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# EXPERIMENTAL INVESTIGATION AND PRODUCTION OF BIO-METHANOL THROUGH GASIFICATION OF BIO-MASS

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## ABSTRACT

**In this project, the process of converting the waste Biomass into the value added fuel, Bio-Methanol. Currently researches are looking for Methanol production from waste Biomass. The waste biomass feedstock is converted to Syn-gas, a mixture of Carbon monoxide, Hydrogen and other molecules through Gasification. The required $H_2$ for Syn-gas production is supplied by electrolysis method. The Syn-gas is converted into Bio-methanol by chemical reaction on Potassium hydroxide and $Br_2ccl_4$ solution. Thus, the process of production of methanol from biomass is similar to coal gasification process. Presently the researches are looking for the possibilities to use Bio-methanol as transportation fuels.**

**KEYWORDS:** Bio-methanol, Syn-gas, Gasification of Bio-waste,

Methanol is one of the most important platforms for chemical production in chemical industries. Currently methanol is used to make purposes like anti-knocking agents and blended with fuels and as anti-freeze. Present researches are looking into possibilities to use methanol as a transportation fuels. The global production of methanol is based almost entirely in natural gas. Concerns over climate change, fossil fuels depletion and prices of natural gases cause interest in production of bio-methanol from renewable feed stocks.

Bio-methanol can be produced from waste biomass, non-biogenic waste streams or even $CO_2$ from flue gas. The feed stocks are converted into syn-gas, a mixture of Carbon monoxide, Hydrogen and other molecules through Gasification. To decrease the environmental impact of bio-methanol production, the required hydrogen is supplied through electrolysis. Bio-methanol is chemically identical to conventional methanol. The production of bio-methanol will reduce the need for fossil fuels and nuclear energy consumption and will reduce Greenhouse gas emission.

Syn-gas plays a major role as an intermediate in production of methanol. Syn-gas from renewable recourses, such as biomass, exhibits a promising prospective. This is because biomass is a $CO_2$ neutral resource. The syngas is converted into methanol by a catalytic process based on copper oxide, zinc oxide or chromium oxide catalysts. Distillation is used to remove the water generated during methanol synthesis. Oxygen is typically produced via cryogenic air separation (large capacities that are well suited for methanol production), pressure swing adsorption (PSA, small- to mid-size capacity), or electrolysis. The technologies used in the production of methanol from biomass are relatively well known since they are similar to the coal gasification technology, which has been applied for a long time. However, making biomass gasification cost-competitive has proven difficult.

Methanol can be produced from biomass through a thermo chemical process known as gasification. The biomass is subjected to elevated temperatures and pressures (in some processes) to form a synthesis gas (syngas). The syngas (a mixture of carbon monoxide and hydrogen) is conditioned to remove impurities such as tars and methane, and to adjust the hydrogen-to carbon monoxide ratio to 2: l. The syngas is then reacted over a catalyst at elevated temperatures and pressures to form methanol.

## LITERATURE REVIEW

An extensive survey of technical journals, internet and books related to Methanol synthesis was done before embarking on the project. This was done to keep ourselves abreast with the latest developments in the field. A brief summary of the technical articles collected from the technical journals are given below.

### Methanol Synthesis

Specht & Bandi, discussed the main processes in a conventional methanol plant are: gasification, gas cleaning, syn-gas conditioning (reforming of high hydrocarbons, water-gas shift, hydrogen addition, CO2 removal) and methanol synthesis and purification. First, a specific syn-gas composition can be reached by combining syn-gas from different sources or gasifying different feed-stocks simultaneously. The crude syn-gas from biomass usually has a low hydrogen-to-carbon (H/C) ratio, whereas syn-gas from natural gas has a very high H/C ratio. The aim of the syn-gas conditioning step is to produce syn-gas that has at least twice as many H2 molecules as CO molecules. The

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optimal ratio of H2 molecules to CO molecules depends on the initial syn-gas composition, as well as the availability of H2.

Yin Xiuli, discussed that Bio-methanol can be produced from virgin or waste biomass, non-biogenic waste streams or even CO2 from flue gases. These feedstocks are converted (typically through gasification) into syngas, a mixture of carbon monoxide, hydrogen and other molecules. The syngas is subsequently conditioned through several steps to reach the optimal composition for methanol synthesis (e.g. by removing CO2 or adding hydrogen). To decrease the environmental impact of bio-methanol production, it has been proposed to use renewable electricity to supply the required hydrogen through electrolysis. After conditioning, the syngas is converted into methanol by a catalytic process based on copper oxide, zinc oxide or chromium oxide catalysts. Distillation is used to remove the water generated during methanol synthesis.

C.M. Van der meijden, H. Veringa, suggested that Methanol can be produced from biomass through a thermochemical process known as gasification. The biomass is subjected to elevated temperatures and pressures (in some processes) to form a synthesis gas (syngas). The syngas (a mixture of carbon monoxide and hydrogen) is conditioned to remove impurities such as tars and methane, and to adjust the hydrogen-tocarbon monoxide ratio to 2: l. The syngas is then reacted over a catalyst at elevated temperatures and pressures to form methanol.

Sudeep mohapatra, Lalit Mohan Sahu, concluded the Methanol fuels produced from biomass feedstocks can reduce net greenhouse gases from automobile emissions. The biomass feedstock takes up carbon dioxide during growth— in amounts equal to those emitted during combustion—creating a "carbon cycle." Methanol's high heat of vaporization results in lower peak flame temperatures than gasoline and, therefore, lower nitrogen oxide emissions. Its greater tolerance to lean combustion (higher air-to-fuel) ratios results in generally lower overall emissions and higher energy efficiency. In addition, production of methanol from biomass can turn municipal, industrial, agricultural, and forestry wastes into energy resources.

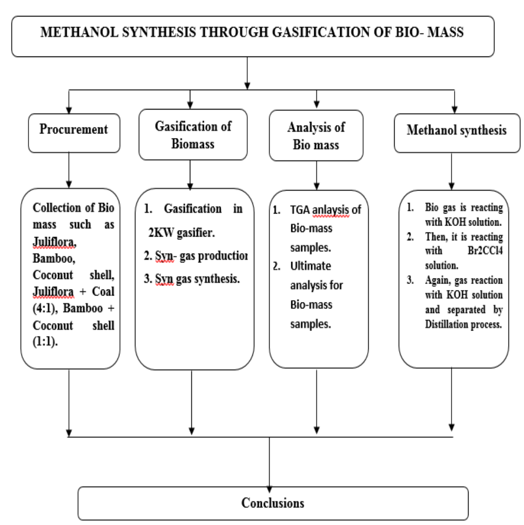
**Syn- gas producion**

Demirbas- A, discussed that Syngas production from direct biomass gasification, which may be more economically viable. The ratio of H2/CO is an important factor that affects the performance of this process. In this study, the characteristics of biomass gasification gas, such as H2/CO and tar yield, as well as its potential for liquid fuel synthesis is explored.

Demirbas- A, concluded the making H2 and CO (syngas) from biomass is widely recognised as a necessary step in the production of various second generation biofuels. There are two major ways to produce a bio syngas: fluidised bed gasification with catalytic reformer or entrained flow gasification. The latter option requires extensive pre-treatment such as flash pyrolysis, slow pyrolysis, torrefaction, or fluidized bed gasification at a low temperature. Cleaned and conditioned bio syngas can be used to synthesize second generation biofuels such as Fischer-Tropsch fuels, methanol, DME, mixed alcohols, and even pure hydrogen.

A. van der Drift, H. Boerrigter, suggested the quality of syngas will affect the technical and economic aspects of the whole system, and dictate the selection of downstream facilities. It is thus important to know what the gas composition would be under different gasification conditions and to identify those conditions that would be optimal for methanol production. Theoretically, a syngas with a H2/CO ratio of 2.0, which is appropriate for methanol synthesis to get high yield without the need to perform the shift reaction.

## METHODOLOGY



## EXPERIMENTAL SETUP AND DISCRIPTION

**Figure 1: 2KW Gasifier.**

The above figure is 2KW gasifier. The total capacity of the gasifier is 8Kg.

**Figure 2: 3 Stages of Reaction for Methanol Synthesis**

3 Stages of reaction: 1st bottle contains KOH solution, second $Br_2CCl_4$ solution and 3rd bottle is again KOH solution.

### Experimental Procedure

*1)* Preparation of Raw materials:

Bio mass samples are collected and sorte according to catagories. Finally, it was shreaded and cutted into small pieces for ease of feeding the raw materials and for good heat transfer. 5 Kg of each samples was weighed and feed to reactor and the reactor was properly sealed to protect the gas leaking. adequate precautions were put in place to make sure there is no leakage before start of experiment.

*2)* Process discription:

*a)* Gasification Of Different Bio Mass:

All bio-mass samples (Juliflora, Bamboo and Coconut shell, Juliflora + Coal (4:1), Coconut shell + Bamboo (1:1)) are taken for Gasification process. First, the compositions of each biomass samples were analysed through Proximate and Ultimate analysis and then each 5 Kg of samples were combust in 2KW gasifier and temperature maintained at $700^0$-$750^0$C for complete combustion of bio mass feed stock. The gas from gasifier is stored in gas container and gas composition is analysed through Gas analyser.

*b)* Syn gas production:

Syngas was produced through gasification of biomass and bio charcoal. Syngas production is the basic step of methanol synthesis from biomass. Although many gasification methods have been developed in recent decades, there is still limitation on applying the technology in a large scale economically and much more research works are needed. Most of the postulated concepts to produce methanol from biomass are based on steam-oxygen gasification, and the important factors that affect the commercial viability of methanol synthesis are the system efficiency and investment cost. Air-steam gasification, however, has been considered a better solution which can balance between gas quality and investment. Oxygen-rich air is also a substitute for pure oxygen to reduce investment and cost. Experiments based on air-steam gasification and catalytic gasification were carried out using a fluidized bed gasifier to explore the possibility of producing syngas from biomass. Experiment based on oxygen-rich gasification was also performed using a CFB gasifier to investigate the economic feasibility as a substitute for pure oxygen gasification. The gas composition is analysed by Gas Analyser.

*c)* Methanol synthesis:

The syn gas produced from gasifier was taken for chemical reaction. The chemicals used for methanol production are KOH, Br2Ccl4. First, the syngas is passed through KOH solution, the reaction takes place and KOH solution absorb carbon dioxide in the syngas. Then syngas is made to react with red colour Br2CCl4, syn gas is converted to Methyl Bromide. Again, it is made to react with KOH solution which convert Methyl Bromide to Methanol. Methanol is dissolved in KOH solution which is separated through distillation process such as evaporation and condensation process from KOH solution.

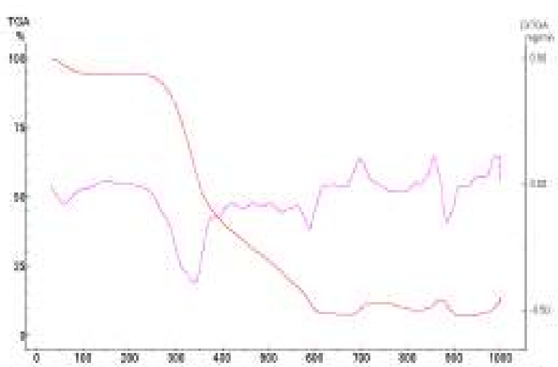
## RESULTS AND DISCUSSION

### Thermo Gravemetric Analyser

*3)* Analysing Procedure

- The sizes of all the particles of the samples were less than 0.8 mm. The initial weights of the samples for all conditions were 8 mg with variation of 0.5 mg.
- The TGA was carried out for all the bio materials. The sample temperature was measured with S type thermocouple directly under Platinum crucible under nitrogen atmosphere. The flow rate of gas is 20 ml/min. And the heating rate was 20 °C /min.
- Bio mass samples such as Juliflora, Coconut shell, Bamboo and Juliflora mixed with Coal (20%) are taken 0.75 mg to 1.5 mg each for our experimentation on Thermo Gravimetric Analyzer.
- That Bio mass samples can be tested by increasing temperature on Thermo Gravimetric Analyzer machine and then the weight loss can be noted down at every temperature.
- Normally wood samples losses most of its weights under 650° - 900°c as per the result graph plotted.

*4)* TGA Results



**Fiure 3: JULIFLORA**

From the above graph, TGA curve was indicating that, the weight was started from the temperature of 800c. The maximum weight was lost between temperature of 3000c to 4000c. The two peak was found in this TGA curve at temperature of 700°c(approx.) and 850°c(approx.).

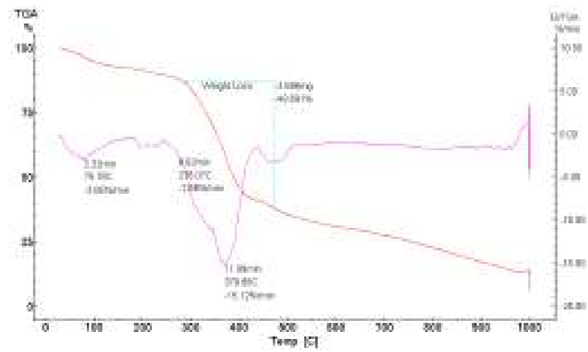


**Figure 4: Juliflora (80%) + Coal (20%)**

From the above graph, TGA curve was indicating that, the weight was started from the temperature of $80^0$c. The maximum weight was lost between temperature of $350^0$c to $500^0$c. Then gradual reduction of weight of sample from $500^0$c to $950^0$c.

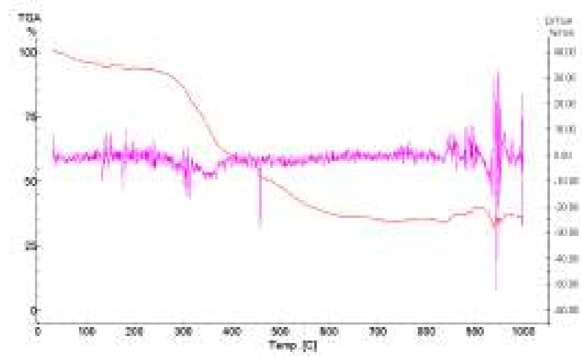


**Figure 5: Coconut Shell**

From the above graph, TGA curve was indicating that, the weight was started from the temperature of 300°c. The maximum weight was lost between temperature of 300°c to 550°c. The one peak was found in this TGA curve at temperature of 900°c.

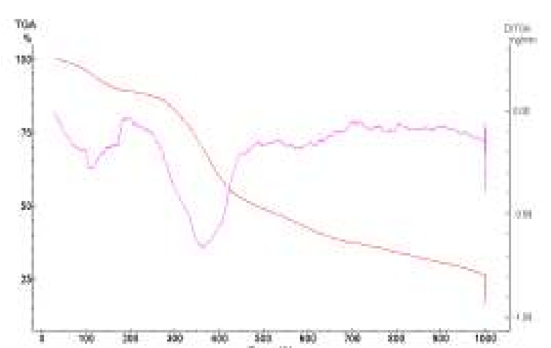


**Figure 6: BAMBOO**

From the above graph, TGA curve was indicating that, the weight was started from the temperature of 800°c. The maximum weight was lost between temperature of 350°c to 600°c.

*B.* Ultimate Analysis

The biomass substance consists of organic compounds of carbon, hydrogen and oxygen matter. The ultimate analysis shows the following components on mass basis: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S), moisture content (M), and ash (A). Therefore,

C + H + O + N + S + M + A =100% 0f mass. (1)

Moisture content of the bio mass is calculated by two methods: Wet basis or Dry basis. In case of wet basis, the moisture content is equal to the mass of water in the fuel divided by total mass of the biomass. The moisture content has big effect to net calorific value reached at burning process. The moisture content is stated as weigh % of the wet base.

To calculate the moisture content of biomass.

Moisture content = WET – DRY/ WET x 100 (2)

**Table I: Ultimate Analysis of Bio Mas**

| S. No | Sample | Weight of Wet Sample (g) | Weight of Dry Sample (g) | Moisture Content in % | Calorific Value (KJ/Kg) |
|---|---|---|---|---|---|
| 1. | Juliflora | 15.47 | 15.33 | 0.9 | 390.30 |
| 2. | Bamboo | 20.85 | 20.39 | 2.2 | 370.06 |
| 3. | Coconut shell | 23.44 | 23.21 | 0.9 | 413.86 |

To calculate calorific value [7]

Btw/pound = 145C + 610 ($H_2$-1/8$O_2$) + 40 S+ 10 N (3)

To calculate C, H, O, N, S, ASH

C in % = 0.495 x WEIGHT OF SAMPLE

H in % = 0.006 x WEIGHT OF SAMPLE

O in % = 0.427 x WEIGHT OF SAMPLE

N in % = 0.0002 x WEIGHT OF SAMPLE

S in % = 0.001 x WEIGHT OF SAMPLE

ASH in % = 0.015 x WEIGHT OF SAMPLE

*C.* Gas Composition From 2kw Bio Gasifier For Different Samples

**Table II: Gas Composition for Different Biomass Samples**

| S. N. | Samples | % Of Gas Composition | | | | | Calorific Value [KJ/Kg] |
|---|---|---|---|---|---|---|---|
| | | $H_2$ | $CO_2$ | CO | $CH_4$ | $O_2$ | |
| 1. | Juliflora | 5.81 | 6.53 | 5.73 | 1.28 | 10.61 | 491 |
| 2. | Coconut shell | 6.11 | 5.2 | 6.42 | 2.24 | 10.89 | 685 |
| 3. | Bamboo | 6.89 | 6.2 | 6.01 | 3.6 | 11.2 | 593 |
| 4. | Juliflora + Coal (20%) | 8.23 | 6.77 | 7.47 | 2.35 | 10.66 | 619 |
| 5. | Coconut shell + Bamboo | 6.32 | 8.28 | 5.20 | 1.12 | 11.16 | 406 |

5 Kg of sample feed stock is burned in 2KW Bio gasifier and the temperature is maintained at $700^0$-$950^0$C for complete combustion of feed stock. The temperature is maintained by thermocouple and gas compositions are measured using gas analyser.

The gas produced in 2KW Gasifier is collected and stored for Methanol synthesis. The syn gas produced is analysed and by comparing all bio mass samples gas composition further it is proceded for methanol synthesis.

## DISSCUSION

The gas composition of five samples are tabulated above which are analysed by gas analyser.

Sample 1: Juliflora

The calorific value of juliflora is comparatively low when compared to other samples. The ratio of H2 and CO is 1:1 which is in acceptable range for methanol synthesis. CO2 in gas composition is nearly 7% so it is reduced by reacting with KOH solution.

Sample 2: Coconut shell

The calorific value of coconut shell is higher than other samples. The ratio of H2 and CO is nearly 1:1 and it is higher than other samples which is best suitable for methanol synthesis.

Sample 3: Bamboo

For bamboo calorific value and Hydrogen percentage is higher than others but the carbon dioxide in bamboo is 2 times higher than other samples. CO2 affect the methanol synthesis. CO2 is removed by reacting Bio gas with KOH solution, which absorb CO2 molecule from the biogas.

Sample 4: Juliflora + Coal (20%)

Coal is mixed with Juliflora at the ratio of 1:4. By comparing the gas composition with Juliflora the calorific value as well as H2 and CO are increased. But CO2 also gradually increased.

Sample 5: Coconut shell + Bamboo

These samples are mixed in the ratio of 1:1. The calorific value is drastically reduced compared to individual samples. Comparing all other samples, these have high CO2 percentage which leads to compulsory catalytic reaction with KOH solution to reduce carbon dioxide.

Comparing all the samples, coconut shell and the mixture of juliflora and coal has high H2 and CO ratio. And all the above samples require KOH reaction for CO2 reduction.

**Methanol Synthesis**

- Methanol synthesis from syngas is carried under 3 stages of reactions.
- The syn gas produced through gasification is made to react with 20% of KOH solution. Carbon dioxide in syn gas is absorbed by KOH solution.
- Then, syn gas was made to react with $Br_2CCl_4$ solution. This converts syn gas into methyl bromide which is collected and stored in a container.
- The Methyl bromide is made to react with excess amount of KOH solution which convert Methyl bromide to Methanol.
- The Methanol is separated from KOH solution through Distillation process.
- Thus, Methanol was separated by Evaporation and Condensation from KOH solution.

## CONCLUSSION

The maximum calorific value is obtained in the range of 685 KJ/Kg. And the maximum $H_2$ and CO ratio is 1:1. Further testing is required to be carried out in order to better assess and to improve the overall performance. Issues arises during the trial run is elaborately discussed and kept open for deeper investigation.

The issues are requirement of input power for supplying steam through electrolysis and presence of oxygen and excess $CO_2$ in syn gas. Oxygen is reduced by steam gasification where steam is passed through electrolysis process. $CO_2$ is reduced by reacting it with KOH solution before methanol synthesis.

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