Green Diesel from Fischer-Tropsch Synthesis: Challenges and Hurdles

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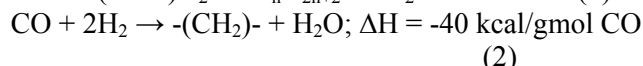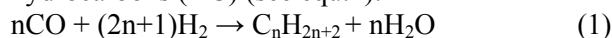http://www.chimique.usherbrooke.ca/gch/profs/Abatzoglou/index.htm

Abstract: Kyoto's protocol respects the view that, within the context of worldwide preservation and improvement, the quality of life is impossible to maintain without bringing forward new and replacement technologies. Energy supply is perhaps the most significant contributing vector and it is, in consequence, intrinsically linked to nearly all environmental actions. Liquid fuels, such as diesel oil, for transportation and heating needs, are in the centre of these preoccupations. The Fischer-Tropsch Synthesis is an "old" technology but it can be adapted for use with syngas, biosyngas or biogas, for the production of diesel oil. Such diesel fuel oil, when coming from renewable sources, such as "biomass", is called "green diesel".
This present work outlines the actual status of the FTS technology and details the scientific challenges, and the technical hurdles, associated with the use of renewable feedstocks and the newly developed "nanometric catalysts". A recently commenced Canadian R&D project in this technical area is also briefly presented.

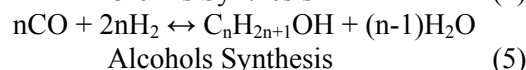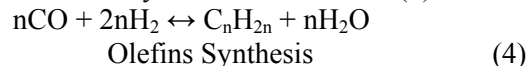*Key-Words:* Fischer-Tropsch Synthesis, Green Diesel, Renewable Energy, Nanocatalysts

1 Introduction and Literature review

There is obvious urgency in the finding/generating "less polluting" fuels. The combination of a technically robust and environmentally acceptable solid residues management technology, i.e. gasification, with the associated use of the producer gas for the production of liquid fuels, via Gas-to-Liquid (GTL) Fischer-Tropsch Synthesis (FTS) technologies, is a possible way of achieving the mentioned target. Such a technology, if systematically commercialized, would lead the way to "green chemistry" and would constitute an incremental step towards the realization of bio-fuel production refineries. Organic residues, related to human activities as well as "farmed" biomass, can be gasified, using proven technology [2] to produce biosyngas. This in turn can be converted, via the process proposed here, to useful liquid fuels in a way benign to the environment. The FTS then converts a mixture of CO and H_2 to hydrocarbons (HC) (see equ.1):
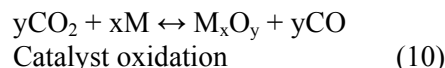
$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \qquad (1)$$
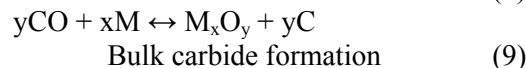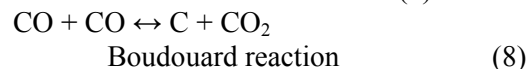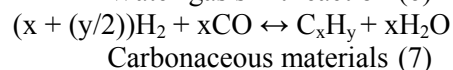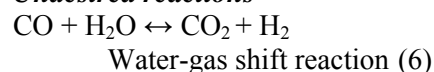$$CO + 2H_2 \rightarrow -(CH_2)- + H_2O; \Delta H = -40 \text{ kcal/gmol CO} \qquad (2)$$

Desired (i.e. paraffins, olefins and alcohols) and undesired products (i.e. aldehydes, ketones, acids, esters, and various types of carbon-rich structures) are obtained during FT (see reactions 1 and 3-9), depicting the complexity of the process:

Desired reactions
$$nCO + (2n+1)H_2 \leftrightarrow C_nH_{2n+2} + nH_2O$$
Paraffins Synthesis   (3)
$$nCO + 2nH_2 \leftrightarrow C_nH_{2n} + nH_2O$$
       Olefins Synthesis   (4)
$$nCO + 2nH_2 \leftrightarrow C_nH_{2n+1}OH + (n-1)H_2O$$
       Alcohols Synthesis   (5)

Undesired reactions
$$CO + H_2O \leftrightarrow CO_2 + H_2$$
       Water-gas shift reaction (6)
$$(x + (y/2))H_2 + xCO \leftrightarrow C_xH_y + xH_2O$$
       Carbonaceous materials (7)
$$CO + CO \leftrightarrow C + CO_2$$
       Boudouard reaction   (8)
$$yCO + xM \leftrightarrow M_xO_y + yC$$
       Bulk carbide formation   (9)
$$yCO_2 + xM \leftrightarrow M_xO_y + yCO$$
Catalyst oxidation   (10)

Commercialized FTS technologies [1] use coal or natural gas (NG) "gasification" to produce synthesis gas (process feedstock) and belong to one of two categories, based on the reaction temperature: High and Low Temperature FTS. Their basic characteristics are summarized as follows:

(a) High Temperature FTS (HTFTS):
❏ 330°-350°C: high selectivity for gasoline and light olefins production

- ❑ Fe catalysts are more active at higher T
- ❑ Complex products generated and high level investments required
- ❑ 2-phases : Multi-tubular Fixed or Fluidized beds

(b) Low Temperature (LTFTS)
- ❑ 220°-250°C: high selectivity in liquid distillate and waxes
- ❑ Preferred for diesel production
- ❑ Co catalyst is more active at low T
- ❑ 2-phases: Multi-tubular Fixed or Fluidized beds
- ❑ 3-phases: Slurry Phase Bubble Column Reactors (SBCR)

1.1 Biomass-to-Liquid (BTL)

When biomass is used as a renewable raw material for FTS, depending on the gasification agent (air or oxygen-enriched air), the biosyngas so produced [2, 3] is a mixture of the desired H_2 and CO but it also typically contains ~ 5 to 10% carbon dioxide, less than 10% of hydrocarbons, 25-55% N_2 and some acidic (H_2S), alkaline (NH_3) and metallic (K, Na) contaminants. Although FTS is a mature technology for CO/H_2 mixtures, arising from coal (and natural gas) gasification (i.e. Shell and Sasol technologies), little is known on the process efficiency side when diluted biosyngas feedstock(s) are used. Besides, the available "commercial" catalysts are very sensitive to the presence of sulphur and halogens and the required feed gas purification, down to the ppb level, is both difficult and expensive. The situation is similar to that when the biogas from a fermentation process is the FTS feedstock. In this case, the average feedstock composition is 50%vol CH_4-50%vol CO_2, but impurities, such as siloxanes, NH_3, H_2S/mercaptans and light halogenated compounds, pose considerable technical hurdles.

1.2 The Catalysts and their contaminants

Cobalt and iron based catalysts are currently preferred for gas to liquid (GTL) transformation technologies because of their activity, their relatively high life expectancy and their low cost [1, 4]. Co is 1000 times more costly than Fe, but it is more efficient, more selective, and either not or, at least, much less deactivated by water (an FTS co-product), and consequently, it has a longer life span, especially if the Co crystallite sizes are greater than 10nm, and water content is less than 20mol%. Ni-based catalysts are also very active but their high hydrogenation activity leads to a higher level of CH_4 selectivity. Ru-based catalysts are equally good but their high cost tends to exclude

them; thus, the use of Ru is considered only as a promoter in support of the more economic Fe and Co catalysts. Regarding the efficiency and robustness of the catalytic formulations used, and although there are several literature references to catalyst deactivation studies [5, 6, 7, 8], there is currently little data on the reaction mechanisms as a function of the catalyst's surface properties and its chemical composition. Additional information about the commercial catalysts used is summarized in the following notes:

(a) Iron based catalysts
- ❑ Carbides and oxycarbides are the active phases
- ❑ Higher water gas shift (WGS) activity; this means that lower H_2/CO ratios are generally needed
- ❑ The conversion is proportional to the sum of the $CO + H_2$ components
- ❑ Low Temperatures and H_2/CO ratios favour high molecular weight (MW) hydrocarbons (HC)

(b) Cobalt based catalysts
- ❑ The metal itself is the catalytically active phase
- ❑ More active at higher conversions of the feed gas
- ❑ The conversion is proportional to the H_2/CO feed gas ratio
- ❑ High CO partial pressures and low H_2/CO ratios favour high MW HC selectivity
- ❑ Longer life but more expensive initially.

There are "limited" published works on the tolerance of the Fischer-Tropsch (FT) catalysts for the metallic, sulphur and halogen based, contaminants, as found in syngas, biogas and biosyngas. Significant levels of contradictions exist in this field. Although it is well known in industrial circles that sulphur concentrations greater than 5ppb are detrimental to the catalysts used, experimental bench, pilot and industrial scale testing shows that sulphur can be tolerated at ppm levels and that, in some cases at least, its presence enhances their catalytic activity [9]. Curtis et al. [10] have reported that small amounts of sulphur in TiO_2 and SiO_2-supported Co catalysts improve the strength and activity of the catalysts, due to the improvement in the CO-metal adsorption efficiency and the creation of higher concentrations of CH_x species at the catalyst surfaces. Recently, Wu et al. [11] prepared a precipitated iron catalyst containing sulphates and proved that the presence of sulphur in this form is beneficial to both the catalysts activity and its selectivity towards heavier hydrocarbons. Thus, the role of the sulphur as a

"reaction" contaminant is controversial; the controversy being attributed to different role(s) for the S in the different catalysts used, and under the different FTS conditions. No references have been found to the tolerance of FTS catalysts to metallic and halogen contamination (e.g. chlorine). Nevertheless, Bangala et al. [12] have reported on the protective role of chromium against S, in a MnO-Al$_2$O$_3$-supported, Ni-based reforming catalyst formulation.

1.3 The reactors

Fluidized bed and multi-tubular fixed-bed reactors have historically been developed and used commercially for FTS [1, 13]. Since 1980, three-phases slurry, continuous stirred tank, reaction systems have been both studied and proposed as alternative reaction systems for FTS; the basic advantages of the slurry reactors being their greater ability for efficiently removing the heat produced during the exothermic FTS reactions, and the solvent action of the "inert", heat conveying, liquid phase on waxes, deposited on the catalyst surfaces. Their major disadvantages are, however, the slower gas/liquid-solid interface diffusion rates obtained, in comparison to those of both fixed and fluidized bed reactors. In summary:

(a) 2-phases (Gas-Solid) reactors
- ❑ Catalyst average size must be greater than 1mm for acceptable bed pressure loss (ΔP)
- ❑ "Effectiveness factor" lower than 1 (diffusion control)
- ❑ Catalyst improvement does not "help" the reaction kinetics
- ❑ Difficulty of reaction heat removal
- ❑ Catalysts poisoning - deactivation

(b) 3-phases (Slurry) CSTR
- ❑ Low selectivity in high MW HC
- ❑ Effectiveness factor close to unity, but lower Gas-Hourly Space Velocity (GHSV)
- ❑ Catalyst-waxes separation (the target: to reach effective catalyst concentrations in wax at values lower than 2ppm)
- ❑ Catalysts poisoning - deactivation

2   Research Background

Since the discovery of the initial catalytic synthesis by Sabbatier & Sanders, 1902, and the "decisive" developments of Fisher-Tropsch in 1923 [4], differently supported and unsupported metal catalysts, such as Fe, Co, Ni, Ru and Rh, have been mainly used in three different reaction systems, these being the fixed-bed, the bubbling and circulating fluid bed, and the 3-phase(s) slurry, all utilised with the aim of improving the syngas (e.g., CO + H$_2$) conversion reaction to thereby generate synthetic liquid fuels.

Current developments aim at improving the FTS technology for the production of high-molecular weight waxes, followed by their "hydrocracking" to generate liquid fuels. Due to their high level activity and long life, cobalt and iron based Fischer-Tropsch catalysts are still the preferred materials for this role [14]. Co catalysts provide the best compromise between low investment costs, high CO conversion levels and they also offer favourable C$_{5+}$ selectivity, as well as low, water gas shift (WGS) activity [15, 16]. Supported Co catalysts, having high specific "reaction promotion" rates, require the initial synthesis of small metal crystallites at high local densities, when dispersed on their support surfaces. It is the use of the "supports" or alloys that increases the rate per unit surface of Co atoms [17].

It is well known that the exothermic Fischer-Tropsch reaction, when combined with the high catalytic activity levels, creates problems in the tubular form , fixed-bed reactor, due to the poor mixing and heat transfer properties of the fixed-bed reactor; the temperature control also being more problematic than that experienced in a slurry-phase reactor. Van der Laan et al. [18] have worked on a Bubble column slurry reactor and associated Fe/Cu/K/SiO$_2$ catalyst, dispersed in the liquid phase. With particles at the 50μm size, it was found that the reaction kinetics controlled the rate, mainly due to the combination of low catalyst activity and high transfer coefficients in the bubble column slurry reactor. To improve the rate, the catalyst activity needs to be greater and, since the phenomenon enters the internal diffusion control range, the internal surface must also be expanded. Such an expansion is possible with the "improved", non-porous, nanometric catalysts. Bai et al. [19] have worked with a Mn-promoted, Ultrafine Fe catalyst in a slurry form. CSTR reactors have shown that this catalyst exhibits slower deactivation rates and less "heavy" wax production, leading to an easier, catalyst-wax separation process than that observed for conventional, "precipitated" iron catalysts. Mahajan et al. [8] have achieved low space-time-yields (STY) and non-selective, hydrocarbons (HC) distributions, using nanosized Fe particles, produced by Fe$_2$O$_3$ reduction. It is surprising that the reducing agent played an important role in determining the final Fe catalyst efficiency. Some agglomeration of

the nanosized iron, and a decrease in the conversion of microsized Fe to nanosized particles, has been observed, but without some understanding of the phenomenon being advanced. Kikuchi et al. [20] tested an Ultrafine Co catalyst in the slurry form CSTR. The catalyst was produced using a liquid phase reduction process and generated a non-porous, structure product. The precipitated Co catalysts show lower activities, due to their porous structure, signifying the diffusion limitations; however, the Cr, Ti, Mn, Zr and Mo doping proved otherwise to be more efficient.

The effects of CO_2, water and other impurities, such as hydrocarbons and nitrogen, on the syngas conversion, on various catalyst selectivity and catalyst deactivation, are all governed by the FT reactions mechanism. As syngas conversion in the FT is a quite complex process, a number of researchers have worked on the understanding of the FTS reaction mechanism [21, 22, 23]. In the case of iron-based, FT catalysts, the effects of water are well understood as the water reoxidises the iron during FT [21]. In this case, the syngas consumption rate decreases as the water concentration increases [16, 17, 18, 24].

The performances of the catalysts used depend on the reactor configuration:

❑ High BET-Surface supported catalysts are used in both fixed-beds and fluid beds. A typical example is the $Co-ZrO_2/SiO_2$ catalyst, prepared by consecutive impregnation of silica with $Zr(OCH_2CH_2CH_3)_4$ and $Co(NO_3)_2.6H_2O$ [25]. The loading of this catalyst is typically ~10%w/w Co and ~11%w/w Zr. The catalyst is reduced in a 10% H_2-90% N_2 stream, at 400ºC for 12h. Such a catalyst, when operated at a total pressure of 2.2MPa, a N_2 content of 40%vol., a temperature of 206ºC and a GHSV of 2000hr^{-1}, provides a CO conversion rate of ~3 mmol/hr.g_{cat} but there is insufficient information available to calculate the % of CO conversion. Jess at al. [26] have reported data obtained using a Fe-based catalyst, contained in three "fixed-beds in series", at a pressure of 2.4MPa, N_2 content of 50% and at a temperature of 260ºC. A total CO conversion of 55% is reported. A further calculation, made under the assumption that the bulk density of the catalyst was of 1.5kg/l, lead to a CO conversion rate of 4.6 mmol CO/h.g_{cat} at an average GHSV of around 1700h^{-1}.

❑ Supported and unsupported micro- (i.e. 50μm in commercialized reactors) and nano- (i.e. 10-50nm in R&D units) powders of Fe and Co, are used as

FTS catalysts in slurry reactors. These catalysts are promoted by other metals (i.e. Mn, Cu and alkalis). Bai et al. [19] have reported data on a Mn-promoted Fe ultrafine particle catalyst, used as a slurry in a continuously stirred-tank reactor. CO conversions as high as 91% have been reported at a temperature of 270ºC, a pressure of 2.3MPa, a $H_2/CO=2$ and a GHSV of 2l(STP)/h.g_{cat}, equivalent to 1.0h^{-1} with respect to the feed gas composition. It is obvious that slurry reactors have very low GHSV compared to fixed and fluidized beds, under similar reaction conditions. This is due mainly to low diffusion rates and implies high reactor volumes and process costs.

The role of the nitrogen input has been also studied. Kuntze et al. [27] worked with an alkalized precipitated iron in a fixed-bed reactor and concluded that;- a) particle sizing is a major factor because of wax filling of the pores (diffusion limitations); b) the nitrogen acts only as a diluent. Jess et al. [26, 28] concluded that, for equal partial pressures of the reactants, the FTS reaction rates are N_2-neutral and N_2 plays a positive role as heat-carrier for this exothermal reaction, thus allowing for higher, individual tube diameters in multitubular, fixed beds reactor configurations, and consequently lower pressure losses. The role of N_2 as a diluent has been investigated by Collier et al. [25]; experiments, performed in a fixed-bed reactor with a Co/ZrO_2-SiO_2 catalyst and a simulated syngas, have shown that the N_2 content decreases the CO conversion because the rate is of "first order" with respect to the H_2 input. The order of one with respect to H_2 has been also been confirmed for a precipitated Fe catalyst, as used in the SASOL fixed-bed unit [26]. In the same work, it was shown that the reaction is of the zero order with respect to CO. There is no information in the literature regarding the role of the N_2 in slurry CSTR.

3 The Canadian GTL project

3.1 Objective
The Canadian project, started this year (2007), is aimed at developing novel nano-catalysts that can maximize the wax fraction of the FTS in both slurry reactors and fixed-bed reactors, using renewable feedstocks (i.e. biogas or biosyngas, produced by air or O_2-enriched air gasification of the biomass and wastes.
The basic research hypothesis is that new nano-catalysts, produced by Thermal Plasma Synthesis using

induction plasma technology and Wet Impregnation techniques, can be designed to improve the efficiency of the slurry and fixed-bed reactors, used in the FT synthesis from biosyngas.

3.2 Specific objectives

The specific objectives of the project are to face some of the previously described challenges, and to overcome some of the known technical hurdles; such as:

(a) To produce new formulations of nanometric iron and cobalt based FTS catalysts which improve their product selectivity, while being less sensitive to the presence of contaminants. Both the incipient wetness, thermal plasma vapour deposition (TPCVD) and cluster spray techniques (TPCS), are used to produce nanosized,, non-porous and ceramic- or nanocarbon-supported, metallic crystallites. The basic ideas are:

(a1) Since the average catalyst particle size for fixed-bed reactors must be typically greater than 1mm to have acceptable pressure drop losses, unsupported nanospheres are therefore "prohibitive". Ceramics, composed of nanocarbon-supported catalysts, will be produced by the techniques described above (point 3.2a).

(a2) For slurry reactors, the size reduction and the production of non-porous nanocatalysts minimize the liquid-solid diffusion resistances and render the FTS dependent upon the gas-liquid diffusion and the surface reaction rates.

(b) In order to compare the performances of two reactor types: 2-phases fixed-bed and 3-phases slurry reactors, using established indicators such as the CO and H_2 conversions, turnover rates (GHSV), HC selectivity, C_{5+} selectivity, HC molecular weight distribution, are employed.

(c) To evaluate the effects of the presence of inert components (i.e. N_2), H_2O, CO_2 and hydrocarbons in the synthesis gas, on the reactivity and selectivity of slurry reactors.

(d) To develop technical knowledge on nanometric catalysts separation from the liquid products and to develop "scale-up" criteria for industrial applications.

The fixed targets are therefore:

o To maximize the CO conversion; this is the index used to measure the process effectiveness.

▪ For fixed-beds, the target is to reach CO conversions greater than 80% at GHSVs of more than 2000hr^{-1}. This can be achieved by increasing the active specific surface of the catalyst and to decrease the extent of the reoxidation reactions.

▪ For slurry CSTRs, the target is to reach CO conversions greater than 90% at GHSVs of more than 10hr^{-1}. This can be achieved by decreasing the "effective" size of the catalyst powders (supported or unsupported, non-porous nano-sized spheres) and improving the gas-liquid-solid diffusion rates, without increasing the reaction pressure.

o To increase the selectivity and conversion rates to high molecular hydrocarbons;-

▪ Mills [4] reported that the SASOL I Arge operation, using a precipitated alkali-promoted Fe catalyst at T=220-255ºC, at P=2.5MPa and H_2/CO=1.7-2.5, produced a C_{5+} selectivity of 78% and with a C_{19+} selectivity of 41%. A target in the actual Canadian project is to achieve levels over 85% and 55% respectively, without additional severity and costs. Moreover, CO_2 selectivity must remain lower than 5%.

▪ Bai et al. [19] reported that slurry-CSTR is characterized by much lower selectivity in the desired products. In such reactor configurations, the C_{5+} selectivity is typically lower than 40%, the C_{4-} selectivity is as high as 35% and the CO_2 selectivity more than 35%. The target is to increase the C_{5+} selectivity to above 70%, while at the same time reaching a C_{19+} selectivity greater than 40%.

o To enhance the sulphur tolerance: The optimum catalysts will remain active (more than 90% of their initial activity) for at least 4000h for input gas streams containing an average of 20ppmv sulphur. In the case of Fe carbide(s) catalysts, this can be achieved by decreasing the re-oxidation rates.

3.3 Methodology

The method of "incipient wetness" will be used to produce the silica and/or alumina-supported cobalt and iron catalysts. This method consists of 1) co-precipitating salts (usually easily decomposable nitrates) in aqueous suspensions, then 2) separating the wet solids from the superfluous liquid phase and to proceed with the drying and calcination steps to facilitate the homogenisation and cementing of the catalytic matrices. These steps will be followed by the additional steps of grinding, new homogenisation and

use of "moderate" calcinations. A reduction of the metal oxides under mild hydrogenation conditions might also be needed. The catalysts will be extensively characterized, using several novel techniques.

The methods of TPCVD and TPCS are used to ensure the production of higher levels of catalytic surfaces and wider dispersion of the active elements. The technique of reagent deposition in the vapour phase provides for high growth rates of the desired species (to 100μm/min), while preserving control on the coating quality. It is indeed possible, by varying the composition of the suspension precursors, to influence the microstructure controlling the nucleation and growth, which are otherwise influenced by the temperature and composition profiles at the "boundary layer", located between the receiving surface and the deposited particles. The TPCS technique is used to vaporize metallic species (e.g. Fe, Co, promoters) under reductive (i.e. presence of a carbon-precursor, such as CH_4, C_2H_2 or ethylene glycol) or an otherwise inert atmosphere, and to rapidly quench the aerosol formed to produce non-porous, spherical, nanosized metals, oxides, carbides or "doped" cluster structures. This technique has recently been developed by two of the authors [29] and it will be applied to produce new catalytic formulations in this project. The adaptation of thermal plasma technology to combinatorial synthesis is now available in the Plasma laboratories of the UdeS and this will be used to accelerate the search for new catalysts. The recently installed infrastructure (Canadian Foundation for Innovation and Quebec Government as well as institutional and industrial funding on Combinatorial Chemistry) is to be used to produce many catalytic formulations by varying the predefined parameters and variables in a precise and reproducible manner.

A major research technique used in this research is that of multi-walled carbon nanofilaments (CNF) and nanotubes (CNT), produced by CO_2 sequestration via dry reforming, to be used as catalysts or catalysts substrates for GTL FTS. Recent publications of the authors [30, 31] have shown that such CNF and CNT; (a) can be produced using low cost catalysts; (b) they have high specific surface values (around $150m^2/g$) and (c) that their iron carbide content confers catalytic properties on them. Moreover, wet impregnation and TPCS techniques can also be used to deposit greater quantities of iron and iron carbides, respectively. Such new catalysts will be used to produce long, linear-chain paraffin (waxes), in fixed-bed and slurry FTS reactors.

4 Discussion

It has been shown that considerable challenges and technical hurdles remain to be overcome in order to render the "Green diesel" option as a commercially viable option. Slurry reactors seem to be very promising but the following discussion is necessary to pinpoint the behaviour and challenges associated with this type of reactor.

The suspension of the solids: According to the literature, the critical mass load of the solids in slurry CSTR and columns is about 65%; commercial slurry reactors, utilize micronic catalysts at mass concentrations close to 30% but not over 40% [1]. When nanometric catalysts are used, their dispersion in the slurry reactor liquid phase is expected to be easier because the Stokes sedimentation phenomenon is practically non-existant, but the liquid-solid superficial phenomena are rather difficult to account for and the clustering during the FTS reaction can also occur. As it is well known that Fe and Co catalysts also participate in the reaction, through a cycle of oxidation/reduction and the formation of carbides, it is expected that such chemical changes have a significant impact on the physical state of the catalysts (i.e. shape, size, internal porosity, agglomeration) which also affect both the suspension properties and the catalysts efficiency [32].

Rate controlling step: In gas phase fixed-bed FTS, internal diffusion usually governs the rate because external and surface reaction rates are faster. The use of supported catalysts, having low internal porosity, and based on well distributed, nanometric metal grains, could considerably reduce the gas-solid internal diffusion resistance and thus render the phenomenon more dependent upon the surface reaction kinetics. Moreover, the high MW HC (waxes) could easily diffuse back to the gas phase, thus avoiding the rate control arising from the product's own internal diffusion, and so offering lesser opportunities for the formation and deposition of porous carbon. In the slurry CSTR, where catalyst particles have an average size of less than 50μm, the external diffusion resistance is negligible [1]. The transfers in the liquid (gas-liquid) and in the solid (liquid-solid) are the overall rate limiting steps. With the non-porous nanosized catalysts, the gas-liquid transfer through the gas-liquid surface is expected to be the rate limiting step. Thus, optimization of the gas-liquid dispersion technique employed is needed. Sarkar at al. [32] have shown that, during FTS with ultrafine Iron powders (2-5 nm), the nanometric catalyst particles reoxidise after their activation as

carbides and the process is accompanied by a considerable increase in the particles average size and morphology, a change that is not due to superficial carbon formation. This means that it is plausible that there may be a critical catalyst's particle size, above which the liquid-solid transfer rate, and the surface reaction rate, will both be decreased to a point where they could become the FTS rate limiting steps.
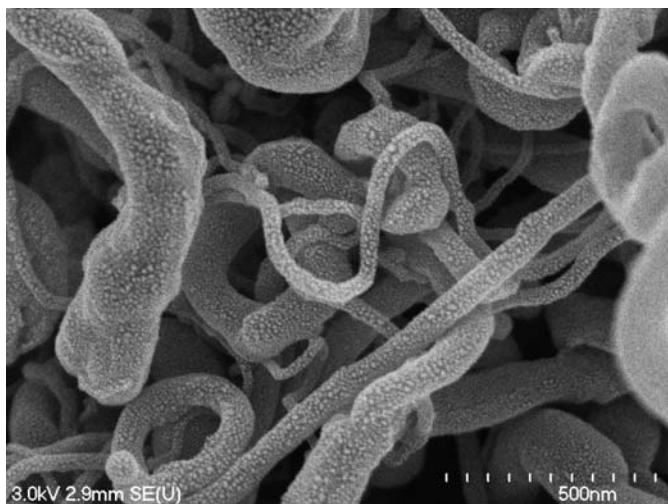

Figure 1: CNT/CNF metallization with Au

When CNT and CNF are to be used, there is internal porosity (the internal surfaces of hollow tubes and filaments) but the catalytically reactive iron carbides or the metallic Co deposits, produced through TPCS, must be mainly applied to the external surface of this substrate in order to avoid internal diffusion limitations. If a homogeneous, non-dense metal grains, distribution is generated at the CNT/CNF surface, the grains relative immobility will be a determinant in avoiding agglomeration/sintering phenomena, due to chemical changes of the metal catalysts. Recently, the authors have tested metals coatings deposition at the surface of CNF/CNT, obtained by the dry reforming of ethanol [30, 31]. The proof was made by metallizing these nanostructures with Au. In the resulting coated fibres, shown in Fig. 1, the spots appearing at the surface of the CNT/CNF are the Au nanograins. Similar deposition techniques can be used for Fe, Co and ultimately, directly for the Iron carbides (i.e. Cementite: Fe_3C), using Thermal Plasma Spray, or as Iron oxides by Wet Impregnation techniques.

The stoichiometry: In slurry CSTR the real stoichiometry is not the same as that with the imposed phenomenological stoichiometry, at the entry point of the gas phase, since the gases diffuse at different rates in the liquid phase. Particular attention must be given to

"couple" the gas solubilities prediction in the Slurry reactor FTS.

Carbon formation: The Boudouard carbon disproportionation reaction (equ. 8) is the main source of inert solid carbon deposition. In a fixed-bed reactor, it is impossible to modify the H_2/CO ratio without affecting the reaction. In the 3-phase Slurry CSTR, the ratio can be modified if the reaction variables are linked with the solubility and the rates of diffusion of these two gases. Local carbon formation inside the pores of the catalysts may cause a loss of their structural integrity and of the catalytic sites. In the cases of non-porous, nanosized catalysts, it has been shown [32] that carbon formation is not the most problematic factor. In fact, carbon formation did not prove to be the determining factor in particle size growth, and further, amorphous carbon rim formations at the surfaces of Fe grains generally have thicknesses typically lower than 5-6 nm. Nevertheless, this rim carbon is thought to contribute to the catalyst's activity; the effect being either positive or negative, since; a) such carbon hinders the reactants access to the catalyst surface but, b) it surely contributes to the reforming of carbides, thus reducing the role of the less active iron oxides. In the case of Co, the results of carbon formation are more negative, such as the surface poisoning through "coking", and because Co carbides are less active than metallic Co itself.

Catalyst-Waxes separation: The "challenges" described above are the concern the FTS reaction module and they are all important factors. Equally important, and perhaps crucial, in these processes is the challenge to succeed in devising an efficient wax-catalyst separation process. The catalyst itself can be reused, while the waxes can be treated "downstream" of the FTS (i.e. by hydrocracking) without the presence of the remaining solids which would otherwise constitute a considerable technical "hurdle". In 1991, a DOE Report [33] described the then available technical options, the authors concluding that the ideal situation was to achieve effective catalyst/wax separation while the mixture remained inside the reactor, i.e. through the use of a parallel, continuous solids, filtration loop; the final objective being to recover the waxes product containing less than 1-2 ppm of the introduced catalyst. This particular arrangement proved to be rather inefficient, due mainly to the high liquid phase viscosities and the difficulties encountered with the on-line pressure filtration step. Besides these experiences, if this particular processing with micronic particles is difficult, then the comparable situation, in the case of

nanocatalysts use, is expected to be "worse". The other available option is the external removal of the catalyst, through such techniques as: sedimentation, centrifugation, or magnetic separation. Gravity "settlers" and hydrocyclones have been tested with relative success (though without reaching the desired sub 1-2ppm wax content in metal) but all of these were performed with micronic particles. It is, in the authors' view, rather difficult to imagine that expecting such techniques to succeed with various nanoparticle products, even if their specific gravities are high (e.g. metals, oxides, carbides) The most promising method for such nanoparticles is that of magnetic separation. Some more recent works [34, 35] present a magnetic separation technique (MM-PS, patent pending), applied to Fischer-Tropsch process wax-catalyst slurries, extracted at 260°C and containing 18%wt solids. The actual catalyst particles are micronic agglomerates of 2-60 nm individual particles. The technique uses a magnetic field of 0.2 Tesla to remove up to 97% of these valued solids. The residual solids, retained in the wax rich phase, were both ferromagnetic and paramagnetic, while it was also shown, by Mössbauer measurements, that 17% of the solids particles were superparamagnetic. This level of separation efficiency is not yet sufficient for a "one step/stand alone" commercial operation, but the technique can be adapted for regular "on line" use. However, it must presently be complemented by the installation of a secondary magnetic separator, capable of recovering / retaining the remaining paramagnetic and diamagnetic components of the catalyst solids. The High Gradient Magnetic Separation (HGMS) technique, potentially suitable for this application, is presented in [34]. This two-stages, magnetic separation technique leads to the recovery of the valuable waxes, with remnant catalyst contents ranging between 100-500ppm.

5 Environmental advantages of green diesel

Each m^3 of the "fossil origin diesel fuel" used in today's transportation or energy sector emits into the atmosphere the equivalent of approximately 2.5t of CO_2. In Canada, the road use diesel consumption in 2002 was at the 15 Mm^3 level. This converts to atmospheric emissions of some 40Mt of CO_2/per year. The replacement of 25% of this diesel by the CO_2 "emission neutral green diesel" will annually decrease

the GHG emission by ~ 10Mt. Taking into consideration the fact that Canada's GHG production was about 750Mt in 2005, a reduction in consumption of 10Mt means a neat decrease of more than 1.3%, or more than 20% of the total Kyoto protocol commitment made by Canada..

The basic hypotheses set for these calculations are similar to those for all the industrialized nations and therefore it is rather obvious that an eventual "commercial success" in this field will constitute a strong technical tool for every nation to adopt in its endeavour to respect its commitment made in the now "decade old" Kyoto protocol.

6 Conclusion

Green diesel production, using the FTS technologies, is now considered to be an achievable target. Nanometric particle catalysts, as used in slurry reactors, is believed to be a promising option but considerable Research, Development and Demonstration efforts must be expended in order to face the challenges and technical hurdles in such a mission. They can be categorized as follows:

- ❑ Low cost controlled preparation of catalysts in a commercially reproducible manner.
- ❑ Efficient dispersion of nanometric catalysts in the slurry reactor processing.
- ❑ Fast and efficient gas-liquid-solid transport phenomena-operations.
- ❑ Predictable behaviour of catalysts during their life cycle.
- ❑ Cost and quality of the effective separation of the wax-catalyst by-product mixture.

A Canadian project has been started in 2007, aimed at providing practical answers to the majority of the above listed technical points and R & D support requirements.

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