

Production of Biogas Fuel from Alcohol Distillery Plant

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Abstract- Due to limited availability of natural fuels like Gasoline, diesel, LPG etc, scientists are going to research on agricultural based fuels. Many countries like Brazil, USA, New Zealand, India, etc, are using alcohols blended gasoline and biodiesel blended diesel. The increase in capacity of the distilleries to produce fuel-grade and chemical grade ethanol will immensely increase the water pollution problem ,due to generation of large volume of distillery waste water (DWW) having high biological oxygen demand(BOD), chemical oxygen demand (COD) with high color intensity.

Thermal treatment at pH 0-1 and $T = 1400^{\circ}\text{C}$ with a C_w of 3 kg/m^3 are maximum COD reduction of about 70% from its initial value of 34 kg/m^3 . The COD and BOD reduction were due to formation of solid residues.

From the distillery units we can not only get ethanol ,chemicals but we can also get bio-gas fuel and solid residues fuel by treatment of waste water from same unit .These can be our future fuels.

Index Terms- Thermal treatment, catalytic thermolysis, biodigester effluent, charred residue, distillery Spent wash.

I. INTRODUCTION

In India the alcohol is produced in the distilleries mostly by fermentation of molasses. Alcohol is separated from the fermented product in distillation column as top product. The bottom product is waste, which is known as distillery waste water (DWW). The distillery waste water which produces from molasses/sugar cane juice is dark brown in color and has very high COD ($60\text{-}200\text{kg}/\text{m}^3$) and BOD ($50\text{-}75\text{kg}/\text{m}^3$) in comparison to other raw materials like sugar beet and grains. This is also very difficult to treat. About $12\text{-}17\text{m}^3$ of waste water per m^3 of ethyl alcohol is generated. Most of the distilleries in world use anaerobic systems to recover the maximum amount of energy through biomethanation reactors (biodigester). These reactors operate at around 80-90% BOD removal efficiency and around 70% COD removal efficiency. Thus the effluents of these systems still contain very high COD ($\sim 30\text{-}45\text{kg}/\text{m}^3$) and very high BOD ($\sim 4.5\text{-}7\text{kg}/\text{m}^3$). [6, 7]

The government of India has recently order to market 5-10% ethanol-blended gasoline from the oil outlets in the country. This singular decision has increased the demand of fuel-grade ethanol, which cannot be met from the molasses based fermentation units only. Hence the shift to juice of sugar cane, sweet sorghum and beet and non-edible great food grains (wheat, rice, maize etc) as the additional and alternative raw materials for alcohol fermentation is a near possibility to meet the projected ethanol requirements of 500million liter alcohol per annum as 5% ethanol & in the next stage for 10% ethanol blending with

gasoline an additional 500 million litres of ethanol will be required. While the use of ethanol –blended gasoline and bio-diesel will reduce the environmental pollution due to reduction of the noxious gases and particulates from vehicle exhausted emissions, the increase in the capacity of the distilleries to produce fuel-grade and chemical grade ethanol will immensely increase the water pollution problem, due to generation of large volume of DWW having high BOD, COD with high colour intensity.

As the bio methanation is attractive process to recover the energy contains in these wastewater as methane rich gas but this effluent still contain very high COD ($\sim 10\text{-}45\text{kg}/\text{m}^3$) and very high BOD ($\sim 1.5\text{-}7\text{kg}/\text{m}^3$), which is treated to further to meet the discharge water quality standards for release into surface waters (BOD $< 0.03\text{kg}/\text{m}^3$) and sewers (BOD $< 0.10\text{kg}/\text{m}^3$, COD $< 0.30\text{kg}/\text{m}^3$) applicable in India. Most of the disillery units used bioaeration process for treatment for bio digester effluent. For this oxygenation system like either surface aerators or submerged high pressure bubblers are used. The cost of operation of such oxygenation system is very high even than they are unable to meet for standards for discharge quality of waste water as the residual COD is still $8\text{-}15\text{kg}/\text{m}^3$ and the residual BOD is in the range of $3\text{-}7\text{kg}/\text{m}^3$. One of the disadvantage of this process is that he hydrocarbon is wasted due to its oxidation .These hydrocarbon is wasted due to its oxidation. These hydrocarbons may be recovered as fuel material after separating from the biodigester effluent. For treatment of BDE, a three step process: thermal heat followed by flocculation and wet oxidation has been suggested.

In the present paper the Thermolysis of biodigester effluent (BDE) is presented to treat the BDE and to recover the energy in the form of residues. In the laboratory, various oxides of metals, viz, Cu, Mn, Zn either singly or in mixed forms were used as catalysts. However, CuO was found to be the best among them and, therefore, CuO catalyst was chosen further studies. . Utilization of ethanol as fuel and generation of biogas from distilleries is also being covered.

II. ETHANOL AS FUEL

Ethanol is now being used as fuel in many countries. Brazil introduced a program to produce ethanol for use in automobiles in order to imports. Brazilian ethanol is made mainly from sugarcane. Pure ethanol (100% ethanol) is used in approximately 40% of the cars in Brazil. The remaining vehicles use blends of 24% ethanol with 76% gasoline. Sweden is using large quantities of ethanol as a fuel. They have used ethanol in chemical production for many years. As a result Sweden's crude oil consumption has been cut to half since 1980. During the same time period the use of gasoline and diesel for transportation has

also increased. Some Canadian provinces promote ethanol use as a fuel by offering subsidies of upto 45 cents per gallon of ethanol. [8]

III. BIOGAS FUEL FROM DISTILLERY WASTEWATER

There are about 300 distilleries in India producing 3.0 billion litres of alcohol and generating 40 billions of waste water annually. These distilleries have potential to produce 1300 million cubic meters of biogas. A nearby distillery unit with an annual alcohol production of about 2150 kiloliters has been found to generate about 32700 m³ of spent wash. The plant was claimed to achieved a COD removal efficiency of 86% with a HRT of 10 days and the biogas production was around 450-500 m³/day. Another moderate sized chemical unit, having captive distillery is manufacturing 55000 KL of alcohol per year. Its distillery produces an effluent spent wash of about 1400 m³/day with a BOD value between 45000-50000 nm³/day. The biogas was composed of 50-60% methane, 1-3% hydrogen sulphide and 31- 49% of carbon dioxide.

A comparative study of the treatment of the sugarcane based vinasse of different countries has been made by Drissen et al, the results of which are shown in Table 1. These results confirm the fact that varying characteristics of the spent wash affects the efficiency of treatment.

IV. THERMOLYSIS OF BIODIGESTER EFFLUENT

4.1 Materials

The biodigester effluent was obtained from a nearby sugar plant. Typical of the effluent, before and after thermal, is presented in Table 2.

4.2 Preparation of catalyst

The CuO catalyst was prepared in the laboratory from the cupric nitrate by alkali precipitation followed by drying and calcinations. To prepare 10gm CuO catalyst, 30.40 mg/lit copper nitrate solution was prepared in distilled water and liquid ammonia was added to the solution gradually (drop by drop) while stirring the solution at a constant speed. The resultant precipitate was washed thoroughly with distilled water and then it was dried in an oven at 105⁰C for 18 h. The dried matter was calcined in a furnace at 400⁰C for 4 hours. The calcined solid was ground in a laboratory grinder and sieved. The solid particles with an average size of 220 nm were used in the experiments.

4.3 Experimental setup and Procedure

The Thermolysis experiments were performed in a 1dm³ High pressure stainless steel (SS-316) reactor (SSR). The SSR was equipped with electrical heating, temperature indicator-cum-controller, liquid sampling port, pressure indicator, and a cooling coil. The reactor contents were agitated using a magnetic stirrer. After the start of an experimental run at a desired temperature, the effluent samples were withdrawn from the reactor at definite time intervals. The samples were filtered and the filtrate was analyzed for its COD values [2]. The effect of such variables as initial pH (pH₀=1-10) and temperature (T=100-140⁰C) on the COD removal efficiency were studied. The experiments were performed at temperature(100-140⁰C) and self-generated pressure the autogenously pressures of the solution at 100⁰ C,

120⁰C, 130⁰C, 140⁰ C were, respectively, 2.8, 5.1, 7.20 and 8.80 bar as against the vapor pressure of water which were 1.2, 2.7 and 3.6 bar at the corresponding temperatures. This pressure enhancement is due to the pressure of organic matter in the effluent. The effluent was preheated from the ambient temperature to the required temperature; the preheating period varying with the temperature. The starting time of the start was considered as the 'zero time' when the temperature was attained due to preheating of the waste water from its ambient temperature. All the experimental runs were carried out for 6h duration. Chemical oxygen demand (COD) was determined by the standard dichromate reflex method. BOD of a sample was determined by incubating the seed sample for 3 days at 27⁰ C.

4.4 Result and Discussion

First to screen the catalyst, the experiments were performed in a atmospheric pressure reactor at 100⁰ C and different pH (pH=1-10) using different catalyst like homogeneous copper sulphate and heterogeneous metal oxide/mixed oxide of Cu, Mn, Zn, Pb, Fe. Oxide etc. among this CuO catalyst gave best results at pH=1, therefore CuO catalyst was chosen further for thermolysis and kinetic studies.

4.4.1 Effect of initial pH

The effect of pH on the catalytic thermolysis of BDE was studied at 140⁰C temperature and the autogenous pressure (self pressure). The pH₀ of the effluent batch in the reactor was varied between 1 and 10. The pH₀ was adjusted with either sulphuric acid or liquid ammonia. The COD reduction at 140⁰C and autogenous pressure versus treatment time (t_R) with pH₀ as the parameter are presented in the Fig.2. It may be seen from the figure that the COD reduction is maximum at pH₀=1. Between pH₀=2-4, the COD reduction efficiency goes down drastically. Above pH₀=4-8, COD reduction increases, although marginally, and then decreases. It is also that the treatment at pH₀=8 is the best within range 4 ≤ pH₀ ≤ 10.

We can draw a plot that shows significant drop in the COD of the effluent at zero time. During the transient (pre-) heating period (t_h) from the ambient temperature to the treatment temperature, thermal degradation/precipitation occurs. Pre-heating periods require for rising the temperature of the effluent from the ambient temperature to the treatment temperature was 23 min for 100⁰C, 2 min for 120⁰C, and 30 min for 130⁰C and 34 min for 140⁰C. At 140⁰C, the COD reductions during the pre-heating period at different pH₀ were as follows: 52 % (pH₀ =1), 48 % (pH₀ =2), 15 % (pH₀ =4), 18 % (pH₀ =6), 17 % (pH₀ =8) and 16 % (pH₀ =10). These values are shown at the ordinate at zero time, i.e., t=0. It may be seen that COD reduction during the pre-heating period is substantial when compared with the overall COD reduction obtained after 2 h of treatment at the steady state reaction temperature. After 6 h period, the COD reduction was 70.01%, 65.39%, 34.55%, 38.1%, 36.91% and 35.61% at pH₀ = 1, 2, 4, 6, 8 and 10, respectively.

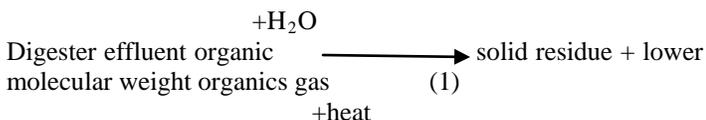
During pre-heating period, thermolysis increases with increase in reaction temperature and consequent reduction in pH. Metal complexation with lignin, carbohydrates and other soluble organics like proteins, etc. make the reaction products insoluble. The insoluble matter/residues (char) of 14.63, 14.63, 9.05, 10.02, 11.18, 9.28 kgm⁻³ were obtained at experimental conditions of

initial pH (pH₀) 1, 2, 4, 6, 8, 10 respectively with T=140⁰c, C_w kg/m³, t_R = 6 h. This data shows that low pH (acidic condition) is favorable for more solid formation and, thus, more COD reduction. For thermolysis, the constituents: lignin, carbohydrates and proteins containing functional groups are more reactive at acidic condition in presence of CuO catalyst. These residues have heating values 14.5-19 MJ/Kg shows its organic nature. It also reflects that COD reduction is due to separation of these organics in the form of solid residues during thermolysis process.

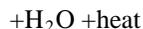
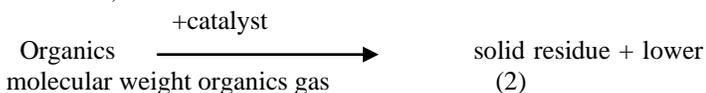
4.4.2 Effect of Temperature

The effect of temperature on thermolysis of BDE was studied in the temperature range of 100-140⁰C and solution autogenously pressure at pH₀=1 using C_w=3 kg/m³ and COD₀=34 kg/m³. The COD reduction was taken as a parameter. The results are shown in figure.3. From the figure it may be seen that the COD reduction is fast during the initial period of reaction (up to 2 h) and slow thereafter. With the increase in temperature, the COD reduction of the supernatant solution also increases. It can be seen that 27% and 51% COD reduction were obtained at the end of pre-heating period (i.e., zero time) to raise the solution temperature from the ambient temperature to 100⁰C and 140⁰C, respectively, which has increased to 41% and 70% at the end of reaction period 6 h. At 140⁰C, 62% COD reduction is obtained in t_R=2 h which increases to 70% in t_R=6 h.

During catalytic thermolysis, two mechanisms, both in parallel but complimentary to each other, take place simultaneously. The organic molecules, smaller and larger – present in the effluent undergo chemical and thermal breakdown and complexation forming insoluble particles which settle down. Further, during the Thermolysis larger molecules also undergo break down into smaller molecules which are soluble. Due to formation of insoluble particles, and slight gasification involving COD and BOD of the supernatant, get reduced. The thermolysis process of the biogas digester effluent can, thus, be represented as



In the presence of the catalyst, the solid residue formation gets hastened and its yield is increased. The reaction equation can be written as,



4.4.3 Analysis of residues

The residue obtained after filtration was dried in an oven, and its composition and physical properties are presented in Table-3. It may be seen that the colour of the residue obtained after treatment at different pH₀ is different from one another. At lower pH₀ easily grind able bulky mass with free flowing properties was formed, while at higher pH₀, flakes or small granular particles were found. The lower the initial pH(pH₀=1-2), the higher is the energy recovery in the form of residue. At pH₀=1, the energy recovery is 42.4%, whereas at pH₀=2, the energy recovery is 47.7%. Reduced drying period for the residue, higher specific energy and high COD reduction for the effluent were achieved when Thermolysis was conducted under acidic condition. The residue is a complex solid with a good heating value (~18 MJ/kg at pH₀=1) and high C/H atomic ratio. It also contains the majority of copper used as the catalyst. The copper content of the residue is a minimum (13.3%) at pH₀=1. This residue could be used as a fuel in a combustor, furnace or an incinerator. The ash contains more than 50% copper and is therefore, a good copper source to enrich organic manure. This blended manure could be a very good fertilizer for agricultural crops.

V. CONCLUSION

The ethanol is good fuel material for gasoline engine as it produces low emission of CO₂ and hydrocarbon.

Biomethanation is the well recommended process to treat the waste water originated from the distillation column of ethanol production plant. It produces methane rich gas, which has high heating value.

Thermolysis has been found to be effective process for the treatment of biodigester effluent. Thermolysis at 140⁰C, pH 1 with a C_w of 3 kg/m³ gave maximum COD reduction of about 70% from its initial value of 34 kg/m³. The BOD reduction was found to be 83% from its initial value of 6.3 kg/m³. The COD reduction is accompanied with the formation of settle able solid residue which is enriched in carbon having heating value 17.92 MJ/kg.

The fuel may be obtain from distillery in three ways

- I. As ethanol
- II. As methane rich biogas
- III. As solid residues during thermolysis of biodigester effluent

Table-1 –Result of UASB process treatment of the sugarcane based vinasse for different countries

| Parameter | Brazil | India | Venezuela |
|-------------------------------------|--------|-------|-----------|
| COD removal (%) | 88 | 65-70 | 65-70 |
| BOD removal (%) | 96 | 85-90 | 85-90 |
| Biogas, l/g COD removal | 0.5 | 0.5 | 0.5 |
| Organic loading rate (g COD/l. day) | 22 | 10 | 16 |

Table-2 – Typical composition of biodigester effluent before thermal and after thermal (at T = 140 °C, pH₀=1)

| Parameter | Biodigester effluent | Biodigester effluent thermal |
|-------------------------------|----------------------|------------------------------|
| COD | 34000 | 10200 |
| BOD | 6300 | 1075 |
| Organic Carbon | 9636 | 1845 |
| Inorganic Carbon | 3528 | 1468 |
| Total Carbon | 12864 | 3313 |
| Reduced Carbohydrate | 32500 | 6550 |
| Dissolved lignin | 16100 | 1230 |
| Protein | 3280 | 32 |
| NH ₄ -N | 687 | 140 |
| Organic Nitrogen | 190 | 73 |
| Total Kjeldahl Nitrogen | 877 | 213 |
| P ₀₄ ²⁻ | 157 | 54 |
| KH ⁺ | 5170 | 3840 |
| S ₀₄ ²⁻ | 7120 | 4230 |
| Cl ⁻ | 3000 | 2820 |
| Fe ⁺⁺ | 10 | 8 |
| Ca ⁺⁺ | 558 | 170 |
| Cu | 8 | 210 |
| Total Dissolved Solids (TDS) | 28320 | 25710 |
| Total Suspended Solids (TSS) | 12180 | ---- |
| pH | 7.8 | 1.54 |
| Color | Blackish brown | Orange |

Note: All the values except pH are in mg dm⁻³

Table - 3. : Analysis of the Residue Obtained after Catalytic Thermolysis at Different pH₀ values (T =140°C, t_R=6h)

| pH ₀ | | | | | | |
|-------------------------------------|---|---|---------------------------------|-----------------------------------|----------------------------------|-----------------|
| | 1 | 2 | 4 | 6 | 8 | 10 |
| Wt. of residue (kg/m ³) | 14.63 | 14.63 | 9.05 | 10.02 | 11.18 | 9.28 |
| Color | Dark brown | Dark brown | Dark brown | Black | Blackish brown | Greyish brown |
| Nature | Bulky mass, 1-2 mm flakes, easily grindable | Bulky mass, 1-2 mm flakes, easily grindable | 1-2 mm flakes, easily grindable | 3-5 mm flakes, difficult to grind | 2-3mm flakes, difficult to grind | 1-2 mm granules |
| Approx. drying period (h) | 3.0 | 4.0 | 4.5 | 6.0 | 8.0 | 10.0 |
| Specific energy (MJ/kg) | 17.92 | 18.73 | 16.22 | 19.0 | 16.77 | 14.5 |
| % Convertible COD | 70.01 | 65.39 | 34.55 | 38.1 | 36.91 | 35.61 |
| % Energy recovery | 42.43 | 47.66 | 25.51 | 33.09 | 32.60 | 23.39 |
| % Copper in residue (g) | 13.26 | 14.50 | 1.26 | 22.72 | 17.14 | 25.50 |

$$\% \text{ Energy recovery} = \frac{(\text{Specific energy} \times \text{Mass})_{\text{residue}}}{(\text{Specific energy} \times \text{Mass})_{\text{Biodigester effluent}}} \times 100$$

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