



Recent Developments in Biogas Manufacture and Biogas Utilization: A Review

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ABSTRACT

The various developments in the areas of biogas manufacture and utilization have been surveyed. This includes alternate / multiple substrates that could be economically employed for biogas production, biogas enrichment (carbon dioxide removal), biochemical desulfurization of biogas, utilization of enriched, desulfurized biogas as automobile fuel (in place of CNG, LNG), for the production of syngas and a host of chemicals (including nitrogenous fertilizers) therefrom, production of phosphatic biofertiliser from ADS (anaerobic digester sludge) and synthesis of liquid fuels (mainly, motor gasoline) using Fischer – Tropsch process. The technical details and economic viability of each process have also been analyzed and highlighted.

Keywords: biogas manufacture, multiple substrates, biogas enrichment, biochemical desulfurization, syngas and chemical synthesis, Fischer – Tropsch synthesis, ADS and phosphatic biofertiliser

INTRODUCTION

Biogas technology is more than one century old. A lot of developments have taken place in the areas of biogas manufacture and utilization. However, needless to comment, large scale utilization of biogas for various industrial and commercial applications has not caught sufficient momentum till this date. A review of current developments in production and utilization of biogas has been reported by Gromke, Rensberg, Denysenko, Stinner, Scmalfuß and Scheftelowitz (2018: 17). As reported by them, crop silages and manures are the most prominent substrates used in Germany for biogas production. Though the use of biomethane in transport sector is not yet well-developed, more than 74% of the electric power generated from biomass in Germany is reportedly from biogas and biomethane. In a similar way, Jingura and Matengaife (2009: 1116) have presented an overview of biogas production by anaerobic digestion in Zimbabwe and have recommended a few technical options for optimizing the biogas production.

The various advancements in the area of biogas manufacture and successful case studies with respect to diversified utilization of biogas on industrial / commercial scale have been surveyed in this paper. Economical viability of biogas utilization has also been analysed and emphasized.

MULTIPLE SUBSTRATES FOR BIOGAS PRODUCTION

Biogas is produced by the anaerobic digestion of organic matter using a complex culture of microbes (hydrolytic, acidogenic, acetogenic and methanogenic microbes). Out of these, the function (activity) of methanogens is rate – controlling and these are principally obligate microbes and are accordingly quite sensitive to the operating temperature and pH. The optimum temperature for biogas production is 30 – 35°C (mesophilic environment) and optimum pH is 7-8. The organic matter would have to be, therefore, mixed with water in 1:1 ratio (by mass). Use of thermophilic microbes (that multiply at elevated temperatures of 45-65°C) has not been proved to be beneficial, since the additional cost of maintaining high temperature is not adequately compensated by the increase in biogas yield achieved.

Cow dung is the oldest raw material for biogas production. It has the distinct advantage that it is capable of developing the microbes by itself and thus does not demand seeding of any inoculums. However, many alternate animal wastes and plant wastes including cellulosic wastes have been proved to be potential substrates for biogas generation. Waste paper, microalgae, sewage

Table 1. Biogas production from different substrates

Substrate(s)	Yield of Gas, ml CH ₄ /(g.VS)	Reference No
Raw sewage sludge	278.0	6
Algae	168.0	6
Sewage (88%) + algae (12%)	309.0	12
Sewage (85%) + algae (15%)	294.0	21
Food waste (88%) + algae (12%)	420.0	7
Corn straw + algae	325.0	19
Waste paper (40%) + algae (60%)	321.0	20

Table 2. Comparison of biogas yield from mono-substrate, two substrate and three substrate digestion

Substrate(s)	Yield of Gas, ml CH ₄ /(g.VS)	Reference No
Waste grown algae	266.0	70.0
Sewage sludge	190.0	70.0
Waste paper	338.0	69.5
Waste paper + sewage sludge (1 : 1)	520.0	69.3
Waste paper + sewage sludge + waste grown algae (1 : 1 : 1)	700.0	70.0

Source: References (Ajeej et al., 2015: 270, 2016: 74)

sludge, water hyacinth are examples. In many cases, a mixed feed composed of multiple substrates (two or more substrates) has been found to be beneficial (discussed below). Typical data reported by different authors are summarized in **Tables 1 and 2**.

Olsson et al. (2014: 203) conducted experiments on anaerobic co-digestion of sewage sludge with algal mass in different proportions and found that maximum biogas yield of 309 ml CH₄/(g.VS) was obtained when these two were mixed in the ratio 88 : 12. The reported yield is 11% higher than that obtained when raw sewage sludge was digested alone and 84% higher than that obtained when microalgae were used as the single substrate (Golueke et al., 1957: 47). Similar observation has been reported by Yuan et al. (2012: 396). Krustok et al. (2012) report that when algal mass is mixed with food waste and digested together anaerobically, the yield of biogas achieved is still higher, almost 2.5 times that obtained from anaerobic digestion of algal mass alone. In a similar way, addition of algae to corn straw (Weizhang et al., 2012: 281) and to waste paper (Yen and Brune, 2007: 130) reportedly result in significant increase in biogas yield (**Table 1**).

Meng, Jin, Yi, Mengdi, Peng, and Pan (2020: 12350) have studied co-digestion of wheat straw and vinasse (which is the byproduct of alcoholic fermentation of straw) and report that the biogas yield is 92.1% higher than that of straw mono-digestion. Also, vinasse – manure co-digestion yielded 7% higher biogas output as compared to vinasse-straw co-digestion.

Similar investigations on enhancing the biogas / biomethane yield from straw by blending it with alternate energy-rich substrates have been reported by other authors as well. Examples are three substrate co-digestion of wheat straw, dairy waste and chicken manure (Wang, Yang, Feng, Ren, and Han 2012: 78), two substrate co-digestion of oat straw and cattle manure (Lehtomäki, Huttunen, and Rintala, 2007: 591) and three substrate digestion of rice straw, kitchen waste and pig manure (Ye, Li, Sun, Wang, Yuan, Zhen, and Wang, 2013: 2653). In all the cases, higher cumulative biomethane yield of 200 – 400 ml/(g.VS) had been observed as compared to 120 ml/(g.VS) when straw was digested alone as single substrate.

Co-digestion of waste paper and sewage sludge (in 1:1 ratio) has been reported by Ajeej et al. (2015: 270, 2016: 74). In this case, the biogas yield increased from 190 ml/d (mono-substrate digestion of sewage sludge) to 520 ml/d (175% increase or 2.75 times) and from 338 ml/d (mono-substrate digestion of waste paper) to 520 ml/d (54% increase). The methane content of the gas remained close to 70% in all the three cases.

Laboratory studies on anaerobic co-digestion of sugarcane bagasse and fruit-vegetable waste with waste activated sludge as inoculum are reported by Vats, Khan, and Ahmad (2019: 331). Results obtained by them demonstrate that 79, 58 and 56% increase in biogas generation is achieved when sugar cane bagasse and fruit-vegetable waste are co-digested in the ratio of 30:70, 50:50 and 70 : 30 respectively as compared to the mono anaerobic digestion of bagasse.

Another option is to mix thermal acid pretreated cellulosic waste (bagasse) with food waste and subject to anaerobic co-digestion (Vats et al., 2019). In this case, the biogas production when a mixture containing bagasse and food waste in the ratio 35 : 65 is used as the substrate has been reported to be 81% higher than that when bagasse was digested alone. The potential of mixing poultry droppings with cellulosic waste for enhancing the biogas production has also been reported Vats, Khan, and Ahmad (2019). Based on experimental studies in laboratory batch reactors, they report a cumulative biogas yield of 8400 ml (methane content = 50%) at the end of 30 days when a 1:1 mixture of cane bagasse and poultry droppings was anaerobically digested, as compared to 1500 ml (methane content = 63%) when the bagasse was digested alone as mono-substrate. They also observed that in this case, thermal pretreatment of bagasse increased the biogas yield only marginally.

Co-digestion of sewage sludge and food waste in an anaerobic digester that operates with pulse feeding has been analysed by Liu, Huang, Li, Peng, Maurer, and Kranert (2020: 818). They have observed that the system responds favorably to such flexible feeding scheme and this also reduces the required storage capacity of biogas by 40% (as compared to that in continuous feeding mode).

Three substrate digestion has proved to be still more beneficial. Ajeej et al. (2016: 74) report that when waste paper, sewage sludge and waste grown algae are digested together in the ratio 1 : 1 : 1, the biogas yield increases to 700 ml/d, which is 268% higher than (or 3.68 times) that obtained during mono-substrate digestion of sewage sludge and 35% higher than that in two substrate (waste paper and sewage sludge) digestion (**Table 2**). Similar inferences are reported by Samson and LeDuy (1983: 677)

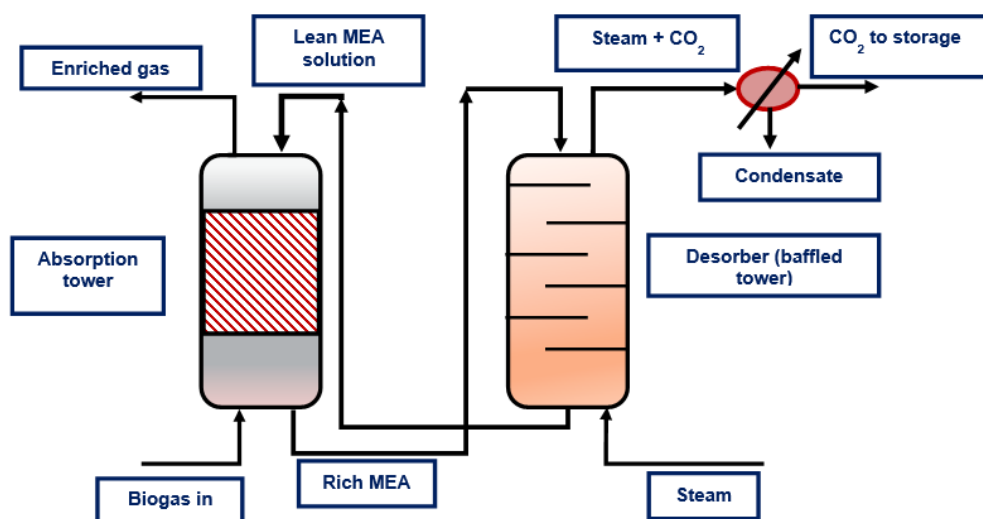


Figure 1. Absorption – desorption Unit for Biogas Enrichment

who investigated anaerobic co-digestion of domestic sewage sludge, spent sulfite liquor and peat hydrolysate and also by Momoh and Nwaogazie (2008: 95) who report biogas synthesis from co-digestion of waste paper, water hyacinth and cow dung.

Anaerobic digestion of oil residue (waste cooking oil) mixed with vegetable and fruit wastes (three substrate digestion) has been investigated by Thanikal, Yazidi, Torrijos, and Rizwan (2015: 18379). They report that co-digestion of oil with fruit and vegetable wastes caused 30% increase in the yield of methane as compared to when oil is used as mono substrate. Okewale and Adesina (2019: 271) have conducted anaerobic co-digestion of three substrates such as pig dung, water hyacinth and poultry droppings in laboratory batch digesters. They report a cumulative biogas yield of 307 ml CH₄ per g VS at the end of 52 days when the three substrates (pig dung, water hyacinth, poultry droppings) were used in the ratio 15 : 40 : 45, as compared to a cumulative yield of 219 ml CH₄ per g VS when only two substrates were used such as water hyacinth and poultry droppings in the ratio 40 : 60. The cumulative biogas yield reported is as low as 75 ml CH₄ per g VS when a two substrate co-digestion was performed using pig dung and water hyacinth in the ratio 60 : 40.

As a whole, multiple substrates provide encouraging results with respect to biogas yield and quality and this also helps in combined waste treatment / waste utilization.

ENRICHMENT OF BIOGAS

Typically, biogas contains around 60% methane and 40% carbon dioxide (by mole). At this composition, its calorific value is around 33000.0 kJ/kg. Enrichment of biogas means removal of its CO₂ content (which is the incombustible constituent) and thereby increasing its calorific value. Pure methane has a calorific value as high as 55000 kJ/kg.

Enrichment of biogas (to almost pure methane) is desirable only when it is being used for industrial purposes such as in furnaces and boilers, in automobiles or as a feedstock for the manufacture of many valuable industrial chemicals. When used as a domestic cooking gas, the CO₂ content is retained in the gas mixture since CO₂ acts as a diluant and helps in checking the high inflammability of the fuel. Highly inflammable gaseous fuels are not recommended for use in domestic kitchens due to safety considerations.

Enrichment of biogas can be commercially and economically accomplished in an absorption – desorption system that employs aqueous monoethanolamine (MEA) solution as the absorbent and steam as the stripping fluid (Narayanan et al., 1990: 17; Bhattacharya et al., 1992). The scheme is sketched in **Figure 1**. Aqueous MEA is a selective and efficient solvent for carbon dioxide. It not only dissolves CO₂, but also reacts with it:



The above reaction has been found to be of second order (first order with respect to CO₂ concentration and first order with respect to MEA, the overall order of reaction being 2.0). Typical value of second order rate constant (k_2) at 30°C is (Bhattacharya et al., 1992),

$$k_2 = 10200 \text{ m}^3 / (\text{kmole} \cdot \text{s})$$

The process is thus that of chemisorptions and as a consequence, the rate of absorption is quite high. Biogas is admitted to the packed absorption tower from the bottom and aqueous MEA solution is fed from the top to affect countercurrent contacting. The packing material employed is inert and corrosion resistant (such as ceramic material or those made of polymer composites). Due to the presence of packing, both fluids (the biogas stream and the MEA solution) execute a tortuous path through the column and this assists in achieving intimate contacting between the two. The carbon dioxide present in the biogas gets selectively absorbed in the descending stream of aqueous MEA solution and as a result, the biogas leaving from the top of the tower shall be essentially free from carbon dioxide. The rich MEA solution (containing all the dissolved CO₂) is discharged from the bottom of the

absorption tower and it is then fed to the top of the desorption column which is usually a baffled tower that is fed with high pressure steam from the bottom. Here also, countercurrent contacting occurs. All the dissolved CO₂ is stripped off by steam and the lean MEA solution containing very little dissolved CO₂ (that leaves from the bottom of the desorption column) is recycled back to the top of the absorption tower (see **Figure 1**). Steam that exits from the top of the desorption column is condensed and the carbon dioxide separated sent to storage.

Since the absorbent (MEA solution) is continuously recovered and recycled (there is no net consumption of MEA during the process), the economy of the process is quite high. The absorption tower operates at ordinary temperature and since the rate of absorption is quite high (it is a chemisorptions process), the packed height required for the absorption column shall not be substantially large.

Mathematical analysis of this process has been performed by Narayanan et al. (1990: 17) and a well-tested CAD (software) package has been developed. Since the process involves absorption accompanied by chemical reaction (chemisorptions), the rate of absorption of CO₂ at any cross – section *i* of the packed tower (R_i) is given by

$$R_i = E_i k_L P y_i / \left[H e + E_i (k_L a) / (k_g a)_i \right] \quad (2)$$

where

R_i = local rate of absorption, kmole / (m².s)

E_i = enhancement factor

k_L = liquid phase mass transfer coefficient, m/s

P = absorption pressure, atm

He = Henry's law constant for CO₂ dissolution in MEA, (m³.atm) / kmole

y_i = mole fraction of CO₂ in gas phase at any cross – section *i* of the column

k_g = gas phase mass transfer coefficient, kmole / (m².s. atm)

a = specific interfacial area for mass transfer, m² / m³

The mass transfer coefficients (k_L , k_g) and the specific interfacial area for mass transfer (a) are to be computed from selected experimental correlations available in literature. For example, for the present case of CO₂ absorption in aqueous MEA, Narayanan et al. (1990: 17) have used an extension of the correlation proposed by Dwyer and Dodge (1941: 485) for the estimation of the gas phase mass transfer coefficient ($k_g a$), the correlation proposed by Van Krevelen and Hoftijzer (1947: 49, 1948: 529) for the estimation of liquid phase mass transfer coefficient (k_L) and the correlations proposed by Onda et.al (1968 : 62) for the estimation of the specific interfacial area for mass transfer (a). It need not have to be over-emphasized that the selection of each of these empirical correlations is to be done with adequate caution, keeping the limitations and the range of applicability of each very much in mind.

As stated earlier, due to the chemical reaction between the absorbent and the solute (namely, CO₂), the liquid phase mass transfer coefficient (k_L) gets enhanced. The degree of enhancement is predicted by the enhancement factor (E_i) which is a function of the kinetics of the chemical reaction involved, diffusivity of CO₂ in solution (D_{AL}) and that of amine in solution (D_{Lm}). For the present case of absorption accompanied by a second order, irreversible chemical reaction, the following implicit correlation, that is based on the graphical data reported by Van Krevelen and Hoftijzer (1948: 563) , may be employed:

$$E_i = \Phi / (\tanh \Phi) \quad (3)$$

where

$$\Phi = [\beta(E_0 - E_i)/(E_0 - 1)]^{1/2} \quad (4)$$

$$\beta = (D_{AL} k_2 C_{Li}) / (k_L)^2 \quad (5)$$

E_0 = value of effectiveness factor when the chemical reaction is instantaneous

$$= 1 + (D_{Lm} C_{Li}) / (2 D_{AL} C_A^*) \quad (6)$$

D_{AL} , D_{Lm} = diffusivity of carbon dioxide and that of amine in solution, m²/s

C_A^* = interfacial concentration of CO₂ (assumed equal to the equilibrium concentration), kmole/m³

$$= (y^* P / H e) \quad (7)$$

The free amine concentration at any cross-section (C_{Li}) can be estimated from a material balance as

$$C_{Li} = C_{L0} - [2(1 - y_0)Q/Q_L] [Y_i - Y_e] \quad (8)$$

where

$$Y_i = y_i / (1 - y_i) \quad (9)$$

$$Y_e = y_e / (1 - y_e) \quad (10)$$

Q = molar feed rate of biogas, kmole/s

Q_L = volumetric feed rate (recirculation rate) of lean MEA solution (absorbent) at the top of the tower, m³/s

y_0, y_e = mole fraction of CO₂ in feed gas and that in exit gas (enriched biogas) respectively

C_{L0} = molar concentration of amine in the lean MEA solution (absorbent) fed from the top, kmole/m³

Since $(R_i a) = (k_g a)_i P (y_i - y^*)$,

$$y^* = y_i - (R_i a) / [(k_g a)_i P] \quad (11)$$

The rate of absorption of CO₂ at any cross – section i of the packed tower (R_i) is thus computed by solving the above equations (2 to 11) simultaneously by trial. For example,

Step 1 : First assume $y^* = y_i$.

Step 2 : Compute C_A^* from equation (7) and E_i from equations (3) to (10). To note that equation (3) is to be solved by trial since it is implicit in E_i .

Step 3 : Compute R_i from equation (2).

Step 4 : Now, compute y^* from equation (11) and C_A^* from equation (7). Then, estimate E_i by trial from equations (3) to (10).

Step 5 : Re-compute R_i from equation (2).

Step 6 : If the above – computed value of R_i differs significantly from that computed earlier, repeat the trials starting from step – 4.

Once all the values of R_i have been thus computed (for $i = 1$ to 100), then the required packed height of the absorption tower (L_p) can be estimated as

$$L_p = [G_L / (2a \rho_L)] \int_{C_{Le}}^{C_{L0}} (1/R) dC_L \quad (12)$$

where

G_L = average superficial mass velocity of absorbent solution, kg/(m².s)

ρ_L = density of absorbent solution, kg/m³

C_{Le} = molar concentration of amine in the rich MEA solution leaving the bottom of the absorption column, kmole/m³

The integral of above equation is evaluated numerically by Simpson's rule. Typical results reported by Narayanan et.al (1990 : 17) are given below :

Biogas feed rate = 22400 m³/d

CO₂ removal = 98 %

Required packed height of absorber (L_p) = 1.8 m

Column diameter (D) = 1.0 m

They have considered the desorber to be a packed tower and determined its required dimensions (L_d, D_d) using the conventional HTU – NTU concept. The results are

Required packed height of desorption tower (L_d) = 1.3 m

Tower diameter (D_d) = 1.5 m

Steam consumption = 1.8 kg per kg of biogas fed.

It can be seen that this absorption – desorption process is quite cost – effective, since it does not demand too large packed height for the absorber for affecting more than 98% CO₂ removal. Steam consumption of the desorber is also not large. The fact that the absorbent solution is continuously regenerated and recycled (there is no net consumption of the absorbent) adds to the overall economy of the process.

BIOCHEMICAL DESULFURIZATION OF BIOGAS

Hydrogen sulfide is another contaminant often present in biogas. Even when present at low percentages, it could cause serious corrosion problems as it leads to the formation of SO₂ gas and sulfuric acid mist, both of which are extremely harmful to the process equipment employed as well as to the environment (if exhausted to the atmosphere).

The conventional Claus process (for converting H₂S to elemental sulfur) is an expensive process and is best suitable for handling pure H₂S gas or a process gas with large percentage content of H₂S. With lean gases, it is not well-compatible nor cost – effective.

Biochemical desulfurization is an efficient and economical process particularly for handling gas streams containing low percentage of H₂S as is in the present case (Narayanan, 2012: 187; Rajvaidya, 2002). The scheme is sketched in **Figure 2**.

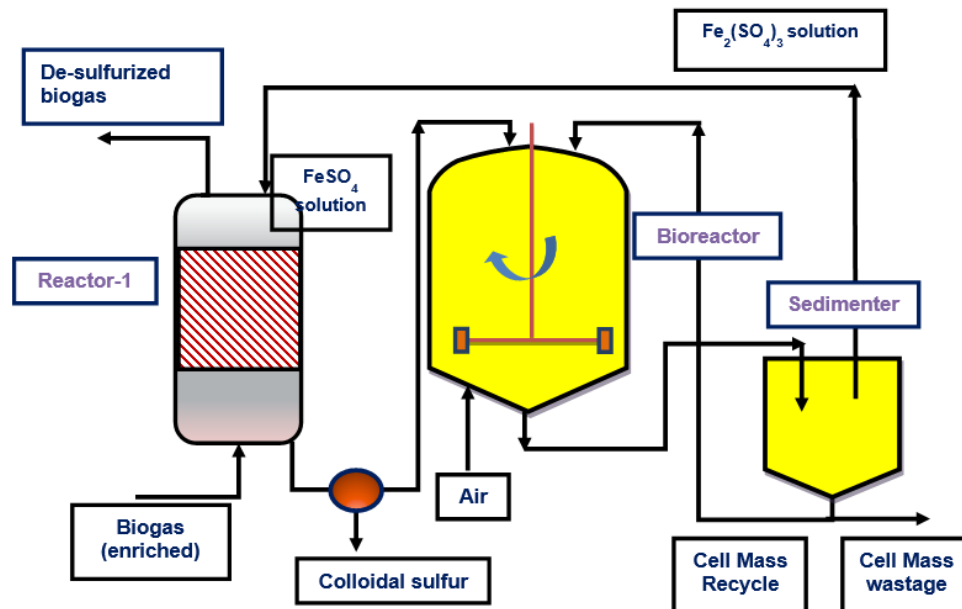
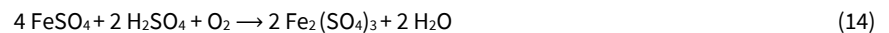


Figure 2. Biochemical desulfurization of biogas

The enriched biogas is first bubbled through ferric sulfate solution in Reactor -1, which is a stirred tank chemical reactor. Hydrogen sulfide present in the gas stream gets oxidized to elemental sulfur (colloidal sulfur), while ferric sulfate is reduced to ferrous sulfate:



The colloidal sulfur that gets precipitated is separated by filtration and the acidified ferrous sulfate solution (filtrate) is pumped into Reactor-2 which is a microbial bioreactor that has been seeded with a culture of recombinant *Thiobacillus ferrooxidans* microbes (sulfur eating bacteria) and is sparged with sterile air from the bottom. The following bioconversion occurs here:



The product solution is fed to a sedimentation tank in which all the microbial cells settle down as sludge. A part of this microbial sludge is recycled back to the bioreactor (to maintain the optimum population of microbes in the reactor), the rest wasted. The clear ferric sulfate solution that overflows is pumped back to reactor-1.

This biochemical process has the following distinct advantages:

- (1) Both the reactors operate at ordinary temperature and pressure. No high temperature, no high pressure required. There is no consumption of thermal energy.
- (2) Ferric sulfate solution is continuously regenerated in reactor - 2 (bioreactor) under microbial action and recycled to reactor - 1. This boosts the economy of the process as it does not demand consumption of any valuable chemicals.
- (3) The microbial culture (inoculum) is to be seeded to the bioreactor (reactor - 2) only at the startup, since being a microbial process, it is autocatalytic in nature. No chemical catalyst is required.
- (4) The process involves fully green technology. There is no emission of harmful gases, no discharge of toxic effluents or sludges, no formation of undue solid residues.
- (5) Almost complete desulfurization of biogas (more than 98% removal of H_2S) is possible even when if H_2S content of the feed gas is low.

ENRICHED, DESULFURIZED BIOGAS (BIOMETHANE) AS AUTOMOBILE FUEL

Enriched, desulfurized biogas, which is almost pure biomethane, can be conveniently used as an automobile fuel in road vehicles (passenger vehicles) in place of CNG (compressed natural gas) or LNG (liquefied natural gas). Natural gas is chiefly composed of methane (more than 95%) and hence biomethane (either as compressed gas or in the liquefied state) shall become a viable substitute to the same. Three wheelers (auto-rickshaws) and four wheelers (passenger cars) powered by CNG and LNG are already on the road in India and other countries.

Use of CNG or compressed biomethane in automobiles has distinct advantages:

- (a) It eliminates the need for atomization of fuel, which is an expensive process (atomization is invariable with all liquid fuels such as petroleum oils),
- (b) Being highly inflammable, the delay period is reduced to a minimum (often eliminated) and this provides smooth and steady engine performance,

- (c) It undergoes almost complete combustion and since it is devoid of aromatic hydrocarbons and sulfur compounds (biomethane has been desulfurized in advance), the exhaust gases shall contain little unburnt carbon particles, little unburnt hydrocarbons and shall be essentially free from corrosive SO₂ gas and sulfuric acid mist,
- (d) It is thus more environment – friendly.

In addition, unlike natural gas which is obtained from petroleum reserves, biomethane is a green fuel derived from biological wastes. Nevertheless, being a gaseous fuel, it does demand a high degree of pressurization and this necessitates thick – walled, large volume fuel tanks.

Liquefaction of methane is, in fact, an expensive process, since critical temperature of methane is very low (- 82C or 191K) and its critical pressure is as high as 42 atm. As a result, it is to be cooled to very low temperature and compressed to very high pressure for converting to liquefied state. However, once liquefied, it occupies very low volume and consequently, a large amount of gas could be stored in a low volume fuel tank. In this case also, no atomization of the fuel shall be required since it is not a liquid fuel but a liquefied gas. The cost of atomization gets thus completely eliminated. Its combustion characteristics, engine performance and above all, distinct environment friendliness remain the same as those of CNG or compressed biomethane.

BIOMETHANE AS FEEDSTOCK FOR THE MANUFACTURE OF INDUSTRIAL CHEMICALS

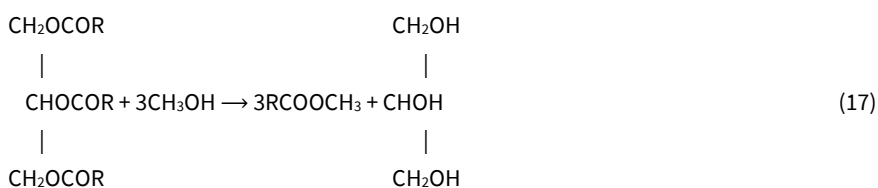
Biomethane (enriched, desulfurized biogas) forms an economically viable raw material for the production of syngas (synthesis gas) and syngas is the starting material for the manufacture of a host of valuable, industrial chemicals. Syngas is typically a mixture of carbon monoxide and hydrogen and is produced by the steam – hydrocarbon reaction (reaction between methane and high pressure steam) at elevated temperature and pressure (T = 750-950°C, P = 10-15 atm) and in presence of nickel catalyst:



The reactor is called *primary reformer* or *steam cracker*. Using syngas as the feedstock, a large number of industrially important products can be manufactured. An example is methanol, which is manufactured by passing syngas through a bed of CuO – ZnO catalyst (supported on alumina) at high temperature (T = 250°C) and high pressure (P = 50 – 100 bar), wherein the CO and hydrogen present in syngas react with each other yielding methanol vapors:



Apart from being used in medicine and pharmaceutical purposes, methanol is also one of the principal raw materials for the manufacture of biodiesels (which are the green fuels of the era) from vegetable oils. Biodiesel is synthesized by the transesterification of vegetable oils (jatropha oil, neem oil, algal oil) with methanol in presence of an alkali catalyst (sodium methoxide) or acid catalyst (dilute sulfuric acid) or enzyme catalyst (lipase enzyme):



Glycerol is the byproduct of the process. Biodiesel is an excellent substitute to petrodiesel for use in automobiles. Unlike petrodiesel, it is photosynthetically renewable, provides smoother and better engine performance and is more environment-friendly (green fuel). It does not contribute to CO₂ pollution and consequent global warming, since the carbon dioxide gas emitted during the combustion of this fuel gets reabsorbed by the plants from which the vegetable oil (the feedstock) is derived and this thus maintains a carbon cycle in nature and the net amount of carbon dioxide in the atmosphere remains unaltered. Petrodiesels, on the other hand, release the carbon that otherwise remains fixed underground, into the atmosphere in the form of CO₂ (which is the greenhouse gas responsible for promoting global warming).

Hydrogen gas is another industrially important product that could be manufactured starting from syngas. Here, syngas from the primary reformer (or steam cracker) is mixed with excess steam and then passed through a bed of iron oxide catalyst (with chromium oxide promoter) in a reactor called *shift converter* that operates at a high temperature of 425°C. Carbon monoxide present in syngas reacts with excess steam producing CO₂ and more hydrogen gas:



The product gas mixture leaving the shift converter (that is composed of CO₂ and H₂) is sent to the absorption – desorption system (discussed in the earlier section) wherein all the carbon dioxide present is removed by absorption in aqueous MEA solution (see **Figure 1**). The resultant hydrogen gas is sent to storage.

Hydrogen gas is an important raw material in a large number of chemical process industries such as for hydrodesulfurization of petroleum oils (also called hydrofining), hydrogenation of vegetable oils, hydrogenation of coal and the like. Syngas from biomethane can be thus used as an economical source for large scale hydrogen production.

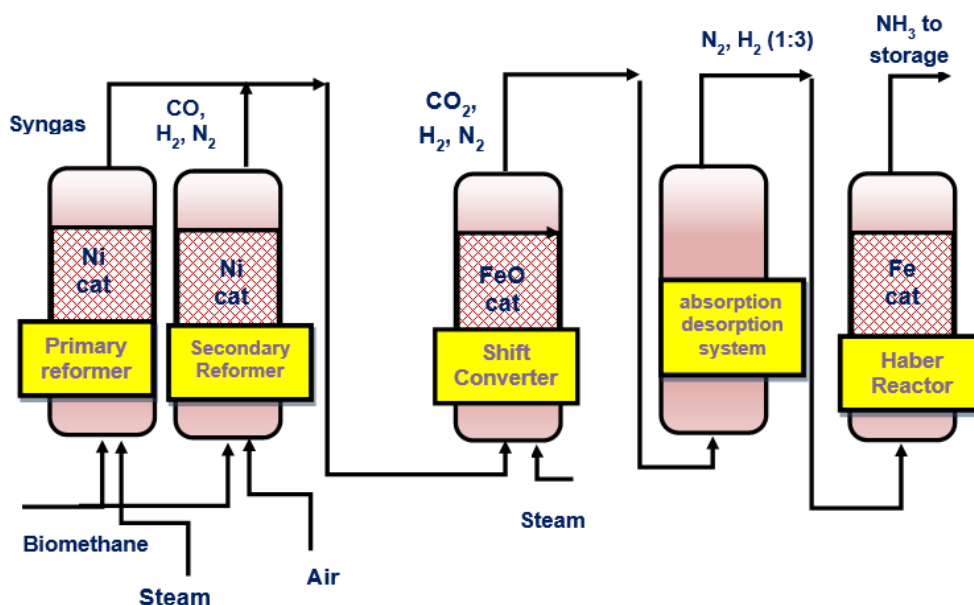


Figure 3. Ammonia Synthesis starting from Biomethane (syngas route)

MANUFACTURE OF NITROGENOUS FERTILIZERS STARTING FROM BIOMETHANE

Biomethane can also be employed as the starting material for the synthesis of nitrogenous fertilizers such as ammonium sulfate, urea, calcium ammonium nitrate (CAN or nitrolim) and ammonium phosphates (MAP, DAP). The process is sketched in **Figure 3**. It involves three catalytic reactors (apart from the Haber reactor) such as the primary reformer, secondary reformer and the shift converter. In the primary reformer, syngas is produced by the steam – hydrocarbon reaction as discussed earlier. The process takes place in a column reactor (as shown in figure) that is composed of a packed bed of nickel – catalyst particles. Both preheated biomethane and high pressure steam are admitted from the bottom and as they move up the catalyst bed, steam – hydrocarbon (steam – methane) reaction occurs and syngas gets generated. As stated earlier, the reaction occurs at a temperature of 750 – 950 C (temperature of catalyst bed) and at a pressure of 10 – 15 atm. Since steam is used in excess, the product gases would contain little unreacted methane. In the secondary reformer, which is also a packed bed reactor composed of a bed of nickel catalyst, preheated mixture of biomethane and dry air (mixed in a prescribed, pre-calculated proportion) is admitted from the bottom and as the gas mixture ascends through the catalyst bed, methane gets catalytically oxidized to CO and H₂. A small amount of carbon dioxide could also be formed. The reactor operates at specified temperature and pressure (T = 500 – 600°C, P = 5 – 6 atm). The reaction may be represented as,



The two gas streams (product gases from the primary reformer and those from the secondary reformer) are mixed (to obtain a gas mixture composed of CO, H₂, N₂ and traces of CO₂) and then admitted to the shift converter (the third packed bed catalytic reactor) into which excess steam is also injected from the bottom. In presence of the iron oxide – chromium oxide catalyst particles present in the shift converter, all CO present in the gas mixture is oxidized to CO₂ by steam, followed by production of additional hydrogen gas (see reaction shown in equation – 18). The gas mixture leaving the shift converter shall be thus composed of N₂, H₂ and CO₂, and is sent to the absorber – desorber system (**Figure 1**) to remove all the CO₂ present by absorbing in aqueous MEA solution. The resulting gas mixture of nitrogen and hydrogen is called *ammonia synthesis gas*. By adjusting the amount of steam admitted to the primary reformer and the amount of air admitted to the secondary reformer, the molar ratio of N₂ to H₂ in this mixture could be adjusted to 1 : 3.

In the renowned Haber reactor, nitrogen reacts with hydrogen in presence of the iron catalyst (Haber catalyst) at high pressure (P = 10 – 15 atm), the most favorable operating temperature for Haber catalyst being 375°C:



Ammonia is the universal raw material for the manufacture of many nitrogenous fertilizers (urea, ammonium sulfate, ammonium nitrate) and nitrophosphates (monoammonium phosphate, diammonium phosphate).

SYNTHESIS OF LIQUID FUELS FROM BIOMETHANE (FISCHER – TROPSCH SYNTHESIS)

Biomethane can very well be used as the starting material for the synthesis of liquid fuels (principally, high octane motor gasoline) through what is called the Fischer – Tropsch synthesis (F – T process). This process was first developed way back in 1949 – 50, on the eve of the second world war for the synthesis of motor gasoline (petrol) from coal.

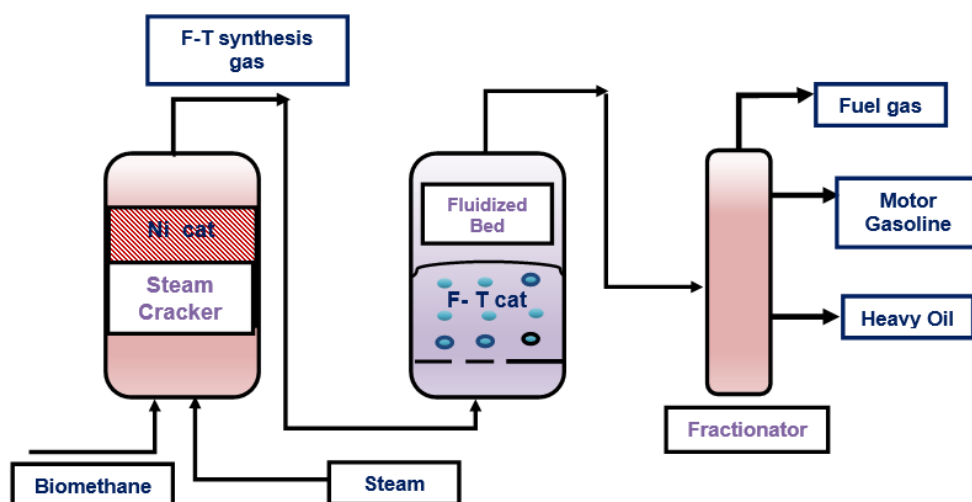


Figure 4. Liquid Fuels from Biomethane (Fischer Tropsch synthesis)

F – T synthesis gas is qualitatively same as syngas and is composed of CO and H₂, but in a molar ratio of 1 : 2 (in syngas, the molar ratio of carbon monoxide to hydrogen is around 4 : 5). As a result, F – T synthesis gas could also be produced either by steam – carbon reaction (when coal or coke is used as the raw material) or by steam – hydrocarbon reaction (equation – 15). This is what has been illustrated in **Figure 4**. In the packed bed catalytic reactor composed of nickel catalyst, biomethane (desulfurized and preheated) and high pressure steam react together forming F – T synthesis gas. Since biomethane has already been desulfurized, the resultant F – T synthesis gas need not have to be desulfurized again (sulfur compounds are extremely poisonous to F – T catalyst), but could be fed directly to the F – T reactor which is a catalytic reactor that uses a bed (packed bed or fluidized bed) of alkali promoted iron catalyst (F – T catalyst) and operates at a high temperature of 300 – 350°C. High operating pressure is not essential here. On the other hand, it has been observed that increased pressure tends to increase the wax content of the liquid hydrocarbons produced. At the above specified temperature and in presence of the F – T catalyst, carbon monoxide and hydrogen present in the F – T synthesis gas react together to form liquid hydrocarbons (C_nH_m). The reaction may be represented as,



When a fluidized bed reactor (sketched in figure) is employed, it is ascertained that the feed gas mixture (sulfur – free F-T synthesis gas) is admitted from the bottom at a superficial velocity that is around 20% higher than the minimum fluidization velocity (to affect complete fluidization), but around 20% lower than the terminal free settling velocity of each catalyst particle (to avoid carry over). In a fluidized bed like this, there will be more intimate contacting between the catalyst particles and the feed gas mixture and the problems due to channeling and inefficient gas-liquid contacting (that could occur in packed beds) shall be absent. The operating cost of the reactor shall be invariably higher. On the other hand, since the catalyst particles remain suspended in the ascending stream of F-T synthesis gas and thereby form an expanded bed, the overall volume of reaction zone available shall also be higher.

The product vapors from the reactor are fractionated in a tall, continuous fractional distillation column to separate the liquid hydrocarbons chiefly boiling in the motor gasoline boiling range, but of fairly high octane number. The entire process is shown schematically in **Figure 4**.

F – T process has a bright future. Once neglected and labeled as uneconomical, this process is being researched all over the world today with lot of momentum and interest. Motor gasoline (petrol) can be thus synthesized from biomethane instead of from petroleum reserves and the fact that biomethane is a product manufactured from waste materials and sludges talk about its economic viability and commercial adaptability.

The challenge before the research community today is the development of a more efficient F – T catalyst (Asaliev, 2020: 69; Mahmoudi, 2017: 11) that could help in increasing the rate of reaction and improving the product quality (high wax content of the liquid hydrocarbons synthesized had been the major drawback of F – T process when it was first introduced). Cobalt – based catalysts have been observed to be promising (Mahmoudi, 2017: 11). Further investigations in this connection are certainly worthwhile.

MANUFACTURE OF PHOSPHATIC BIOFERTILISER (PROM) FROM ANAEROBIC DIGESTER SLUDGE (ADS)

The sludge discharged from the biogas digester, called anaerobic digester sludge (ADS), could be dewatered, dried, pulverized and then used as a low grade nitrogenous manure. However, its N – content is only 2.5% and is thus a poor substitute to synthetic fertilizers such as urea (which contains 46% N), ammonium nitrate (33% N) and ammonium sulfate (21% N). However, pulverized ADS could be efficiently used for the commercial manufacture of a phosphatic biofertilizer (called PROM) from refined rock phosphate ore (Narayanan, 2012: 187; Sekhar and Aery, 2005).

Table 3. Comparison of PROM with synthetic fertilizers in agriculture
Crop yield, quintal / hectare

	SSP	DAP	PROM
1. Wheat	28.9	-----	29.0
2. Soyabean	10.37	-----	11.65
3. Groundnut	-----	30.29	31.20
4. Rice (kg / hectare)	3000	3910	4375
5. Barley	-----	56.23	70.0
6. Cabbage (quintal / acre)	-----	46.66	54.44
7. Onions	-----	165.19	166.66

PROM (Phosphate Rich Organic Manure) is a biofertiliser that is manufactured by the biochemical conversion of rock phosphate ore using ADS, Vermicompost or cow dung. An inoculum of a phosphate solubilizing bacteria such as *Bacillus mega therium var phosphaticum* could also be used to improve the rate of bioconversion and product quality. The specific attractive features of PROM manufacture are

- (1) The primary raw material for PROM production is refined rock phosphate ore itself, which is the universal raw material for the manufacture of elemental phosphorus, phosphoric acid and phosphatic fertilizers.
- (2) Being a biochemical process, PROM manufacture takes place at ordinary temperature and pressure. No high temperature required (no consumption of thermal energy), no high pressure and no chemical catalyst needed.
- (3) There is no consumption of any valuable chemical such as dilute sulfuric acid, phosphoric acid or ammonia.
- (4) The manufacturing cost of phosphoric acid is completely eliminated (which is otherwise indispensable for the manufacture of synthetic phosphatic fertilizers and nitrophosphates).

The process of manufacture of PROM is thus relatively simple:

Well – powdered, refined rock phosphate ore is mixed with pulverized ADS in 1:2 ratio (by mass) and then blended with water in 3 : 7 ratio (mixture : water) in an open stirred tank bioreactor. The slurry is continuously agitated and kept exposed to air for about 7 – 8 days. This is called the thermophilic stage and during this stage, the p_H of the slurry is maintained close to 7.0 and the operating temperature at 30 – 35°C (the temperature should not be allowed to increase beyond 6°C). The microbes liberated by ADS in the aqueous medium act on the rock phosphate ore particles and convert them to soluble phosphates. Since the reactor is kept open, atmospheric oxygen diffuses into the slurry and no external supply of compressed air is required (though the process is aerobic in nature). The operating cost of huge air compressors can be thus fully dispensed with.

At the end of the thermophilic stage, an inoculum of *Bacillus mega therium var phosphaticum* is seeded to the bioreactor (size of inoculum = 3 – 5%) and agitation of the slurry is continued for another 3 – 5 days. PROM synthesis shall be more or less complete at the end of this stage.

An additional step, though optional, may also be performed in which the bioreactor is seeded with a culture of nitrogen fixing bacteria (such as *azotobacter*, *rhizobia*) and the slurry is allowed to ferment for an additional period of 4 – 5 days. This shall increase the effective N – content of PROM and thus boost the product quality.

The product slurry is then filtered to separate the PROM particles and these particles, after drying and grinding, could be packaged and used in agriculture directly. PROM so prepared shall have a P – content of 16.5 % (as soluble P_2O_5) and a C : N ratio of 19:1. It thus forms a promising biofertiliser that competes excellently with synthetic phosphatic fertilizers such as SSP (single superphosphate), DAP (diammonium phosphate) etc. Typical data from successful field trials (Narayanan, 2012: 187; Sekhar et al., 2005) are shown in **Table 3**.

PROM is thus a viable substitute to synthetic phosphatic fertilizers and in addition, its cost of manufacture is much lower. Being a biochemical process, it is however slow and does demand larger reactor volume. Needless to comment, in spite of its many-sided advantages, government subsidy to PROM manufacture has been granted only five years ago in India.

CONCLUSIONS

A lot of diversifications and improvements have taken place in the field of biogas manufacture and utilization. Use of multiple substrates is encouraged, since this increases the yield of biogas significantly. Once biogas is produced on large scale, it could be enriched to almost pure methane (biomethane) by an absorption – desorption process which uses aqueous MEA solution as the selective solvent for CO_2 absorption. It can also be desulfurized by the cost – effective biochemical process. Thereafter, biomethane could be used as an automobile fuel (as a substitute to CNG, LNG) or for the manufacture of a host of valuable industrial products such as methanol, hydrogen gas and nitrogenous fertilizers through syngas route. It could also be used for the synthesis of liquid fuels (mainly motor gasoline) through Fischer – Tropsch process. The anaerobic digester sludge (ADS) discharged from the biogas digester could be employed for the biochemical production of an efficient phosphatic biofertilizer (PROM). All the processes have been commercially developed and well – tested CAD (software) packages are available for the design and installation of each scheme / process.

NOTATIONS

- a : specific interfacial area for mass transfer, $m^2 m^{-3}$
 C_A^* : equilibrium concentration of carbon dioxide in solution, $kmole m^{-3}$
 C_{Le} : concentration of amine in rich MEA solution, $kmole m^{-3}$
 C_{Li} : free amine concentration at any cross section i , $kmol m^{-3}$
 C_{Lo} : concentration of amine in lean MEA solution, $kmol m^{-3}$
 D : diameter of absorption column, m
 D_{AL} : diffusivity of carbon dioxide in solution, $m^2 s^{-1}$
 D_d : diameter of desorption column, m
 D_{Lm} : diffusivity of amine in solution, $m^2 s^{-1}$
 E_i : enhancement factor at any cross section i , dimensionless
 G_t : average superficial mass velocity of absorbent solution, $kg m^{-2} s^{-1}$
 He : Henry's law constant, $m^3 atm kmol^{-1}$
 k_2 : second order rate constant, $m^3 kmol^{-1} s^{-1}$
 k_g : gas phase mass transfer coefficient, $kmol m^{-2} s^{-1} atm^{-1}$
 k_L : liquid phase mass transfer coefficient, $m s^{-1}$
 L_d : packed height of desorption column, m
 L_P : packed height of absorption column, m
 P : absorption pressure, atm
 Q : molar feed rate of biogas, $kmol s^{-1}$
 Q_L : volumetric feed rate of absorbent (lean MEA solution), $m^3 s^{-1}$
 R_i : rate of absorption of carbon dioxide at any cross section i , $kmol m^{-2} s^{-1}$
 y_e : mole fraction of carbon dioxide in enriched biogas, $mol mol^{-1}$
 y_i : mole fraction of carbon dioxide at any cross section i , $mol mol^{-1}$
 y_0 : mole fraction of carbon dioxide in feed gas, $mol mol^{-1}$
 ρ_L : density of absorbent solution, $kg m^{-3}$

REFERENCES

- Ajeej, A., Thanikal, J. V. and Narayanan, C. M. (2016). Studies on production of biogas by co-digestion of sewage sludge, wastepaper and waste grown algae. *J Mod Chem Chem Technol*, 7(1),74–81.
- Ajeej, A., Thanikal, J. V., Narayanan, C. M. and Kumar, R. S. (2015). An overview of bio augmentation of methane by anaerobic co-digestion of municipal sludge along with microalgae and waste paper. *Renew Sust Energy Rev*, 50, 270-276. <https://doi.org/10.1016/j.rser.2015.04.121>
- Asalieva, E. Y., Kul'chakovskaya, E. V., Sineva, L. V. and Mordkovich, V. Z. (2020). Effect of zeolite on Fischer–Tropsch synthesis in the presence of a catalyst based on skeletal cobalt. *Petroleum Chem*, 60(1), 69-74. <https://doi.org/10.1134/S0965544120010028>
- Bhattacharya, B. C. and Narayanan, C. M. (1992). *Computer Aided Design of Chemical Process Equipment*. Kolkota: New Central Book Agency.
- Dwyer, O. E. and Dodge, B. F. (1941). Rate of absorption of ammonia by water in a packed tower. *Ind Eng Chem*, 33(4), 485-492. <https://doi.org/10.1021/ie50376a012>
- Golueke, C. G., Oswald, W. J. and Gotaas, H. B. (1957). Anaerobic digestion of algae. *Applied Microbiol*, 5(1), 47-55. <https://doi.org/10.1128/AEM.5.1.47-55.1957>
- Gromke, J. D., Rensberg, N., Denysenko, V., Stinner, W., Schmalfuß, T., Scheftelowitz, M., Nelles M. and Jan Liebetrau, J. (2018). Current developments in production and utilization of biogas and biomethane in Germany. *Chem Ing Tech*, 90(1-2),17-35. <https://doi.org/10.1002/cite.201700077>
- Jingura, R. and Matengaifa, R. (2009). Optimization of biogas production by anaerobic digestion for sustainable energy development in Zimbabwe. *Renew Sust Energy Rev*, 13(5), 1116-1120. <https://doi.org/10.1016/j.rser.2007.06.015>
- Krustok, I., Nehrenheim, E. and Odlare, M. (2012). Cultivation of microalgae for potential heavy metal reduction in a wastewater treatment plant. In *proceedings of International Conference on Applied Energy*, Suzhou, July 5–8.
- Lehtomäki, A., Huttunen, S. and Rintala, J. A. (2007). Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: effect of crop to manure ratio. *Resour Conserv Recycl*, 51(3), 591-609. <https://doi.org/10.1016/j.resconrec.2006.11.004>

- Liang, M., Jin, K., Yi, R., Mengdi, C., Peng, J. and Pan, Y. (2020). Enhancement of bioenergy recovery from agricultural wastes through recycling of cellulosic alcoholic fermentation vinasse for anaerobic co-digestion. *Bioresour Technol*, 311, 123511. <https://doi.org/10.1016/j.biortech.2020.123511>
- Liu, Y., Huang, T., Li, X., Huang, J., Peng, D., Maurer, C. and Kranert, M. (2020). Experiments and modeling for flexible biogas production by co-digestion of food waste and sewage sludge. *Energies*, 13, 818-831. <https://doi.org/10.3390/en13040818>
- Mahmoudi, H., Mahmoudi, M., Doustdar, O., Jahangiri, H., Tsolakis, A., Gu, S. and Wyszynski, M. L. (2017). A review of Fischer Tropsch synthesis process, mechanism, surface chemistry and catalyst formulation. *Biofuels Eng*, 2(1), 11-31. <https://doi.org/10.1515/bfuel-2017-0002>
- Momoh, O. L. Y. and Nwaogazie, L. I. (2008). Effect of waste paper on biogas production from co-digestion of cow dung and water hyacinth in batch reactors. *J Appl Sci Environ Manage*, 12(4), 95-98. <https://doi.org/10.4314/jasem.v12i4.55245>
- Narayanan, C. M. (2012). Production of phosphate rich biofertiliser using vermicompost and anaerobic digester sludge – a case study. *Adv Chem Eng Sci*, 2(2), 187-191. <https://doi.org/10.4236/aces.2012.22022>
- Narayanan, C. M. and Bhattacharya, B. C. (1990). Computer aided analysis and optimization of biogas enrichment process. *J Energy Heat Mass Transf*, 12(1), 17-24.
- Okewale, A. O. and Adesina, O. A. (2019). Evaluation of biogas production from co-digestion of pig dung, water hyacinth and poultry droppings. *Waste Disposal & Sustainable Energy*, 1, 271-277. <https://doi.org/10.1007/s42768-019-00018-8>
- Olsson, J., Feng, X. M., Ascue, J., Gentili, F. G., Shabiiimam, M. A., Nehrenheim, E., et al. (2014). Co-digestion of cultivated microalgae and sewage sludge from municipal waste water treatment. *Bioresour Technol*, 171, 203-210. <https://doi.org/10.1016/j.biortech.2014.08.069>
- Onda, K., Sada, E. and Takeuchi, H. (1968). Gas absorption with chemical reaction in packed columns. *J Chem Eng Japan*, 1, 62-66. <https://doi.org/10.1252/jcej.1.62>
- Rajvaidya, A. S. (2002). Pre-combustion desulfurisation of gaseous fuels. In *Proceedings of All India Seminar on Recent Trends in Automotive Fuels*, Nagpur, Aug 23-24.
- Samson, R. and LeDuy, A. (1983). Improved performance of anaerobic digestion of *Spirulina maxima* algal biomass by addition of carbon-rich wastes. *Biotechnol Lett*, 5(10), 677-682. <https://doi.org/10.1007/BF01386361>
- Sekhar, D. M. R. and Aery, N. C. (2005). *PROM manual*. Udaipur: Himanshu Publishers.
- Thanikal, J. V., Yazidi, H., Torrijos, M. and Rizwan, S. M. (2015). Biodegradability and bio methane potential of vegetable, fruit and oil fraction in anaerobic co-digestion. *Int J Current Res*, 7(07), 18379-18382.
- Van Krevelen, D. W. and Hoftijzer, P. J. (1947). Studies of gas absorption. I. Liquid film resistance to gas absorption in scrubbers. *Receuil des Trav Chim des Pays-Bas*, 66, 49-70. <https://doi.org/10.1002/recl.19470660106>
- Van Krevelen, D. W. and Hoftijzer, P. J. (1948). Enhancement factor in gas – liquid absorption. *Receuil des Trav Chim des Pays-Bas*, 67, 563-570. <https://doi.org/10.1002/recl.19480670708>
- Van Krevelen, D. W. and Hoftijzer, P. J. (1948). Mass transfer coefficients in gas-liquid absorption in packed towers. *Chem Eng Progr*, 44, 529-533.
- Vats, N., Khan, A. A. and Ahmad, K. (2019). Anaerobic co-digestion of thermal pre-treated sugarcane bagasse using poultry waste. *J Environ Chemi Eng*, 7(5), 103323. <https://doi.org/10.1016/j.jece.2019.103323>
- Vats, N., Khan, A. A. and Ahmad, K. (2019). Effect of substrate ratio on biogas yield for anaerobic digestion of fruit vegetable wastes and sugar cane bagasse. *Environ Tech and Innovation*, 13, 331-339. <https://doi.org/10.1016/j.eti.2019.01.003>
- Vats, N., Khan, A. A. and Ahmad, K. (2019). Observation of biogas production by sugarcane bagasse and food waste in different composition combinations. *Energy*, 185, 1100-1105. <https://doi.org/10.1016/j.energy.2019.07.080>
- Wang, X., Yang, G., Feng, Y., Ren, G. and Han, X. (2012). Optimizing feeding composition and carbon–nitrogen ratios for improved methane yield during anaerobic co-digestion of dairy, chicken manure and wheat straw. *Biores Technol*, 120, 78-83. <https://doi.org/10.1016/j.biortech.2012.06.058>
- Weizhang, Z., Zhongzhi, Z., Yijing, L., Wei, Q., Meng, X. and Zhang, M. (2012). Biogas productivity by co-digesting Taihu blue algae with corn straw. *Bioresour Technol*, 114, 281-286. <https://doi.org/10.1016/j.biortech.2012.02.111>
- Ye, J., Li, D., Sun, Y., Wang, G., Yuan, Z., Zhen, F. and Wang, Y. (2013). Improved biogas production from rice straw by co-digestion with kitchen waste and pig manure. *Waste Manag*, 33(12), 2653-2658. <https://doi.org/10.1016/j.wasman.2013.05.014>
- Yen, H. W. and Brune, D. E. (2007). Anaerobic co-digestion of algal sludge and waste paper to produce methane. *Bioresour Technol*, 98, 130-134. <https://doi.org/10.1016/j.biortech.2005.11.010>
- Yuan, X., Wang, M., Park, C., Sahu, A. K. and Ergas, S. J. (2012). Microalgae growth using high-strength wastewater followed by anaerobic co-digestion. *Water Environ Res*, 84, 396-404. <https://doi.org/10.2175/106143011X13233670703242>