Carbon Neutral Fuels and Chemicals from Standalone Biomass Refineries

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Abstract: The urgency to eliminate man-made greenhouse gas emissions and achieve energy security/independence by all countries justifies an energy policy that considers the major role of renewable biomass as a source of organic feedstock for producing adequate organic chemicals and biofuels on a sustainable basis and economically. This paper investigates a three-stage thermochemical process to convert wet biomass into a tailored mix of syngas for producing green methanol, hydrogen, and Fischer-Tropsch products. The three-stage thermochemical process involves the torrefaction of wet biomass using hot carbon monoxide gas, pyrolysis of torrefied biomass to produce biochar, and final gasification of the pyrolysis gases by auto thermal reforming up to 1400° C temperature. The proposed process is suitable to utilize a wide variety of biomass materials such as freshly harvested biomass without field drying, agro waste, forest/plantation litter, organic municipal solid wastes, sludge from sewage water treatment plants, solid biomass rejects from anaerobic digesters, bagasse from sugar or first-generation ethanol plants, organic solid rejects from second-generation ethanol plants, waste glycerides from biodiesel plants, industrial organic waste, etc. The proposed process offers valorization of biomass so that the net income of farmers is enhanced a fewfold by selling freshly harvested biomass. The economic analysis found that carbon-neutral hydrogen, methanol, etc. can be produced below the prevailing costs of such products derived from fossil crude oil or natural gas without considering carbon credits. It is feasible in a standalone biomass refinery to use any biomass as only one bulk raw material/feedstock without any harmful emissions to water bodies or the atmosphere except carbon neutral carbon dioxide gas if not sequestrated.

Keywords: Fossil Fuels, Gasification, Pyrolysis, Torrefied Biomass, Torrefaction

I. INTRODUCTION

A biorefinery is a facility that integrates various biomass conversion processes and equipment to produce fuels and chemicals. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and chemicals from fossil crude oil. By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates to optimize the value derived from the biomass feedstock. The overall environmental impact of a biorefinery is positive as liquid effluents are fully converted into useful consumptive/potable water and the ash generated is also used as fertilizer, etc.

The water footprint of these refineries is very low as they are suitable for extracting the moisture available in the fresh biomass for consumptive uses. Only surplus carbon-neutral carbon dioxide is emitted to the atmosphere if no commercial use is found locally or not used for carbon sequestration to earn carbon credits. The use of carbon-neutral biomass, as is done till now, exclusively for the generation of power or heat source, is uneconomical since adequate green electricity/heat energy can be generated cheaply from renewable energy sources like solar energy and wind power. The embedded carbon in the biomass is as valuable as carbon extracted from the air. Also, biomass contains substantial oxygen which is useful in the gasification process without much external oxygen supplementation [1]. Unlike fossil coal, dry biomass contains hydrogen (5 to 7% by weight), to enhance process efficiency, though to a lesser extent compared to crude oil (15%) and natural gas (25%).

Biomass has various components such as lignin, cellulose, hemicellulose, extractives, low-temperature volatiles, high-temperature volatiles (tars), etc. A standalone biorefinery can take advantage of the unique properties of each biomass component to enable the production of various carbon-neutral products. Biomass, rich in low-temperature volatiles, is more suitable for anaerobic digestion to produce methane/natural gas [2]. Biomass that is rich in fermentable sugars like sugarcane, sugar beet, corn, sweet sorghum, etc can be used in conventional first-generation ethanol plants. Similarly, biomass rich in cellulose and hemicellulose is suitable for ethanol production in second-generation ethanol plants [3]. Biomass, rich in lignin, yields more methane and biochar in the pyrolysis process [4][24][25]. Waste oils/fats from the food industry, sewage treatment plant sludge, and cheaper nondible bio-oils can be converted to biodiesel using methanol by the esterification process. Finally, solid wastes from these processes and any other biomass found not suitable for the above processes can be used to produce syngas for conversion to hydrogen or methanol, or Fischer-Tropsch (FT) products in the proposed three-stage gasification process. The conversion process of syngas into hydrogen/methanol/Fischer-Tropsch (FT) products is of exothermic reaction that produces steam while extracting the heat generated. Similarly, liquid effluents from these processes with high Biological Oxygen Demand (BOD) are used in anaerobic digesters to produce methane gas. The excess steam available from the gasification plant and methanol/FT/H2 reactors is also used to produce potable water from treated liquid effluents in a multi-stage flash distillation process to eliminate liquid effluents discharge to water bodies.
The sulfur content in the biomass is separated by the desulfurization unit converting zinc oxide (ZnO) to zinc sulfide (ZnS). While regenerating the ZnS to ZnO by roasting in the presence of O₂ at 900°C, sulfur dioxide gas (SO₂) is produced and further converted into sulphuric acid by electrochemical/electrolysis process (SO₂ + 2H₂O → H₂SO₄ + H₂ at 80 to 120°C) using renewable electricity for use in the second-generation ethanol production process [5]. The by-product nitrogen from the air separation unit (ASU) needed for generating oxygen can also be used to produce ammonia with hydrogen for consumption in second-generation ethanol generation plants or sold to local consumers like fertilizer plants, food processing industries, etc. The possible synergy among the various methods of biomass conversion to organic chemicals/fuels is shown in Figure 1. Thus a standalone biorefinery is complete in itself (except renewable electricity consumption) by using a wide variety of biomass as feedstock and incorporating the most suitable and economical production methods to produce various organic chemicals and biofuels without negative impact on the environment. The scope of this paper is limited to the proposed three-stage gasification process which plays a pivotal role in a standalone biorefinery. The main objective of this paper is to investigate a suitable process or method to utilize any fresh biomass available spatially and temporally for continuous operation (minimum 8,000 hours/year at rated capacity) to produce carbon-neutral fuels and organic chemicals at a profitable cost with the following aspects.

- Suitable to use varied biomasses such as fresh/live biomass up to 90% moisture by weight, industrial biomass waste, agro waste, organic municipal solid wastes, sewerage treatment plant sludge, organic matter to be incinerated, plastic scrap, etc.
- Suitable to generate the required tailored mix of syngas (H₂ to CO ratio) to produce methanol, hydrogen, and FT products such as synthetic kerosene/aviation turbine fuel, ethane, propane, butane, methane, etc.
- To encourage farmers, traders, etc. within 300 km of distance to supply any biomass throughout the year by offering attractive purchase prices equal to food grains price at the same moisture content.
- Suitable to produce carbon-neutral fuels and chemicals at par with prevailing market prices of fossil fuel derivatives.
- A standalone biorefinery that is suitable for achieving the scale of the economy employing proven technologies. No use of costly catalysts in the process by using auto thermal reforming at high temperatures with heat recuperation for producing syngas.
- To earn moderate carbon credits or tax exemptions for carbon-neutral fuels and chemicals and sale of carbon-neutral CO₂ for sequestration or industrial use.
- Suitable with overall positive environmental impact with little liquid and solid effluents.
- To minimize water footprint in producing carbon-neutral products by using the moisture available in the biomass.
- Excess intermediate products like torrefied biomass and biochar from using low-moisture biomass are stored for use while using high-moisture biomass. Also suitable for use of externally procured charcoal or pet coke or high moisture lignite with low ash content if required [6].

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**Figure 1:** The Synergistic Effects of Various Methods of Chemicals/Fuels Production from Biomass
II. DESCRIPTION

The schematic of the process is given in Figure 2. Suitable-size biomass mostly free from sand, soil, stones, metallic pieces, dripping water, etc is loaded into a rotary kiln-type torrifier or Torrefaction Unit (TU). A rotary kiln consists of a rotating cylinder that sits horizontally on an incline. Wet biomass is fed into the upper or "back end" of the kiln, while adequately hot (nearly 900°C) carbon monoxide (CO) gas is injected into the lower end or “front end” of the kiln. The biomass is heated by the hot CO gas and the heat is liberated by the reaction of CO with the steam emitted from the wet biomass as it moves down the kiln toward the front end. Biomass is totally dried at about 250°C and converted to torrefied biomass by losing some of its low-temperature volatile content which is about 5 to 10% of the dry biomass. Water gas shift reaction (WGSR), an exothermic equilibrium chemical reaction, takes place when CO gas reacts with steam (H₂O) to produce hydrogen (H₂) and CO₂ gases. The unused steam and the volatile gases are carried along with H₂ and CO₂ gases to exit from the back end of the rotary kiln. Radial scrapper rods are mounted on the stationary axle shaft which can move to and fro horizontally inside the rotary kiln to prevent sticking of hot biomass to the interior surface of the rotary kiln. The horizontal shaft is actuated by a camshaft to cause to-and-fro motion.

At the outlet of the rotary kiln, the gases are passed through a scrubber to separate solids and the condensed steam. The gases are further passed through a bed of zinc/metallic oxide to remove the sulfur-containing gases like H₂S, Carbonyl Sulphide (COS), etc. The cleaned gases pass through a final low-temperature WGSR reactor to eliminate any unreacted CO gas in the presence of a suitable catalyst. The gas mixture is further cooled close to ambient temperature by generating medium to high-pressure steam to condense steam and low-temperature volatile gases. During the gradual cooling of the gases, the low-temperature organic volatile compounds are condensed and extracted as value-added organic chemicals such as acetic acid, phenol, cresol, acetone, etc. These organic liquids are also injected into the Pyrolysis Unit (PU) for conversion into syngas if not found of any commercial use. The high BOD water condensed from the gases is sent to an anaerobic/biogas digester unit to convert the dissolved organic compounds into CH₄ gas. The cleaned gas rich in H₂ and CO₂ gases is passed through a sour gas separator to remove the excess CO₂ gas. Thus H₂-rich gas with noncondensable gases such as CO₂, CH₄, CO, etc is produced at near ambient temperature and the wet biomass is converted to torrefied biomass for further use or storage. The gas is also dried by passing through a desiccator.

The hot torrefied biomass (at around 250°C) is further transferred to another rotary kiln called Pyrolysis Unit (PU) by a vertical bucket conveyer or Olds elevator into the backend of the PU where hot CO gas is also injected to heat the biomass further to accelerate the pyrolysis process [7]. Waste plastic along with torrefied biomass can also be added to the PU for converting into syngas. Pyrolysis of biomass is a self-sustaining process at temperatures above 280°C and the process heating rate is maintained between 20 to 25°C/minute [8]. During the pyrolysis process up to 900°C, most of the biomass is converted to pyrolysis gases containing H₂, CO, CH₄, tar gases (volatile organic compounds), and unreacted carbon or biochar. Biochar along with ash is extracted from the front end and soaked in an insulated storage bin/hopper at high temperature for a few hours to liberate the residual volatile compounds. The alkali salts (particularly potassium) in the ash act as a catalyst to liberate CH₄, etc from the left-out hydrogen in the biochar [9].

The pyrolysis gases exit from the front end of the rotary kiln to pass through a scrubber to remove solid and liquid particles. The pyrolysis gases are passed through a sensible heat recuperator/heat exchanger to raise the gas temperature up to 1400°C. At this high temperature, the gases undergo an auto thermal gasification process without the requirement of any catalyst where methane and tar gases react with CO₂ and H₂O to generate syngas which is a mixture of CO, H₂, and CO₂ gases. The syngas is cooled close to ambient temperature by passing through recuperative heat exchangers to heat the pyrolysis gas and later to heat the CO₂ gas up to 700°C which is used for generating the needed CO gas with the biochar. The H₂-rich gas available from the TU is also sent to the Auto Thermal Reactor (ATR) through separate recuperator units to heat up to 1400°C. In the ATR unit, the feed gases rich in volatile gases and CH₄ undergo triple reforming (wet reforming with H₂O, dry reforming with CO₂, and partial oxidation) to yield syngas which is cooled (in recuperative gas coolers) and sent to a cleaning unit to suit the requirements of downstream methanol or H₂ or products of Fischer Tropsch [10][27]. The H₂/CO ratio of the syngas is controlled by varying the hot CO gas feed to the PU.
The CO-Production Unit (COPU) is also a rotary kiln that uses CO₂ gas extracted from the TU and the biochar produced from the PU. The heated CO₂ gas up to 700°C by the hot syngas from the ATR unit is further heated in the sensible heat recuperator by the hot CO gas up to 1400°C that is exiting from the COPU. The CO₂ gas at nearly 1300°C is fed to the rotary kiln where it comes in contact with the biochar and O₂ gas to convert CO₂ gas into CO gas at around 1400°C. No catalyst is required as the CO₂ gas conversion to CO gas at high temperatures is feasible. The purpose of O₂ gas is to produce needed heat energy in an exothermic reaction by reacting with biochar to produce CO. The generated heat is used to achieve the endothermic reaction of CO₂ with carbon to produce CO gas. The hot CO gas from the rotary kiln/COPU is cooled to 800°C by the incoming CO₂ in the recuperative heat exchanger before sending it to the TU and PU. Ash is extracted in semi-liquid form from the COPU rotary kiln with negligible unburnt carbon.

The liquid effluents from the TU are sent to an anaerobic digester for generating biogas and the effluents are later sent to an oxidation pond to reduce the BOD totally by aeration. The treated water available from the oxidation pond is filtered before being sent to a multi-stage flash distillation to produce potable water using the medium-pressure steam generated from the TU, etc. CH₄ gas is separated from the biogas which is a mixture of CH₄ and CO₂ gases. The solid organic sludge or digestate produced from the anaerobic digester unit is also fed to the TU.

### III. DISCUSSION

A three-stage gasification process is selected to have more control over the process with reliability, to separate excess moisture available in the biomass, and to achieve a tailored mix of the syngas from three syngas streams each one rich in CO or H₂ or CO₂ gases. Single-stage biomass gasification technologies used in the industry are fraught with the requirement of dry biomass (up to 20% moisture) feed requirement, ash fusion problems in the reactor and there is no scope to recuperate the heat energy available in the syngas back into the process except for producing electricity as a by-product from the syngas cooling. There has been no remarkable technological advancement in the last 10 years despite the universal acceptance of substituting fossil fuels with carbon-neutral fuels [11, 12, 13]. As the heat is recycled back to the process, the final product (methanol, H₂, and FT products) generation is optimized from the unit weight of dry biomass.
In the torrefaction process, hot CO gas reacts with the steam emitted from the wet biomass and generates H₂ by liberating heat. Thus whole biomass gets dried up and also liberates low-temperature volatile gases and CH₄ (by methanation reactions). Some sulfur content present in the biomass reacts with the CO gas to form carbonyl sulfide (COS) and H₂S gases which are separated by using suitable metal/zinc oxide as an absorbent. A rotary kiln is selected as it is suitable for the hot CO gas to come in contact with the biomass without much pressure loss and the rotary kiln is also suitable for larger unit capacities. Rotary kilns are used extensively in the cement industry to heat the raw material up to 1500°C to produce cement clinker in dry or wet processes. Rotary kilns are also used in coal-based sponge iron manufacturing to produce direct reduced iron [14]. The same proven technology can be adopted readily for TU, PU, and COPU in biorefineries to achieve the scale of economics.

| Table 1: Process Parameters at Various Moisture Contents of the Biomass for Methanol Generation |
|-----------------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Moisture in wet biomass by weight.            | 20%           | 35%           | 41%           | 50%           | 60%           | 75%           | 80%           | 85%           | 90%           |
| Biochar (kg) extracted or consumed (-) per kg of methanol produced | 0.21          | 0.67          | 0.0           | -0.12         | -0.25         | -0.47         | -0.51         | -0.57         | -0.64         |
| Dry biomass + extra biochar (kg) consumed per kg of methanol | 1.8           | 1.57          | 1.51          | 1.39          | 1.26          | 1.06          | 1.01          | 0.95          | 0.88          |
| Oxygen consumed (kg) per kg of methanol | 0.26          | 0.30          | 0.31          | 0.35          | 0.38          | 0.43          | 0.45          | 0.47          | 0.48          |
| Carbon utilization efficiency or carbon in biomass used in generating methanol (%) | 0.54          | 0.53          | 0.53          | 0.52          | 0.51          | 0.51          | 0.50          | 0.50          | 0.50          |
| CO₂ generated (kg) per kg of methanol | 1.15          | 1.20          | 1.23          | 1.26          | 1.28          | 1.34          | 1.35          | 1.38          | 1.39          |
| Nitrogen gas produced (kg) from ASU per kg of methanol | 0.86          | 0.99          | 1.04          | 1.16          | 1.26          | 1.45          | 1.50          | 1.56          | 1.62          |
| Steam produced (kg) from one kg of methanol synthesis. | 0.95          | 0.90          | 0.96          | 0.96          | 1.14          | 1.41          | 1.38          | 1.44          | 1.63          |

Hot CO gas is added to the PU as it will maintain the needed biomass temperature and also enhance the CH₄ gas formation in the presence of alkali compounds of the ash which act as a catalyst [9]. The added CO gas also works to achieve the tailored mix (H₂/CO gas ratio) of syngas needed for conversion to the final selected product. In PU, sulfur in the biomass reacts with calcium oxide (CaO) to form calcium sulfite (CaSO₃) in the absence of O₂. CaSO₃ melts at 600°C and is removed as molten ash from the gas scrubber along with particulate matter. In case the calcium oxide content is lower than the requirement in ash, CaCO₃ (powdered limestone) is added externally in the PU to remove the sulfur [CaCO₃ + SO₂ → CaSO₃ + CO₂]. Any H₂S gas liberated from biomass also reacts with CaO to form CaS. Any hydrochloric acid (HCl) emitted from the chlorine content of biomass/waste plastic reacts with the CaO and forms calcium chloride (CaCl₂) which melts at 770°C. CaCl₂ further reacts with the phosphates (PO₄) in the ash to form calcium triphosphate [Ca₃(PO₄)₂] releasing HCl vapors. The process repeats till all the phosphates in the ash are converted to Ca₃(PO₄)₂. Chlorine gas also reacts with sodium and potassium salts in the biomass to form sodium or potassium chloride which melts at around 800°C. Carbonates and bicarbonate compounds in the ash are converted to oxides and further to sulfites and chlorides, Ca₃(PO₄)₂, CaCl₂, CaSO₄, and other potassium compounds in the generated ash can be used as fertilizer, particularly in alkaline soils. Any fluorine gas liberated by the biomass reacts with sodium and calcium salts to form fluorides. Thus, ash is converted to useful minerals with fertilizer value with less unwanted silica and aluminum salts. Nitrogen in the biomass may react with H₂ to form ammonia (NH₃) gas and there is little possibility of NO₂ formation due to a lack of O₂, NH₃, NO₃, and residual NO are removed in the final syngas cleaning process to suit the downstream uses. Biochar mixed with ash is extracted from the PU for subsequent use in the COPU where ash is separated from the biochar. In auto-thermal reactions, no external heat input is required except for maintaining a suitable temperature to initiate the reactions as the pyrolysis gases are rich in oxygen to react with the CO₂ and H₂O to form syngas rich in CO and H₂ gases [15]. CH₄ also undergoes a dry reforming process with CO₂ to convert into CO and H₂ (syngas). The auto-thermal reactions take place at high temperatures above 1000°C without the need for any catalyst. It is proposed to use sensible heat recuperators to heat the pyrolysis gases up to 1400°C maximum, before entering the auto thermal reactor (ATR), by the hot syngas exiting the ATR. Conventional tubular heat exchangers with metallic or ceramic tubes are not suitable for high temperatures applications above 700°C with reliable performance. Only recuperative heaters are suitable to withstand the required high temperatures (up to 1500°C) by using ceramic material made of alumina or zirconium oxide. O₂ gas is supplied to the ATR during the unit start-up to achieve the required operating temperature. Steam or CO₂ is used to control the temperature in the ATR. The entire three-stage gasification process is designed for pressurized operation up to 5 bar similar to blast furnaces in the steel industry which are also subjected to 1350°C furnace wall temperature similar to recuperative heaters of the proposed system [16]. The kinetics of WGSR will not affect adversely at pressurized conditions as the molar volumes of product gases (H₂ and CO₂) are unchanged from the reactant gases (steam and CO). A recuperative/thermocline heater consists of a pair of insulated casings filled with ceramic material and phase change material (PCM) with adequate voids to facilitate the passing gas to be heated or cooled [17]. Initially, hot syngas is passed through the heater to transfer the heat contained in the syngas to the heat storage material (i.e. ceramic material and PCM) for some duration till the heat storage material is heated up to the required temperature. Later pyrolysis gases are passed through the hot heater in the reverse/current-direction to extract heat by the pyrolysis gases close to the hot syngas temperature. To achieve a continuous operation, one heater is used for heat extraction from the hot outgoing syngas while the other heater is used for heating the incoming pyrolysis gases to the ATR in a cyclical operation. The recuperative heaters are insulated with layers of high-temperature refractory material made of alumina and silica to withstand high temperatures (up to 1500°C) at the required operating pressure. The applicable technology is extensively used in steel making by blast furnace route to achieve nearly 1400°C temperature inside the furnace.
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It is feasible to design and manufacture recuperative heaters and rotary kilns with operating temperatures up to 1400°C and working pressures up to 5 bar with the available proven technologies by selecting suitable ceramic heat transfer material and PCM. Recuperative heaters are also proposed to heat the CO₂ gas up to 1400°C in two steps first by the syngas and later by the hot CO gas as shown in Figure 2 to conserve the available heat energy. Also, H₂-rich gas (lean syngas) at ambient temperature from the TU is heated to 1400°C before entering the ATR unit to reform the residual CH₄ and other noncondensable organic gases into syngas.

In PCM application, heat is stored by the material in the form of latent heat while phase change from solid to liquid is taking place. A few layers of PCM at the hot gas entry of the heat recuperator would enhance the thermal storage capacity substantially reducing the size of the unit and in turn its cost. Ferro silicon material with different compositions (silica to iron ratio) was found very suitable for high-temperature applications up to 1400°C as it has a very high latent heat of fusion (nearly 1787 kJ/kg) and low variation in density from solid to liquid phase [18]. PCM materials are embedded inside spheres made of ceramic material like alumina/zirconium oxide so that liquid phase change takes place while storing the heat.

Table 2: Process Parameters at Various Moisture Contents of the Biomass for Hydrogen Generation.

<table>
<thead>
<tr>
<th>Moisture in wet biomass by weight</th>
<th>20%</th>
<th>35%</th>
<th>41%</th>
<th>50%</th>
<th>60%</th>
<th>75%</th>
<th>80%</th>
<th>85%</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biochar (kg) extracted or consumed (+) per kg of hydrogen produced</td>
<td>1.10</td>
<td>0.35</td>
<td>0.03</td>
<td>-0.64</td>
<td>-1.28</td>
<td>-2.39</td>
<td>-2.69</td>
<td>-3.03</td>
<td>-3.40</td>
</tr>
<tr>
<td>Dry biomass + extra biochar (kg) consumed per kg of hydrogen</td>
<td>8.93</td>
<td>8.21</td>
<td>7.90</td>
<td>7.90</td>
<td>6.64</td>
<td>5.57</td>
<td>5.29</td>
<td>4.96</td>
<td>4.61</td>
</tr>
<tr>
<td>Hydrogen produced (%) from dry biomass + extra biochar</td>
<td>11.3%</td>
<td>12.2%</td>
<td>12.7%</td>
<td>12.7%</td>
<td>15.1%</td>
<td>17.9%</td>
<td>18.9%</td>
<td>20.2%</td>
<td>21.7%</td>
</tr>
<tr>
<td>Oxygen consumed (kg) per kg of hydrogen</td>
<td>1.35</td>
<td>1.54</td>
<td>1.63</td>
<td>1.81</td>
<td>1.98</td>
<td>2.27</td>
<td>2.35</td>
<td>2.44</td>
<td>2.54</td>
</tr>
<tr>
<td>Energy consumed by hydrogen (cal/kg)</td>
<td>33814</td>
<td>33563</td>
<td>33455</td>
<td>33233</td>
<td>33016</td>
<td>32645</td>
<td>32547</td>
<td>32433</td>
<td>32309</td>
</tr>
<tr>
<td>Nitrogen gas produced (kg) from ASU per kg of hydrogen</td>
<td>4.51</td>
<td>5.17</td>
<td>5.46</td>
<td>6.05</td>
<td>6.62</td>
<td>7.60</td>
<td>7.86</td>
<td>8.17</td>
<td>8.50</td>
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<tr>
<td>Steam produced (kg) from one kg of hydrogen</td>
<td>2.74</td>
<td>3.37</td>
<td>3.63</td>
<td>4.09</td>
<td>4.98</td>
<td>5.96</td>
<td>6.20</td>
<td>6.50</td>
<td>6.75</td>
</tr>
</tbody>
</table>

Mass and heat balance calculations of the process are performed to find out the specific biomass consumption (including biochar), carbon use efficiency, etc. at different moisture contents of wet biomass. To convert CO₂ gas into CO with biochar, external heat input is required which can be supplied by using additional biochar with oxygen. Surplus biochar is preserved while using dry biomass, but less than 41% moisture by weight for later use of higher wet biomass up to 90% moisture content. The required heat supplementation from biochar partial oxidation needs an Air Separation Unit (ASU) to supply O₂ for the combustion of biochar to CO gas. Nitrogen as a by-product is available from ASU which can be sold to food processing units, second-generation ethanol units, and ammonia production units with additional income. It is also possible to use aluminum (Al) scrap (if cheaply available) in place of biochar [19]. When COPU is fired with Al, alumina/aluminum oxide is produced as a solid residue which has good sale value to compensate for the high cost of the Al scrap. There is also the possibility of aluminum carbide (Al₄C₃) formation which reacts with water to give methane gas (CH₄) and aluminum oxide. Various byproducts generated for one kg methanol production are given in Table 1. Also, the cost of green methanol produced is around 450 US$/tonne when the dry biomass purchase price is 200 US$/tonne which is economical when cheaper natural gas is not available. Various byproducts generated for one kg hydrogen production are given in Table 2. On average 12.7% of H₂ by weight can be produced from dry biomass. The estimated production costs of methanol and hydrogen at various dry biomass purchase prices are given in Table 3. It is found from the cost analysis that H₂ gas can be produced from biomass below 2 US$/kg from biomass when dry biomass is procured below 200 US$/tonne whereas the prevailing market price of biomass pellets is nearly 135 US$/tonne (INR 10, 000/tonne). The equivalent natural gas (CH₄) price is nearly 10 US$/per million British thermal units (mmbtu) to match the H₂ production cost from biomass at 200 US$/tonne. The biomass unit is applicable to a natural gas-based unit. No premium is charged to the carbon-neutral H₂ from the biomass when compared with the grey hydrogen produced from the natural gas or the associated carbon sequestration cost is not accounted for.

IV. CONCLUSION

The proposed three-stage biomass gasification process has versatile applications as it can use any fresh biomass up to 90% moisture to produce a tailored mix of syngas for optimum use in the downstream production of methanol, hydrogen, and FT process-derived fuels/chemicals at par with market prices of similar products derived from fossil fuels like natural gas/LNG. The process is highly optimized by reusing the energy available in the process with sensible heat recuperators which is the crucial and novel technology incorporated in the process. The proposed gasification process is versatile as it is also suitable for the use of MSW, STP sludge, medical organic wastes, waste plastic, and industrial organic waste material. Carbon neutral CO₂ gas available from the biomass gasification process is similar to the CO₂ gas captured from the air in carbon capture utilization and sequestration (CCUS) methods to earn carbon credits. The process has an overall positive impact on the environment with minor water pollution, low water footprint, and minor solid waste disposal. When moderate carbon credits are offered to the carbon-neutral fuels or chemicals generated from biomass gasification, the farmers would be the major beneficiaries by reaping higher biomass sale prices at par with food grains prices (wheat or paddy) with a few times more enhanced disposable income from the same cultivated land which will improve drastically the living standards of the rural population.
The carbon-neutral CO₂ gas available from standalone biorefineries can be sequestered by storing in underground caverns permanently or depleted crude oil deposits for enhanced oil recovery so that fossil fuels (crude oil or natural gas) can be branded as a carbon-neutral fuel. CO₂ gas can also be injected into depleted natural gas deposits for sequestration. Nearly 3.11 tonnes of carbon-neutral CO₂ is to be sequestered to brand one tonne of fossil crude oil into carbon-neutral crude oil and nearly 2.75 tonnes of carbon-neutral CO₂ for one tonne of natural gas. In case a carbon credit of US$ 30 per tonne is paid for the sequestration of carbon-neutral CO₂, it would add nearly US$ 93 per tonne (nearly 13 US$ per barrel to procure carbon-neutral CO₂ gas) to the production cost of crude oil (at 85% carbon content). Alternatively, carbon-neutral CO₂ can be used as feedstock to generate green CO₂ gas and H₂ from water along with renewable green energy (like solar PV, solar thermal energy, wind energy, etc.) to produce carbon-neutral CH₄ (nearly 2.75 tonnes of CO₂ to produce one tonne of CH₄), methanol (nearly 1.375 tonnes of CO₂ to produce one tonne of methanol), and FT process fuels/chemicals using solar thermal energy [20,21]. Out of the 12 billion tonnes of dry biomass supply per year globally in 2020, nearly 23 % is used for energy purposes excluding the biomass burnt in the fields [22][26]. It accounts for 2.76 billion tonnes of dry biomass which can produce nearly 1.83 billion tonnes of methanol (0.91 billion tonnes of CH₄ in terms of heating value) at 53% carbon use efficiency. Another 2.23 billion tonnes (refer to Table 1) of carbon neutral CO₂ gas is available which can produce nearly 1.63 billion tonnes of methanol by using solar energy. The total carbon-neutral methanol production potential from the 2.76 billion tonnes of biomass is equal to nearly 3.45 billion tonnes/year or 9.47 million tonnes/day. It is equivalent to nearly 5.79 million tonnes of crude oil/day in terms of heating value or 35 million barrels/day which is 35% of the crude oil production in the year 2022. In case most of the presently used biomass for energy generation purposes is replaced by renewable electricity derived from wind power, solar energy, etc nearly 2.76 billion tonnes of biomass can be made available for the production of organic chemicals, aviation fuels, marine fuels, etc that are uneconomical to produce by renewable electricity/energy with carbon capture from air. The future peak demand for these biofuels at enhanced per capita consumption of the global peak population can be fully met by enhancing the dry biomass availability by 3 billion tonnes/year by converting nearly 6 million km² of desert/semidesert lands into productive agriculture and forest lands by harnessing the global water resources [23]. In addition, carbon-neutral electricity can be produced adequately for the requirement of the global peak population from renewable solar and wind power potential to replace the rest of the fossil fuels consumption totally for achieving a carbon-neutral global economy.

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REFERENCES

Carbon Neutral Fuels and Chemicals from Standalone Biomass Refineries


