Improving Carbon and Process Utilization for Biomass-to-Liquid Fuel Operations
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Abstract:
With the increasing world demand for transportation fuels, declining petroleum reserves and quest for energy security, there is a renewed interest in Fischer-Tropsch (FT) technology as a viable alternative for the production of liquid fuels from carbonaceous resources (natural gas, coal and biomass). Concern about global warming has also created a special interest in the use of biomass (Biomass-To-Liquid Fuels, BTL) as a carbon-neutral route to liquid fuels. However, carbon utilization in BTL via traditional biomass gasification is between 25 – 40 % of carbons in the biomass feedstock. This results in poor process economy. Energy input from concentrated solar power (CSP) into BTL can salvage undue large carbon discharge in traditional BTL. The CSP-BTL hybrid not only improves carbon utilization but is also a plausible strategy for solar energy storage.

Keywords: Biomass-To-Liquid Fuels, BTL, Carbon utilization, Process economy, Fischer-Tropsch Synthesis,

1. Introduction
Fossil fuels constitute the principal source of energy in modern society. The exploitation of fossil fuels is associated with pollution and the emission of green-house gases, especially CO₂ which has been linked with climate change and global warming, which are current environmental concerns [1]. At present, transportation fuels are produced almost exclusively from petroleum. The sector is witnessing the highest growth rate in fuel demand and CO₂ emission. The quest for energy and economic security is motivating the search for alternative fuel sources. Moreover, several reports have indicated that petroleum exploration is most probably at its peak and decline in supply may be expected a few decades from now [2-4]. On the whole, a paradigm shift from fossil fuels to a renewable energy economy is imminent in the future. With this in mind, efforts at developing physical devices and/or chemical systems for harnessing energy from carbon-free renewable sources such as solar, hydrologic, tidal, wind, geothermal [5]. The widespread application of these carbon-free renewable energy sources in the transportation sector does not appear to be feasible in the near future.

Biomass is a natural source of carbon produced through photosynthesis, and its combustion is considered carbon-neutral since the CO₂ released is in a close loop with the carbon cycle. The production of transportation fuels from biomass is attracting attention as a carbon-neutral bridge in the transition to a carbon-free future for the transportation sector [6-7]. Transportation fuels produced from biomass are often referred to as ‘biofuels’ or ‘green fuels’ (e.g biodiesel, green diesel, biogasoline, depending on the technical nomenclature) [8]. The prefix green ascribed to the fuels pre-supposes that their production complies with sustainability criteria (namely: economic, social and environmental performances) from the perspective of green chemistry [9]. Roberto and Ferdi [10] have drawn attention to the probability that biomass, as the starting material for transportation fuels, may not readily lead to sustainable process chains. To support their view, current commercial biofuels do not fully meet the listed sustainability criteria. For example, the increasing production of biodiesel and bioethanol is associated with social concerns regarding their potential effect on the food supply and the ecological impact of the intensive production of the fuel crops on limited arable land [11]. Moreover, bioethanol cannot be used directly in most petrol engines and there is still debate over the net energy balance of bioethanol production from crops such as maize, cassava etc.

One of the efforts at improving the sustainability compliance of biofuel production is through the use of non-food biomass as starting materials. In this regard, the production of biodiesel and bioethanol from non-food crops or biomass is being encouraged. At present the production of bioethanol from cellulosic materials is far less than production from crops (such as sugar cane, maize or cassava). Yet it is desirable to produce transportation fuels from lignocellulosic materials due to their abundance and low cost. To this end, the application of Fischer-Tropsch (FT) technology using biomass as raw material (BTL – Biomass-To-Liquid Fuels) provides a versatil
to a wide range of transportation fuels [12]. However, the full-fledged and widespread application of BTL is beleaguered by low carbon utilization and low energy efficiency. This culminates in poor process economy [13-14]. In this report, we attempt to examine these challenges in BTL and draw attention to plausible options for improving the process economy of obtaining transportation fuels exclusively from renewable sources via BTL.

1. BTL process operations via traditional Fischer-Tropsch technology

Here we attempt to point out the origin of the poor process economy in BTL operations. The operations leading to the production of transportation fuels in BTL involve three main sections: synthesis gas (syngas) production (gasification and purification), Fischer-Tropsch synthesis (FTS) and product up-grade. Syngas is produced by gasification of the biomass raw material feedstock. It involves subjecting the biomass feedstock to high temperature (500 – 800°C) in the presence of steam and or oxygen [15]. Combinations of reactions, which include pyrolysis, partial oxidation, steam gasification, and the water gas shift (WGS) reaction, occur during the process. Gasification is endothermic; the energy required for the process is obtained by combustion of part of the biomass feedstock to supply heat externally or internally to the reactor to drive the reaction. Reported estimates indicate that about 50 % of the starting biomass feedstock is burnt to CO₂ at this stage [15-16]. This partly explains why syngas production accounts for a large part of the cost of fuel production through Fischer-Tropsch technology. The resulting outlet raw syngas from the gasifier reactor usually contains constituents [NOₓ, SOₓ, organic (tar) and inorganic (ash) particles] in amounts above the threshold limit. This gives rise to severe poisoning of the catalyst in the FTS section. The purification of the outlet syngas is critical to a smooth operation in the FTS section. Of special concern in the syngas purification stage is tar removal because it constitutes the greatest technical challenge and it commands a sizable proportion of the cost in the syngas production section. Carrying out the gasification at higher temperatures, above 1000°C, reduces tar formation, but this is at the expense of combustion of extra feedstock [8].

Moreover, the H₂/CO ratio of biomass syngas, after purification, does not satisfy the stoichiometric requirement for FTS. The syngas feed is usually H₂-deficient and CO₂-rich. In commercial FTS operations based on coal or natural gas, a syngas feed with an H₂/CO ratio between 1.5 and 2 is commonly employed, especially where high wax selectivity is the target. Hence, a syngas feed from biomass may require re-conditioning to augment the H₂/CO ratio either by mixing with low cost H₂ or H₂-rich syngas feed (obtained from natural gas). The use of H₂-rich syngas feed may compromise the carbon-neutral BTL process being advocated in this paper. The other common alternative is passing the feed through a WGS (CO + H₂O → H₂ + CO₂) reactor and CO₂ scrubbing. The WGS enriches the H₂ content at the expense of part of the CO in the feed. Thus, following the process line, Biomass feedstock → Gasification → Purification → re-conditioning → Syngas feed for FTS, before the syngas feed enters the FTS reactor, between 60 and 75 % of the carbon in the starting biomass feedstock is released as CO₂. Furthermore, the yield of derivable fuels from the purified and reconditioned syngas depends on the efficiencies of the operations in the FTS (conversion and product selectivity) and product upgrade (hydrocracking, oligomerisation, isomerisation etc) sections.

As illustrated in Figure 1, it is evident that the process economy and carbon utilization in BTL depend largely on the biomass gasification stage. Since syngas production accounts for the largest share of the cost of fuel production via BTL, improvements in the process economy of BTL need to be strategically approached from the gasification stage. At the same time, improved carbon utilization can also be pursued in the FTS and product up-grade sections.
2. Strategies for improving carbon utilization and process economy in BTL

The attractive advantages of using lignocellulosic materials as biomass feedstock for the production of transportation fuels has inspired efforts at improving the process economy of BTL operations. In a recent report by Dominik and co-workers [17], some strategies were suggested for improving carbon utilization in BTL. Their recommendations are: (i) minimising the gasification temperature and recovery of heat from the gasifier exit gases; (ii) co-feeding the biomass with natural gas; (iii) in situ removal of the \( \text{H}_2\text{O} \) produced and addition of \( \text{H}_2 \) in amounts sufficient for the conversion of both \( \text{CO} \) and \( \text{CO}_2 \) to hydrocarbons. These recommendations partly revolve around the conventional practice in commercial FTS based on coal. Considering the fact that syngas production constitutes the bulk of carbon discharge and production cost, the above suggestions did not address improvements at the syngas production stage. Consequently, the expected impact on the carbon utilisation and process economy of BTL will only be marginal. It is also clear that a non-conventional heat source that will salvage the combustion of about 50% of the biomass feedstock in the gasification stage will significantly impact carbon utilization positively in BTL. In line with this, the heat required should come from a renewable resource, it should be cheap and abundant. Solar energy readily fulfils these conditions. Transportation fuels obtained through BTL are classified as second generation biofuels. A mix of solar energy and biomass (constituting solar chemical technology) will upgrade the resulting BTL fuels into third generation biofuels.

3.1. Biomass gasification using solar energy

Solar energy is the largest exploitable renewable energy resource. The energy the sun supplies to the Earth in one hour is more than the present annual global energy consumption. Using solar energy as the heat source to drive endothermic chemical reactions adds to avenues for
harnessing the vastly abundant renewable energy [18]. A mix of solar energy and chemical raw material leading to chemical products constitute solar chemical technology, which can build bridges from an economy based on fossil fuels to an economy entirely based on renewable energy. The concept of solar chemical technology is not new. Initial attempts for its application in fuel processing date back to the energy crisis of the 1970s. However, commercial and research interest in it declined after the energy crisis of the 1970s ended. Nevertheless, as part of the quest for a paradigm shift from a fossil fuels based economy to an economy based on renewable energy, there is a renewed interest in solar chemical technology for fuel processing. Unfortunately, the characteristics of solar energy in its natural form — extreme diffuseness, low and/or uncertain availability due to cloud cover, and the day-night cycle [19] — render it unsuitable for use in BTL processes. These characteristics must be modified or compensated for to make solar energy suitable for BTL processes. To this end, concentrated solar power (CSP) technologies provide modified solar heat sources that are suitable to drive BTL process operations. The basic operating principle in CSP is concentrating solar radiation into a receiver specially designed for high absorption, and reducing heat loss [20]. CSP technologies are currently at a pilot stage. The principles of future commercial CSP plants are shown in Figure 2 and include the following: parabolic trough (PT) collectors, linear Fresnel (LF) reflector systems, dish–engine (DE) systems, and power towers, also known as central receiver (CR) systems.

The tower and dish CSP technologies can be designed as autonomous modules or may be integrated with biomass gasifier. Also, they allow carrying out biomass gasification at temperatures that are sufficiently high (> 1000°C) to drastically reduce tar formation to such low levels that tar removal units become unnecessary in the syngas purification unit. The syngas obtained using CSP technology reportedly contains lower amounts of CO₂ compared to conventional thermal gasifier systems [21]. This also suggests that, by optimising gasification parameters, it may become possible to obtain biomass syngas that will require no re-conditioning before being channelled to the FTS section, with CSP technology acting as the heat source. As can be seen in Figure 3, the use of CSP heat salvages large chunks of biomass that hitherto would have been burnt to provide energy for gasification. In addition, with the CSP operating at higher than 1000°C, the resulting syngas stores more energy that can be extracted when cooled to generate electricity that will be used to drive the plant utilities. In the absence of biomass, the CSP can be operated as a nominal solar-to-electricity system with appropriate thermal storage system.
3.2. Direct use of CO₂-containing syngas in the FTS section

Biomass contains some inorganic components, especially alkali metals in the concentration range 100-1000 ppm [10]; these can promote the water gas shift (WGS) reaction. Hence, it has been pointed out that CO₂ formation may be unavoidable in biomass gasification in the presence of water. Hydrocarbon formation from CO₂ is possible but it requires an additional mole of H₂ per mole CO₂ to form the building unit –CH₂–.

To convert the CO₂ in biomass syngas to CO and then to hydrocarbon, an external hydrogen input will be required. This will augment the H₂/CO ratio sufficiently to make the H₂/(CO + CO₂) ratio lie between 2 and 3. However, conventional commercial hydrogen sources are associated with huge CO₂ emissions, and hydrogen sources without CO₂ emissions may not be economical for BTL operations. Thus, the external input of hydrogen into the biomass syngas may compromise either the economic or environmental sustainability of BTL. Improving the gasification technology towards minimizing CO₂ formation and maximizing the H₂/CO ratio of biomass syngas will be a better strategy that can be sustained.

Commercial FT catalysts are based on iron and cobalt. Table 2 shows the commercial FT process characteristics. The choice of an FT catalyst for BTL syngas should be guided by the biomass/ syngas composition and the desired product selectivity. The pre-requisites for a suitable catalyst for hydrogenation of CO₂ to hydrocarbon are WGS and FTS, since it is generally agreed that hydrogenation proceeds via CO as intermediate. This accounts for why Fe-based catalysts are the preferred choice when dealing with H₂-deficient or CO₂-rich syngas feeds. Hydrogenation of CO₂ using cobalt-based FT catalysts has been reported to give paraffin and wax as the main product.

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Common promoters</th>
<th>Operation mode</th>
<th>H₂/CO of syngas feed</th>
<th>Temperature (°C)</th>
<th>Product selectivities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron-based</td>
<td>Cu, K</td>
<td>HTFT</td>
<td>0.5 - 1.2</td>
<td>280-350</td>
<td>Gasoline range HC, low mol. mass α-olefins and oxygenates</td>
</tr>
<tr>
<td>Iron-based</td>
<td>Cu, K</td>
<td>LTFT</td>
<td>1.5 - 2.0</td>
<td>200-240</td>
<td>Paraffins, high mol. mass α-olefins and wax</td>
</tr>
</tbody>
</table>
According to Iglesia and associates [23], oxygen removal routes (either as H₂O or CO₂) in FTS are exclusively and predominantly via H₂O with cobalt- and iron-based FT catalysts respectively. The removal of oxygen as CO₂ also takes place as a minor contribution which may become favoured at high temperature on alkali-promoted iron-based catalysts [23]. This suggests that HTFT operation modes have a higher tendency toward CO₂ formation than LTFT operation modes. Moreover, CO₂ formation on iron-based catalysts also occurs through WGS during FTS. Co-feeding CO₂ with syngas feed (H₂/CO ratio of 2) has been shown to favour the reverse WGS reaction, resulting in a reduction in CO₂ formation [24]. It lowers the H₂/CO ratio in the reactor, which in turn leads to an increase in C₅+ and olefin selectivity. Hence direct use of CO₂-rich syngas gas feed, as in the case of syngas from biomass feedstock, may have the beneficial effect of suppressing undesired CO₂ formation in FTS using Fe-based catalysts. Using H₂-deficient syngas, it was recently demonstrated that an Fe-Zn based catalyst displayed very low CO₂ selectivity for LTFT. The low CO₂ selectivity was attributed to the presence of sufficient ZnFe₂O₄ phase in the catalyst which provided an alternative in situ pathway to CO₂ hydrogenation other than WGS. Thus, the CO₂ scrubbing in syngas purification becomes unnecessary. This reduces the number of unit operations and contributes to an improvement in the process economy.

### 3.3. Choice of FTS catalyst and operation mode

With the aim of obtaining on-specification fuels exclusively from renewable resources via BTL, it is imperative to take into account the fact that the product fractions of syncrude from the FTS section do not often qualify as fuel. They must be refined or up-graded to meet legislated fuel standards. The ease of refining of the syncrude should guide the choice of the FTS operation mode. According to Klerk [25], the distillate yield from syncrude in an uncomplicated refinery process follows the order: Fe-LTFT > Co-LTFT > Fe-HTFT. Relating this order with the highlights in the FTS section, Fe-LTFT appears to be the appropriate operation mode for BTL. Klerk analysed the task of refining FTS syncrude to on-specification diesel fuel in a simple refinery system (one- or two-unit refining process). He explained that the compositions of FTS syncrudes make it difficult to attain the density parameter in EN 590:2004 diesel fuel specification without a trade-off with either the cetane number or yield. The author described the challenge as a density-cetane-yield triangle. Despite the lower density diesel fuel obtained through the one- or two-unit process refining of syncrude, it readily satisfies the emission requirements more than petroleum derived diesel, provided the density is not critical or a downward review of the density parameter of FT diesel does not compromise its emission specifications. This will remove the limitation of the density-cetane-yield triangle in maximising the diesel fuel yield from the syncrude distillate. It will reduce the process economy in the product up-grade unit of the BTL by saving the need for complicated refining operations. In a situation in which density is a critical parameter, blending with biodiesel is the least complex among the refining options for increasing the density of FT diesel, as suggested by Klerk. A recent report on the effect of blending biodiesel with Fischer-Tropsch diesel indicated a positive result in this regard. On the basis of the engine performance and emission results, a 25% biodiesel-75% Fischer-Tropsch diesel blend was considered a competitive, environmentally friendly, future alternative fuel [26]. This shows that in a situation where the density parameter of diesel is critical, the density of BTL diesel can be upgraded with additives from renewable sources. The use of vegetable oil instead of biodiesel appears more sustainable and can be explored in keeping in line with the intention transportation fuels exclusively from renewable sources via BTL.

### 3.4. Hybrid/non-FT multifunctional catalyst systems

A typical FTS-products spectrum is governed by the ASF-distribution law. The law predicts the limits of the selectivities of the hydrocarbons in syncrude. Traditionally, increasing the yields of selected product ranges is achieved in the product up-grade section. It is envisaged that breaking the limits of the ASF law will provide an opportunity for greater control on FTS-products selectivity aimed at increased proportions of products that are suitable as on-specification fuels in syncrude. The main aim is to selectively produce on-specification fuel in a one-pot process directly from syngas. Here, one or more of the endothermic reactions of the product up-grade section is coupled with the exothermic FTS reaction. This strategy may further help to reduce the number of unit operations from biomass feed stock to end-product fuels. Reduction in the number of unit operations can translate into higher energy efficiency and improvement in process economy in

<table>
<thead>
<tr>
<th>Cobalt-based</th>
<th>Ru, Pt, Zr</th>
<th>LTFT</th>
<th>2.0</th>
<th>200-240</th>
<th>Paraffins and wax</th>
</tr>
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</table>

LTFT – Low Temperature Fischer-Tropsch process

HTFT – High Temperature Fischer-Tropsch process

Table 2: Characteristics of commercial FT processes [22]
BTL. The approaches towards this goal are from reactor arrangement and or catalyst design. The reactor arrangement strategy involves two or more monofunctional catalytic bed systems while the catalyst design approach entails the use of a multi-functional catalyst that has FT and one or more of the activities of the product up-grade reactions.

Several options are being explored in the quest to selectively produce on-specification fuel from syngas in a one-pot process. Worthy of note in the catalyst design approach is the capsule catalyst system. It is prepared by coating a conventional FT catalyst (core) with a zeolite membrane (shell). The capsule concept has been shown to result in catalysts with higher stability than conventional FT catalysts [27]. The concept is that syngas will pass through the zeolite (shell) to reach the FT catalyst (core). FT products are formed in the core and they diffuse out through the shell; they undergo acid-catalysed reactions (hydrocracking, oligomerisation, isomerisation, aromatisation, etc). The tendency of wax hydrocarbon to accumulate in the FT (core) is significantly minimised by the hydrocracking activity of the zeolite shell. Moreover, for a given FT catalyst (core) different product selectivities can be achieved by varying the shell properties (type, thickness) and reaction temperature. Furthermore, more selectivity options are also possible by varying the FT catalyst (core) and reaction pressure. Compatibility between the core and the shell is critical towards achieving the desired product selectivities. A combination of a non-FT catalyst as the core and a suitable shell can also be explored to achieve the selective conversion of syngas directly to on-specification fuels. An example is the selective conversion of dimethylether (DME) to 2,2,3-trimethylbutane (octane number 112) using H-BEA zeolite in the temperature range 453 – 493 K and a pressure range of 60 – 250 kPa pressure [28]. Hence, a capsule comprising a DME catalyst core and an H-BEA zeolite shell could afford selective conversion of syngas to produce a spectrum that is rich in compounds that meet the requirement of high octane gasoline.

3. Conclusion
With the increasing world demand for transportation fuels, declining petroleum reserves and quest for energy security, there is a renewed interest in Fischer-Tropsch (FT) technology as a viable alternative for the production of liquid fuels from carbonaceous resources (natural gas, coal and biomass). Concern about global warming has also created a special interest in the use of biomass (Biomass-To-liquid Fuels, BTL) as a carbon-neutral route to liquid fuels. However, carbon utilisation in BTL via traditional FT technology, viz, biomass gasification and syngas purification; FT synthesis and product up-grade between 25 and 40% of carbon in the starting biomass feedstock. This results in a poor process economy. About 50% of the carbon in the feedstock is discharged as CO₂ during gasification. The use of concentrated solar power as a renewable energy input can enable gasification at temperatures above 1000°C without having to sacrifice about 50% of the carbon in the starting feedstock. It can also give syngas feed that is almost free of tar impurities and containing lower amounts of CO₂ than in conventional thermal gasifiers. Such syngas feed place less demands for syngas purification and results in a smooth operation in the FTS section. Direct use of CO₂-containing syngas feed may be advantageous in suppressing CO₂ formation on iron-based FT catalysts. Hybrid FT and non-FT catalyst systems are also suggested as strategies to reduce the number of processes from biomass feedstock to on-specification fuels.

References
[8] Harold B, Herman DU, Hans-Peter C. Green diesel from biomass via Fischer-Tropsch


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