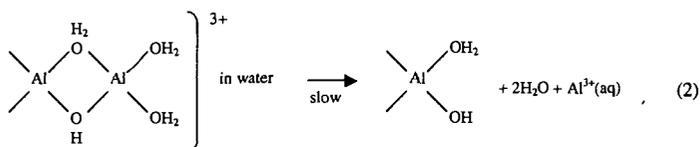
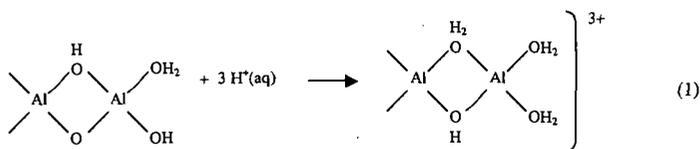


Figure 3: The dissolution behaviour of an alumina support (used to prepare catalyst A) as well as a silica modified alumina support (used to prepare catalyst B).

It can be seen that rapid dissolution occurs within the first hour, followed by a more gradual dissolution that proceeds continuously (i.e. about 30 hours). A mechanism of dissolution is reported in literature⁽¹⁵⁾ (equations 1 and 2). During catalyst preparation, the dissolved aluminium ions can precipitate either as boehmite or in combination with cobalt ions as a cobalt aluminium hydroxalcalcite⁽¹⁷⁾, producing a physically amorphous layer uniformly covering the surface of the bulk support material⁽¹⁶⁾. It is hypothesised that the presence of this amorphous layer, prior to the actual impregnation process, weakens the anchoring of the eventually catalytically active cobalt metal. The cobalt metal crystallites that are weakly anchored to the

alumina support can dislodge and be washed out during slurry phase Fischer-Tropsch synthesis, a process that is enhanced by the increased turbulence associated with large-scale reactors.



To prevent the dissolution of the alumina support during the slurry phase impregnation step of the catalyst preparation procedure, the alumina support was modified with silicon, using Tetra Ethoxy Ortho Silicate (TEOS) as precursor. The support modification step was performed as a slurry impregnation using TEOS dissolved in dry ethanol as impregnation solution. During support modification, TEOS reacts with the hydroxyl groups of the alumina surface. The three remaining ethoxy groups were thermally decomposed during a calcination step at 500°C in air. The maximum amount of silicon that can react with the alumina support depends on the surface area of the alumina support as well as the surface hydroxyl concentration. The dissolution behaviour of the silica-modified alumina was measured (figure 3), and found to be significantly inhibited.

A cobalt catalyst was prepared (catalyst B: 30gCo/0.075gPu/1.5gSi/100gAl₂O₃) on the silicon modified alumina support, using the standard aqueous slurry phase impregnation method. Catalyst B was tested in the pilot plant scale slurry reactor as well as in the semi-commercial demonstration unit under realistic Fischer-Tropsch synthesis conditions during an 8 month continuous test run. Catalyst break-up was not observed during this run, as measured by PSD and SEM analyses. Clean white wax was produced during this entire run, and the cobalt content of the secondary filtered wax remained very low (figure 2). This proved that silicon support modification successfully prevented the generation of cobalt containing ultrafines during large scale Fischer-Tropsch synthesis runs. From table 1, it can be concluded that silicon modification of alumina did not have any substantial effect on the Fischer-Tropsch synthesis performance of the catalyst.

Silicon modification of alumina supports is not only restricted to the utilisation of TEOS. Other silicon precursors can be used, e.g. Tetra Methoxy Ortho Silicate (TMOS). Besides silicon, successful modification of alumina can also be effected with other compounds.

The dissolution of titania supports was also investigated⁽¹¹⁾. Titania also (partially) dissolves in aqueous solutions and silicon modification, using TEOS, effectively inhibited support dissolution.

CONCLUSIONS

It was demonstrated that the production of clean white wax (i.e. free of any cobalt contamination) during large scale slurry phase Fischer-Tropsch synthesis runs, was successfully effected with cobalt catalysts that were prepared on modified supports (i.e. supports displaying inhibited dissolution behaviour in aqueous environments). As an example, the silicon modification of alumina supports was discussed in detail.

REFERENCES

- (1) B. Eisberg, R.A. Fiato, *Studies in Surface Science and Catalysis*, Vol. 119 (1998) 961.
- (2) M.M.G. Senden, A.D. Punt, A. Hoek, *Studies in Surface Science and Catalysis*, Vol. 119 (1998) 943.
- (3) J.W.A. de Swart, R. Krishna, and S.T. Sie, *Studies in Surface Science and Catalysis*, Vol. 107 (1997) 213.
- (4) P.J. van Berge, and R.C. Everson, *Studies in Surface Science and Catalysis*, Vol. 107 (1997) 207.
- (5) A. Hoek, J.K. Minderhout, and P.W. Lednor, EP 110449, 1983.
- (6) C.H. Mauldin, S.M. Davis, and K.B. Arcuri, US 4,663,305, 1987.

- (7) C.H. Mauldin, and K.L. Riley, US 4,992,406, 1991.
- (8) S. Eri, J.G. Goodwin Jr., G. Marcelin, and T. Riis, US 4,880,763, 1989.
- (9) F. Rohr, A. Holmen, and E.A. Blekkan, proceedings of Syngas Conversion to Fuels and Chemicals symposium, 217th ACS national meeting, Anaheim, March 21-25, 1999.
- (10) R.L. Espinoza, J.L. Visagie, P.J. van Berge, and F.H. Bolder, US 5,733,839, 1998.
- (11) P.J. van Berge, J. van de Loosdrecht, E.A. Caricato, and S. Barradas, WO 99/42214, 1999.
- (12) P.J. van Berge, J. van de Loosdrecht, E.A. Caricato, S. Barradas, and B.H. Sigwebela, WO 00/20116, 2000.
- (13) P.J. van Berge, J. van de Loosdrecht, J.L. Visagie, US 09/168604, 1999.
- (14) Schultz, H., and Geertsema, A., *Erdöl and Kohle*, 30 (1969) 193.
- (15) G. Furrer, and W. Stumm, *Geochim. Cosmochim. Acta*, 50 (1986) 1847.
- (16) J.-B. d'Espinose de la Caillerie, and O. Clause, *Studies in Surface Science and Catalysis*, Vol. 101 (part B) (1996) 1321.
- (17) J.-B. d'Espinose de la Caillerie, C. Bobin, B. Rebours, and O. Clause, *Prep. of Cat. VI* (eds G. Poncelet et al, Elsevier Science B.V.) (1995) 169.

FISCHER-TROPSCH DIESEL FUEL PREPARATION AND TESTING

Paul F. Schubert, Robert Freerks, H. Lynn Thomlinson, Branch Russell

Syntroleum Corporation

1350 S. Boulder, Suite 1100, Tulsa, OK

KEYWORDS: FISCHER-TROPSCH, SYNTROLEUM, SYNTHETIC DIESEL FUEL

ABSTRACT

Synthetic diesel fuel which is sulfur and aromatic free has been produced using the Syntroleum Process. The main difference between the Syntroleum Process and traditional Fischer-Tropsch (FT) processes is the use of a nitrogen diluted syngas stream to the FT reactors. This Syngas stream is produced in an air-blown autothermal reformer using natural gas. In the FT reactors, a cobalt based catalyst is used to convert the syngas to paraffinic oils and waxes. These products are then separated, saturated, and cracked to produce the desired products.

The emissions from two diesel fuels, this FT diesel and a conventional low sulfur diesel were measured according to the Code of Federal Regulations (CFR) Title 40 specifications in a Cummins 5.9 liter heavy duty diesel engine and a 1.9 liter light duty diesel engine. The FT diesel showed substantially reduced emissions compared to the other diesel fuels.

INTRODUCTION

The Syntroleum process is a modification of the Fischer-Tropsch (FT) process originated¹ by Franz Fischer and Hans Tropsch in 1923 to convert coal to fuels and lubricants. This process was practiced in Germany¹, and Japan² during the Second World War, and has been practiced in South Africa since it was forced to be essentially energy self-sufficient during its apartheid era. Obviously, the drivers for these uses of the Fischer-Tropsch process were not open market economics. The first commercial development of the FT process involved fixed bed reactors using cobalt based catalysts³. Nine commercial FT plants were completed in Germany between 1935 and 1939. However during this same period research continued targeted at developing higher process efficiency and cost savings with three phase reactor systems⁴⁻⁶.

The earliest work on three phase, liquid circulating reactor systems was conducted by Dufschmidt⁷ for I. G. Farbenindustrie beginning in 1934. Initially this work involved circulating a liquid through a fixed bed of catalyst⁸⁻¹⁰, however, a system with an expanded bed was developed and patented¹¹. This work was largely interrupted by the war. However, it served as the basis for FT slurry reactor development after the war². This early work taught novel features included in many current slurry type FT reactors, including external circulation loops, and inclusion of pumps and separators into those circulation loops⁷⁻¹¹.

The primary steps in the process are generation of synthesis gas (CO and H₂) from a hydrocarbon feed, conversion of the synthesis gas to hydrocarbons, and then refining of the desired products. The initial commercial plants all used coal as the hydrocarbon source, and cobalt catalysts in the FT reactors. The main fuel produced from the process was diesel, because of the excellent cetane number obtained from the highly paraffinic products.

Broader application of Fischer-Tropsch technology has awaited substantial improvement in process economics. In addition, the continued discovery of vast quantities of natural gas around the globe has reduced the emphasis on generating synthetic fuels from coal and "bottom-of-the-barrel" hydrocarbon sources, and emphasized the importance of gas-to-liquid (GTL) processes. It is likely that there are economically viable applications for a number of different hydrocarbon to synthetic fuels processes.

The Syntroleum Process (Figure 1) is designed to reduce costs in critical, capital intensive areas while providing excellent product yields. The critical cost reduction areas are syngas generation, Fischer-Tropsch reactor design, and process integration. In conventional FT processes, the syngas generation step can require 50% to 60% of the total capital investment for the plant. An air-blown process can reduce this to the 25% range because of a combination of the elimination of the air separation unit, use of a small autothermal reformer (ATR), and using a gas turbine to provide the air compression for the air fed to the ATR.

Syngas generation from natural gas has traditionally been done using either steam methane reforming (SMR) or partial oxidation (POX). Both of these require substantially pure oxygen streams from an oxygen plant, which adds significantly to the size and capital cost of the plant. The Syntroleum Process utilizes a proprietary catalytic ATR to convert natural gas to syngas using air as the oxygen source. The reactions occurring in the ATR are shown below.



Small amounts of steam are added to the system to suppress the formation of carbon. Because the system is in heat balance, no heat transfer system is required, and the reactor is much more compact than is possible with SMR or POX. The H₂ to CO ratio of the resulting syngas is close to the approximately 2:1 ratio in the hydrocarbon products from the FT process (4).



The Fischer-Tropsch products are highly paraffinic, but also contain low levels of primary olefins and alcohols. If desired, these can be saturated to produce an essentially totally paraffinic material. Generally, economics are most favored by production of the long chain hydrocarbons which are cracked to the desired products rather than maximizing the amount of product in the fuel range produced directly by the FT process. This is because the latter approach tends to produce undesirably high levels of low value C₁ to C₅ hydrocarbons. Cracking to fuel range products is done using typical refining methods. However, the conditions needed to convert this synthetic crude into products are milder than those required for traditional natural crudes, which generally contain substantial amounts of unsaturated and heterocyclic species.

Because syngas produced in this air-blown process is diluted with nitrogen relative to an oxygen-blown system, there is some increase in the size of the downstream equipment associated with gas processing. However, economic evaluations show that elimination of the entire oxygen plant can be a significantly greater savings than the costs associated with nitrogen in the synthesis gas. An air-blown system allows the use of a turbine for the air compressor thereby enhancing thermal integration as well as allowing an inexpensive method for producing electric power for resale and/or driving other processes. Furthermore, the dilute light hydrocarbon stream that typically would be flared can be used as fuel for the turbine. The air-blown system offers greater flexibility in achieving higher carbon efficiencies and energy integration over a broad range of natural gas compositions. The economic incentives for the air blown system are evident at all plant throughputs and are greatest when evaluating small to mid size plants (< 50,000 bpd).

Cost savings in Fischer Tropsch reactor design are accomplished with a moving bed system, where catalyst microspheres are suspended by the gas in circulating liquid. This system provides more effective multiphase mixing thereby enhancing catalyst productivity and selectivity while minimizing the required heat transfer area. This gives a reactor that is more efficient than tube and shell reactors that have previously been commercialized⁶. Our economic evaluations strongly indicate that the Syntroleum moving bed system with our proprietary cobalt based FT catalyst provides significant

cost savings over the three phase bubble columns previously described in the technical literature^{12, 13}. The improved economic performance of the moving bed system is due to the integration of catalyst performance with reactor design. The catalyst possesses high activity, attrition resistance, excellent hydrodynamic properties and is readily separated from the hydrocarbon products. Additionally, reaction kinetics have been tailored to give the preferred selectivity in the nitrogen-diluted environment.

PILOT PLANT DESIGN AND PERFORMANCE

The ATR and moving bed FTR combination for the Syntroleum process were demonstrated using a pilot plant constructed at ARCO's Cherry Point, Washington refinery. The individual process units were modular in design, constructed in Tulsa, OK, and shipped to the site in Washington state, where they were erected. The objectives of the Cherry Point pilot plant are to confirm the commercial design basis, identify optimum operating conditions for different natural gas feed compositions, and to generate the data necessary to validate Syntroleum process models. The unit was sized to reflect the hydrodynamics and multi-phase flow processes anticipated in commercial operations. Instrumentation was installed to monitor all critical axial and radial variables associated with phase holdups, interphase transport and recirculation rates. Process conditions were varied over a broad range to determine optimal conditions for the production of fuels and/or specialty products. The pilot plant was initially designed with a nameplate capacity of 70 barrels of FT product per day. Higher catalyst productivities and selectivities have been achieved due to better than expected catalyst performance in the turbulent mixing regime associated with commercial sized moving bed reactors. The first portion of the plant started operation in April 1999, and has achieved in excess of 6000 hours of ATR operation and 4500 hours of FT operation. We have successfully demonstrated ATR operation without significant carbon formation, and the FT unit has met or exceeded all design criteria associated with multiphase mass and heats transfer as well as with hydrodynamic and phase partitioning and separation parameters.

The autothermal reformer was designed to generate sufficient syngas to support 70 barrel per day FT product yields as well as allow for production above that nameplate capacity. The ranges of operating parameters being studied involve natural gas formulations containing significant quantities of C₂⁺ hydrocarbons and CO₂. After determining critical residence times and reaction rates, the unit has given excellent performance in terms of carbon conversion efficiency to CO and operating stability.

The catalyst used in the pilot plant is a powder composed of cobalt on alumina-based microspheres. This material was produced in a full commercial- sized batch in commercial manufacturing equipment. Catalyst development involved starting with preparations of gram quantities at the laboratory scale, moving to pound quantity preparation procedures in order to define commercial manufacturing procedures. The final catalyst used in the pilot plant is from a 25,000 lb lot produced using low cost commercial manufacturing equipment.

In order for the catalyst to function effectively in the process, it must first be activated (reduced), because it is cobalt metal that is the actual catalytic species, while cobalt oxide is the form produced during manufacturing. Conditions and procedures were developed and followed at commercial scale, and resulted in catalyst in service in the reactor that met or exceeded the performance requirements in terms of activity and selectivity.

As previously mentioned, catalyst attrition and catalyst-product separation are some of the critical issues to be determined in the unit. After over 4500 hours of operation under widely varying conditions, there is no evidence of significant attrition within the unit. The attrition resistance of the catalyst has been monitored using particle size analysis, the settling characteristics of the particles, and the filter/separator performance. In addition, catalyst life and activity maintenance have met or exceeded expectations.

FUELS PREPARATION AND ENGINE TESTING

Syntroleum has produced a number of fuel range materials by refining Fischer-Tropsch wax, including synthetic analogs of gasoline, JP-5, JP-8, and diesel fuel. Synthetic diesel

is currently receiving considerable attention because diesel engine emissions are under regulatory scrutiny. Syntroleum S-2 fuel is a sulfur free, aromatics free fuel with an exceptionally high cetane index. Table 1 shows S-2's properties compared to typical properties of low emissions EPA D-2 Diesel.

Unmodified Heavy Duty Diesel Engines. Numerous studies have evaluated engine emissions from conventional, unmodified diesel engines using a variety of FT fuels. Engine tests with three S-2-like fuels consistently show decreases of hydrocarbons, carbon monoxide, nitrous oxides and particulate matter emissions¹⁴. We have confirmed these results in work at Southwest Research Institute comparing Syntroleum S-2 with EPA #2 using an unmodified heavy duty 5.9L Cummins engine on a test stand (Table 2) and an unmodified heavy-light duty diesel vehicle with the same engine on a chassis dynamometer (Table 3)¹⁵. None of these tests included engine timing modifications which could have taken advantage of the significantly higher cetane of Syntroleum S-2. In both tests, the Syntroleum S-2 significantly reduced emissions from the 5.9L Cummins engine. The 40% to 45% reduction in particulate emissions using the Syntroleum S-2 is especially notable.

Although our testing did not examine emission reductions from aromatic-containing FT fuels, previous engine tests¹⁶ have shown that those fuels do not achieve the same level of improvement achieved from the more hydrogen saturated FT fuels in this study.

Table 1
Properties of US EPA Diesel and Syntroleum S-2

Property	Test Method	Units	US EPA D-2 Diesel	Syntroleum S-2 Fuel
Specific Gravity	ASTM D-1298	g/cc	0.846	0.771
API, Max	ASTM D-1298	deg	35.9	52
Flash Point	ASTM D-93	deg F	157	148
Cloud Point	ASTM D-2500	deg F	32	<0
Color	ASTM D-1500	Inspection	-	<0.5
Sulfur	ASTM D-2622	wt. %	<0.05	nd
Aromatics	ASTM D-1319	vol %	30	nd
Olefins	ASTM D-1319	vol %	1	nd
Saturates	ASTM D-1319	vol %	69	>99
Cetane Number, min	ASTM D-613	-	45	>74

Table 2
Emissions from a 5.9 liter Cummins B engine on a test stand
Average results from 2 runs

Test (g/bhp-hr)	HC	CO	NOx	Particulates
EPA # 2 Diesel	0.10	1.30	4.00	0.10
Syntroleum S-2	0.10	0.80	3.20	0.06
% reduction for S-2	0	38	20	40

Table 3
Emissions from a Heavy light-duty truck (2000 Dodge Ram 2500) with a 5.9 liter
Cummins B engine on a chassis dynamometer using the US06 test protocol
Average results from 2 runs

Test (g/bhp-hr)	HC	CO	NOx	Particulates
EPA # 2 Diesel	0.19	0.70	5.24	0.11
Syntroleum S-2	0.16	0.50	4.50	0.06
% reduction for S-2	16	29	14	45

Light Duty Diesel Engines. Emissions evaluation of Syntroleum S-2 and EPA #2 were conducted on a 1.9L Volkswagen diesel engine in a 1999 Golf GL TDI (Table 4). This is a current production model, U.S. market passenger car, and is equipped with a catalytic converter. The hydrocarbon, CO, and NOx emissions from both fuels were equivalent within the experimental error of the test. However, the particulate emissions were dramatically lower from the Syntroleum S-2 fuel.

Table 4
Emissions from a light-duty passenger car (1999 Volkswagen Golf) with a 1.9 liter
engine on a chassis dynamometer using the US06 test protocol
Average results from 2 runs

Test (g/bhp-hr)	Particulates
EPA # 2 Diesel	0.42
Syntroleum S-2	0.05
% reduction for S-2	88

CONCLUSIONS

Syntroleum and ARCO have successfully demonstrated a GTL conversion process that utilizes an air blown autothermal reformer and moving bed Fischer-Tropsch reactor. The process is robust, and is ready for scale-up to commercial scale fuels production plants. Economic evaluations of such commercial plants show that production of synthetic fuels is now economically competitive with conventional fuels.

Synthetic S-2 fuel produced substantially lower emissions than EPA diesel under all of the conditions tested. This S-2 fuel has substantial advantages compared to other alternative fuels because, in addition to being environmentally acceptable, it is backward compatible with current vehicles, and is compatible with the existing fuels delivery infrastructure. Syntroleum S-2 also exceeds engine manufacturers desires for ultra-low sulfur fuel which is needed to allow use of NOx absorption catalyst in future vehicle designs.

The need for backward compatibility with little or no modification to the engine is important because owners of current vehicles will not generally volunteer to make their vehicles obsolete because the actions of non-market forces. Furthermore, since it will take considerable time from the introduction of any new engines until they represent a majority of the vehicles on the road, substantial advantage in achieving environmental goals may be made using the existing inventory of vehicles.

The need for compatibility with the existing extensive fuels delivery infrastructure is important for several reasons. It allows consumers to maintain current behavior

patterns while still adopting new technology. In addition, it allows the many fuels distributors to become partners instead of competitors in technology introduction. This eliminates the need to for the new engine and new fuels suppliers to invest billions of dollars in a delivery system (service stations, etc.) and allows existing fuels marketers to pursue their own marketing strategies. The synthetic GTL fuels facilitate this approach because they are compositionally compatible with the existing tanks and pumps in service stations and fueling facilities, and may require little more than clean out of the tanks.

ACKNOWLEDGEMENTS

The authors would like to thank Jeff Bigger, Gary Beer, and Jim Leahy of ARCO, Robert Fannick of Southwest Research Institute and Ray Huang, Cemal Ercan, and Paul Kennedy of Syntroleum for their contributions.

REFERENCES

1. Storch, H. R., Golumbic, N., Anderson, R. B. *The Fischer-Tropsch and Related Synthesis*, 1951, John Wiley & Sons, New York, 1.
2. Stranges, A. N. *Annals of Science*, 1993, 50, 229-265.
3. Henrici-Olive, G. and Olive, S. *Angew Chem (Eng. Ed.)*, 1976, 15, 136.
4. Stranges, A. N. *Annals of Science*, 1997, 54, 29-68.
5. Kolbel, H. and Ralek, M. *Cat Rev-Sci Eng.*, 1980, 21(2), 225.
6. Van Vuuren, D.S. CSIR Report OENG 432, 1982, Pretoria, South Africa.
7. Benson, H. E.; Field, J. H.; Bienstock, D.; Storch, H. H. *Ind. and Eng. Chem.*, 1954, 46, 2278-2285.
8. Duftschmidt, F.; Linckh, E.; Winkler, F. U.S. Patent 2,159,077, 1939.
9. Duftschmidt, F.; Linckh, E.; Winkler, F. U.S. Patent 2,207,581, 1940.
10. Duftschmidt, F.; Linckh, E.; Winkler, F. U.S. Patent 2,318,602, 1942.
11. Duftschmidt, F.; Linckh, E.; Winkler, F. U.S. Patent 2,287,092, 1942.
12. Oukaci, R., Singleton, A.H. et. al., *Applied Catalysis*, 1999, 186, 129-144.
13. Jager, B. AICHE 1997 Spring Nat. Meeting (Houston 3/9-13/97), 1997, N.27c 9p.
14. Ryan, T. W. and Montalvo, D. A.: Emissions Performance of Fischer-Tropsch Fuels; 1997 AIChE Spring Meeting, Houston, TX; March 9-13, 1997 (unpublished).
15. Syntroleum Corporation emissions and toxicological study comparing Syntroleum S-2 CI fuel with commercially available diesel fuels; 2000 (unpublished).
16. Thomas D. Durbin, John R. Collins, Joseph M. Norbeck, Matthew R. Smith; Evaluation of the Effects of Alternative Diesel Fuel Formulations on Exhaust Emissions rates and Reactivity; University of California (Riverside); April, 1999.

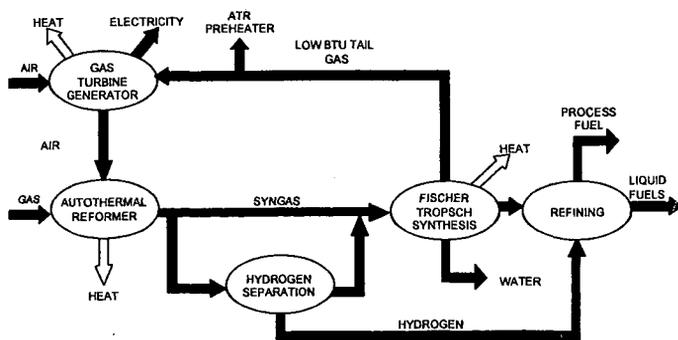


Figure 1. Process schematic for fuels production via the Syntroleum Process.

A TWO-STEP CONVERSION OF SYNGAS VIA DIMETHYL ETHER

Chang-jun Liu, Tao Jiang, and Gen-hui Xu

State Key Laboratory of C1 Chemical Technology,
Tianjin University, Tianjin 300072, China

ABSTRACT In this presentation, we present some of our experimental results of a two-step conversion of syngas into more valuable chemicals or high performance fuel additives. In the first step, dimethyl ether (DME) is formed from syngas. With the second step, the formed DME is applied for the further synthesis via an "electronic" catalysis. The conversion of DME by this way can reach a high-energy yield. The products of such conversion include oxygenates and/or alkanes. The two-step conversion of syngas via DME could lead a new synthesis from syngas. Especially, the conversion of DME in the second step can be operated at ambient condition. The synthesis reported here could lead to a new application of DME.

KEYWORDS: DME, electronic catalysis, plasma

INTRODUCTION

The formation of Dimethyl Ether (DME) from syngas conversion has recently attracted more and more attention. DME is becoming a major product, especially for the gas reserves at remote sites or coalbed methane. It is important for us to seek for more applications of DME. DME is a useful chemical intermediate for the synthesis of many important chemicals, including dimethyl sulfate, lower olefins and methyl acetate.^[1-3] DME has also been proposed as an aerosol propellant to replace chlorofluoro carbons, which were found to have destroying effect on the ozonosphere.^[4] In addition, DME is a promising alternative fuel to diesel.^[5] Brown *et al.* had a detailed discussion on the possible fuels or fuel precursors from DME^[6]. They also described some possible methodologies for the use chemically of DME, including oxidative coupling, vinylation/hydrogenation, oxidative coupling (with MTBE) and carbonylation. Compared to the utilization of DME as fuel, propellant and so on, the use of DME as a chemical intermediate is particularly attractive and needs to be investigated extensively. Especially, DME has been recognized as an alternative to methanol as a chemical building block.

Here we report a conversion of DME in a dielectric-barrier discharge (DBD) plasma reactor at ambient condition, as a two-step of conversion of syngas. The DBD used in these experiments is a high pressure, non-equilibrium discharge which is initiated when alternating voltages of sufficiently high amplitudes are applied between two electrodes separated by a non-conducting medium (dielectric barrier) in addition to a gas space. The frequency of the ac electric field can vary over a wide range from line frequency to several MHz. Glass, quartz or ceramics can be used as dielectric materials. When the amplitude of the applied ac electric field reaches a critical value, breakdown is initiated in the gas and current flows through the gas space from one electrode to the other. Once breakdown is initiated at any location within the discharge gap, charge accumulates on the dielectric resulting in an opposite electric field. This opposite electric field locally reduces the external electric field in the gap and interrupts the current flow within a few nanoseconds. By this mechanism individual current filaments called microdischarges are formed. Their duration depends on the pressure and the properties of the gases involved and the dielectrics used. A large number of such microdischarges will be generated when a sufficiently high ac voltage is applied. The principal advantages of the DBD are that non-equilibrium plasma conditions can be established at atmospheric pressure and that the entire electrode area is effectively used for discharge reactions. The unusual "electronic" catalysis of DBD for the conversion of DME at ambient condition has been confirmed in this investigation. This could lead to a two-step utilization of syngas. In the first step, dimethyl ether (DME) is formed from syngas. With the second step, the formed DME is applied for the further synthesis via such electronic catalysis. Due to the limited space, we only focus on the second step in this paper and leave the first step for the future discussions.

EXPERIMENTAL

Figure 1 illustrates the reactor system. The gas flow (pure DME) is subjected to the action of the DBD in an annular gap formed between an outer stainless steel tube maintained at constant temperature and an inner quartz tube. The radial width of the discharge space was 1 mm, its length 50mm ~ 150 mm. This reactor system is very similar to the DBD reactor for methane conversion described elsewhere.^[7,8] All the experiments were conducted at atmospheric pressure. The feed and exhaust gases were analyzed by a gas chromatograph (HP 4890) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The exhaust gas from the reactor was first introduced into a condenser to separate the condensable product from the gas. A high voltage generator working at about 25 kHz applies the power. The power can be varied by

adjusting the voltage amplitude, which causes a slight change of frequency. The voltage and current measurements were conducted using a high voltage probe (Tektronix P6015) and a current probe (Tektronix CT-2) with a digital oscilloscope (Tektronix TDS 210).

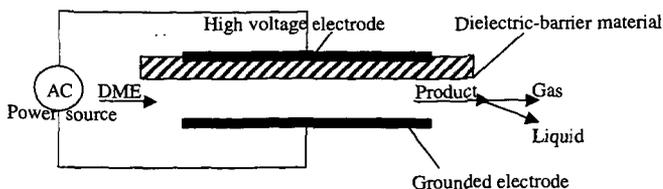
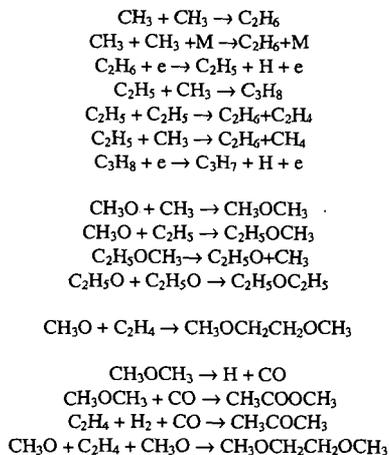


Figure 1. Schematically representative of the DBD reactor system

RESULTS AND DISCUSSION

A surprising high DME conversion has been achieved in the present reactor design. The C-O bond breakdown in a DME molecule does not require a high energy and this leads to the high DME conversion. The bond strength of C-O in DME molecule is only 81 kcal/mol at 298 K. CH_3 and CH_3O radicals can be easily obtained within DME plasmas. Hydrocarbons and ethers are expected to be formed from chain reactions initiated by CH_3 and CH_3O radicals.

Table I shows the composition of gaseous products observed at 60°C and different gas flowrates. The gaseous product is a mixture of hydrocarbons, ethers, H_2 and CO. Methane, ethane, propane, methyl ethyl ether, acetone, methyl isopropyl ether, ethyl ether, 1,2-dimethoxy ethane and dimethoxy methane were detected. Most of methoxy-containing hydrocarbons have been detected in the liquid phase. The composition of gaseous products changed greatly with the variation of gas flowrate. Experimental results showed that most of gaseous products were H_2 and C_1 - C_3 alkanes. The amount of oxygenates was very little in the gaseous phase but abundant in liquid product. Table I also shows the composition of lower alkanes in the gaseous phase increases with the decreasing flowrates. This is a typical characteristic of chain reactions. A mechanism has been presented to explain the observed phenomena. CH_3 and CH_3O radicals are first generated in the DBDs via electronic dissociation or other plasma reactions. Some of chain reactions have been proposed as the following to explain the production of part of hydrocarbons:



In addition, the experiment has shown a formation of some paraformaldehyde, that could be induced from the reaction: $\text{CH}_3\text{O} + \text{H} \rightarrow \text{HCHO} + \text{H}_2$.

The DBD conversion of DME leads to a selective production of liquid product, that is a mixture of various ethers. Figure 2 shows the results of DME conversion and the ratio of liquid production to the total production. It is clear that higher DME conversion accompanies with more liquid products produced. More than 93% of the product is liquid at a gas flowrate of 20

ml/min. This suggests that DBDs could easily convert DME to liquid chemicals at ambient conditions. A more surprising phenomenon with this DBD DME conversion is that no carbon deposit has been observed on the dielectric, while a serious carbon deposit has been formed during plasma conversion of methane or other lower alkanes^[8,9,10]. It has been considered that some aerosols would have been formed during DBD conversion of DME. It is the aerosol inhibits the formation of carbon deposit. Further investigations are being conducted.

Table 1: Effect of gas flow rate on the composition of gas product

Composition / mol%	Gas flow rate / ml/min			
	60	45	30	20
H ₂	9.15	10.83	20.49	31.26
CO	4.29	4.20	8.56	17.70
CH ₄	4.46	5.54	9.82	12.50
C ₂ H ₆	2.66	3.19	5.36	6.02
C ₃ H ₈	0.22	0.28	0.59	1.22
DME	76.48	72.87	50.63	26.71
C ₂ H ₅ O CH ₃	1.32	1.51	2.37	1.83
CH ₃ CO CH ₃	0.04	0.05	0.10	0.20
C ₂ H ₅ (OCH ₃)CH ₃	0.04	0.04	0.09	0.10
C ₂ H ₅ O C ₂ H ₅	0.02	0.03	0.05	0.07
CH ₃ O CH ₂ OCH ₃	0.19	0.22	0.32	0.23
CH ₃ O CH ₂ CH ₂ OCH ₃	0.14	0.15	0.14	0.07
others	1.00	1.09	1.49	2.10

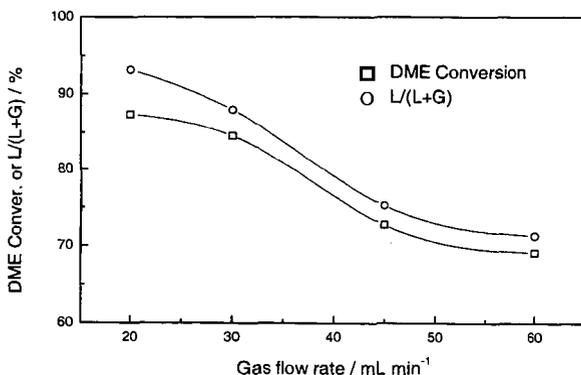
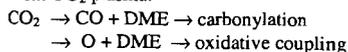


Figure 2. Effect of gas flow rate on experimental results

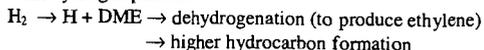
CONCLUSIONS

The potential of plasma conversion of DME has been demonstrated in this work. The present product from this DME conversion can be used as the high performance fuel additive. Moreover, further investigation is being conducted to produce selectively other valuable hydrocarbons. Some other potential pathways for the DME conversion via electronic catalysis are as the following:

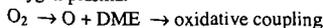
With CO₂ plasma:



With hydrogen plasma:



With oxygen plasma:



With lower alkane (methane, ethane or propane) plasma:

lower alkane plasma + DME \rightarrow high performance fuels or fuel precursors

With steam plasma:

steam plasma + DME \rightarrow special oxygenated hydrocarbons

With syngas plasma:

syngas plasma + DME \rightarrow carbonylation and others

These pathways open more doors to produce series of valuable chemicals. Especially, one of advantages of such electronic catalysis of DME plasma is her high efficiency that is able to convert DME into some special chemicals, that may be difficult to be produced using the conventional technologies. Since the plasma is a complex reactive system that contains a mixture of electrons, ions, radicals, photons, and so on. The control of plasma reactions needs special skills so that a selective conversion of DME can be achieved. We have confirmed that DBD can perform as excellent electronic catalyst for DME conversion. There are some other plasma phenomena, like corona discharge, arc discharge, gliding arc discharge and microwave discharge, that could also be useful for the DME conversion. To compare with the conventional catalysis, the controlling parameters of electronic catalysis are electron temperature, electron density, radical energy and density and so on. The gas temperature and pressure have a little influence on electronic catalysis. More fundamental investigations are necessary to understand the mechanisms. The feasibility of the two-step conversion of syngas via DME using electronic catalysis is being confirmed in our further investigations.

ACKNOWLEDGEMENT

The support from The Research Fund for the Doctoral Program of Higher Education in China is very appreciated. The assistance from Mr. Guo-liang Fang, Mr. Sen Han, Ms. Fei He, Mr. Yang Li, Dr. Zhen-hua Li, Dr. Chun-de Yao and Dr. Ming-fa Yao in Tianjin University is also appreciated.

REFERENCES

- 1 T. Shikada, K. Fujimoto, M. Miyauchi and H. Tominaga. *Appl. Catal.*, **1983**,7, 361.
- 2 W. W. Kaeding and S. A. Butter. *J. Catal.*, **1980**,61,155.
- 3 Guangyu Cai, Zhongmin Liu and Renmin Shi *et al.* *Appl. Catal.*, A **1995**,125, 29.
- 4 K. Guenter, S. Guenter and T. Dieter. DE Patent 4313584
- 5 Alkeos C. Sofianos and Mike S. Scurrell. *Ind. Eng. Chem. Res.*, **1991**,30, 2372.
- 6 D.M. Brown, B.L. Bhatt and T.H. Hsiung *et al.* *Catal. Today*, **1991**, 8, 279
- 7 Chang-jun Liu, Gen-hui Xu and Timing Wang. *Fuel Processing Technology*, **1999**,58, 119.
- 8 Balduur Eliasson, Chang-jun Liu and Ulrich Kogelschatz. *Ind. Eng. Chem. Res.*, **2000** (to be published).
- 9 Chang-jun Liu, R.G. Mallinson and L. Lobban. *J. Catal.*, **1998**, 179,326.
- 10 Chang-jun Liu, R.G. Mallinson and L. Lobban. *Appl. Catal. A*, **1999**, 178,17.