

Production Of Hydromethane from Biomass

Group No - (R17 P)

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Abstract

Biologically produced energy sources have been identified as attractive alternates to traditional fossil fuels due to numerous reasons. There is now universal recognition of the fact that fossil fuels and their derivatives are under extensive exploitation and the process for search of an alternative fuel is of utmost importance. As a result, the idea of synthesis of Methane from biomass has been proposed along with discussion of its overall advantages over fossil fuels, proposal of a more efficient engine and an exhaust unit. Various areas in our daily life can be affected by the successful outcome of this task as many activities depend upon it. Multiple steps have been suggested to reduce the emission of carbon monoxide and other harmful emitted gases from vehicles, as well.

Introduction

Energy is one of the essential ingredients of modern society. Nowadays energy comes for the greater part from fossil fuels like oil, natural gas and coal. The proven fossil fuel reserves are declining in most parts of the world. This demands for the development of sustainable alternative energy sources. On top of the problem of securing the supply, the combustion of fossil fuels produces CO₂, which contributes to global warming. CO₂ emissions from fossil fuels can, to some extent, be countered by sequestration of CO₂. This CO₂ sequestration, however, lowers overall efficiency significantly, resulting in a higher consumption of fossil fuels per unit of energy delivered and consequently a faster decline of fossil fuels reserves. Sustainable alternatives like wind, solar or biomass energy are required to replace the declining production of fossil fuels without increasing the amount of CO₂ in the atmosphere. Energy from biomass is a good addition to wind and solar energy, because of its continuous availability whereas wind energy and solar energy are intermittent energy sources. Natural gas plays an important role as an energy source worldwide. Natural gas is a relatively clean primary energy carrier and is therefore often the fuel of choice in many regions of the world. Replacing part of natural gas by Hydro Methane, produced from a sustainable primary energy source, with the same properties as natural gas facilitates the implementation of sustainable energy since natural gas reserves are not easily accessible in many countries. A Substitute Natural Gas can be produced from biomass (Bio-Methane) with a high efficiency and with low emissions from the plant itself (comparable with modern power plants).

Large scale installations would benefit from a location next to harbors.

Biomass is considered a CO₂ neutral fuel, because the amount of CO₂ released on burning biomass equals the amount taken from the atmosphere during growth of the biomass. Fuels like hydrogen, methane, and methanol produced from biomass have the potential to become a CO₂ negative fuel, because part of the biomass carbon is separated as CO₂ during the production process and can be sequestered. This might be an attractive option for reducing the level of greenhouse gases in the atmosphere. Methane produced from biomass is used for synthesis of methane hydrate. We reviewed an alternative method for efficient and routine synthesis of pure methane hydrate in a form that is highly suitable as a benchmark for measurement of properties. We reviewed an *in situ* "seeding" method for hydrate nucleation and growth, a procedure developed from extensive work on other H₂O-based compounds in which successful growth of polycrystalline test specimens with controlled and

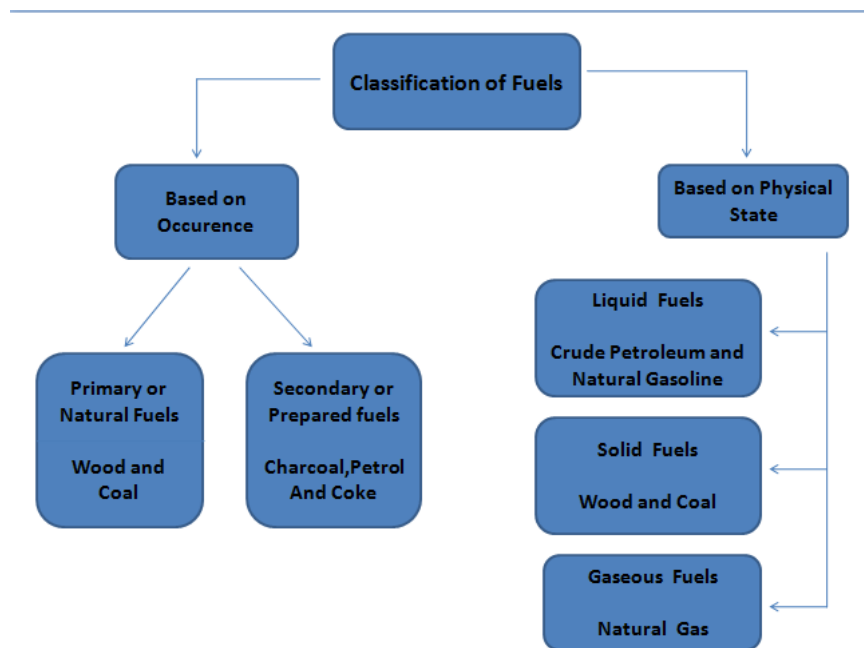
Hydromethane

uniform crystal size, is to be observed. The complete process for synthesis of the Hydromethane has been discussed in the subsequent chapters with great detail.

Fuels

A **fuel** is any material that can be made to react with other substances so that it releases energy in the form of thermal, light, chemical or nuclear energy. The energy released by reactions of fuels is converted into mechanical work using heat engine. Other uses of this energy include warmth from the heat energy, cooking processes, illumination from the combustion itself, industrial processes and other automation processes. In human body, fuels are also used by the cells of the organisms from the process of assimilation of food from a process known as cellular respiration, where organic molecules are oxidized to release heat energy which is used by our cells for various internal processes and activities. Hydrocarbons and related oxygen containing molecules are the most common source of fuel used by humans, but other substances, including radioactive metals, are also utilized.

Classification of fuels



Energy Content of fuels

The amount of energy from different types of fuel depends on the stoichiometric ratio, the chemically correct air and fuel ratio to ensure complete combustion of fuel, and its **Specific energy**, the energy per unit mass.

Fuel	Specific energy (MJ/kg)	Energy @ $\lambda=1$ (MJ/kg _(Air))
Diesel	48	3.310
Ethanol	26.4	2.933
Gasoline	46.4	3.156
Hydrogen	142	4.140
Kerosene	46	2.949
LPG	46.4	2.698
Methanol	19.7	3.045

1 MJ \approx 0.28 kWh

Energy capacities of common types of fuel

Properties of fuels:

Density: Density is defined as the ratio of the mass of the fuel to the volume of the fuel at a reference temperature of 15°C. The unit of measurement for density is kg/m³ and measured by a hydrometer. It is important for assessing ignition qualities and other quantitative calculations.

Specific Gravity

: The specific gravity is a ratio, which is defined as the ratio of the weight of a given volume of oil to the weight of the same volume of water at a given temperature. The density of fuel, relative to water is called specific gravity. E.g. Light diesel oil has specific gravity as 0.85 - 0.87, furnace oil has 0.89 - 0.95.

Viscosity : The viscosity of a fluid is a measure of its internal resistance to flow. Viscosity depends on the temperature and decreases as the temperature increases. Every oil has its own temperature - viscosity relationship and measurement by viscometer. It is important characteristic for storage and use of fuel oil. It influences the degree of pre heating required for handling, storage and satisfactory atomization. Highly viscous oils may become difficult to pump, hard to light the burner, and difficult to handle. the low atomization may result in the formation of carbon deposits on the burner tips/walls. The pre-heating is necessary for proper atomization.

Flash Point : The flash point of a fuel is the lowest temperature at which the fuel can be heated so that the vapor gives off flashes momentarily when an open flame is passed over it. The 66 °C is the flash point for furnace oil.

Pour Point : It is the fuel's lowest temperature at which it will pour or flow when cooled under prescribed conditions. It is a rough estimation of the lowest temperature at which fuel oil is ready to be pumped.

Specific Heat : Specific heat is the amount of calories needed to raise the temperature of 1 kg of oil by 10C. The unit of specific heat is kcal/kg0C. It varies from 0.22 to 0.28 depending on the oil specific gravity.

Calorific Value : The calorific value measures the heat or energy produced. Gross calorific value (GCV) assumes all vapor produced during the combustion process is fully condensed and Net calorific value (NCV) assumes

the water leaves with the combustion products without fully being condensed. Fuels should be compared based on the net calorific value. The calorific value of fuel oils is much more consistent compare to coal (solid fuel), for example kerosene and diesel oil got the GCV 11,100 and 10,800 kCal/kg respectively. Heat of combustion is conventionally measured using a bomb calorimeter.

Fuel	HHV MJ/kg	HHV BTU/lb	HHV kJ/mol	LHV MJ/kg
Hydrogen	141.80	61,000	286	119.96
Methane	55.50	23,900	889	50.00
Ethane	51.90	22,400	1,560	47.622
Propane	50.35	21,700	2,220	46.35
Butane	49.50	20,900	2,877	45.75
Pentane	48.60	21,876	3,507	45.35
Paraffin wax	46.00	19,900		41.50
Kerosene	46.20	19,862		43.00
Diesel	44.80	19,300		43.4
Coal (anthracite)	32.50	14,000		
Coal (lignite - USA)	15.00	6,500		
Wood (MAF)	21.70	8,700		
Wood fuel	21.20	9,142		17.0
Peat (dry)	15.00	6,500		
Peat (damp)	6.00	2,500		

Ash Content : The ash value is related to the inorganic material or salts (compounds of sodium, vanadium, calcium, magnesium, silicon, iron, aluminum, nickel etc.) in the fuel oil and ash levels in distillate fuels are negligible. The residual fuels have higher ash levels. The ash has an erosive effect on the burner tips, causes damage to the refractories at high temperatures and gives rise to high temperature corrosion and fouling of equipment.

Carbon Residue : Carbon residue indicates the tendency of oil to deposit carbonaceous solid residue on a hot surface like burner and injection nozzle when its vaporizable constituents evaporate. The residual oil contains carbon residue of 1% or higher.

Fossil Fuels

Fossil fuels are fuels formed by natural processes such as anaerobic decomposition of buried dead organisms, containing energy from ancient photosynthesis. The age of the organisms and their fossil fuels is millions of years, and sometimes exceed 650 million years. Fossil fuels contain high carbon content and their derivatives include petroleum, coal, and natural gas. Other derivatives include kerosene and propane. Fossil fuel derivatives include gaseous fuels like Methane, Natural gas and liquid fuels like Petroleum and Diesel. Solid Fossil Fuels include coal, bitumen and anthracite. Anthracite Coal consists of almost pure carbon with concentration of carbon revolving around 92.1% to 98%. Fossil fuels in the gaseous form include Methane and they can be found in hydrocarbon fields either alone, or in the form of methane clathrates. Although fossil fuels are continuously being formed via natural processes, they are considered to be non renewable resources because they take millions of years to form and the known viable reserves are being depleted much faster than new ones are being made.

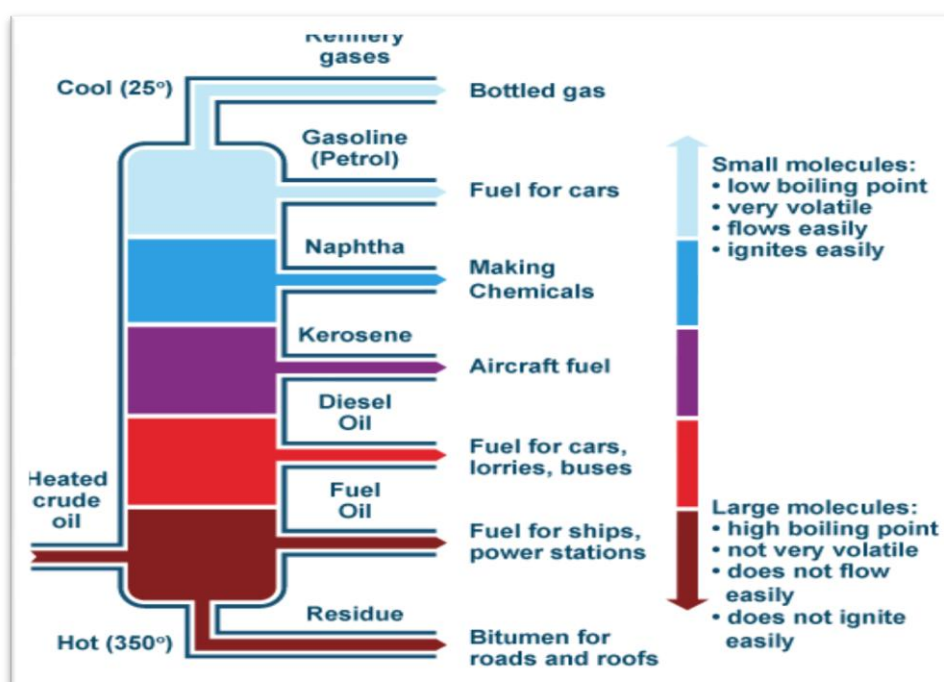


Diagram showing the Products in the Process of Fractional Distillation (Source : pubs.acs.org)

Uses of Fossil Fuels

Fossil fuels are of great importance because they can be burned, producing significant amounts of energy. The amount of energy generated by burning per unit of weight of is called calorific value. Coal is the most popular of fossil fuels having various applications in industries and in generation of other forms of energy. Coal was used to run furnaces for the melting of metal ores.

Natural Gas is also considered a very valuable fossil fuel derivative. Natural gas deposits are also the main source of the element helium. Heavy Crude Oil which is much more viscous than conventional crude oil which is found in oil sands.

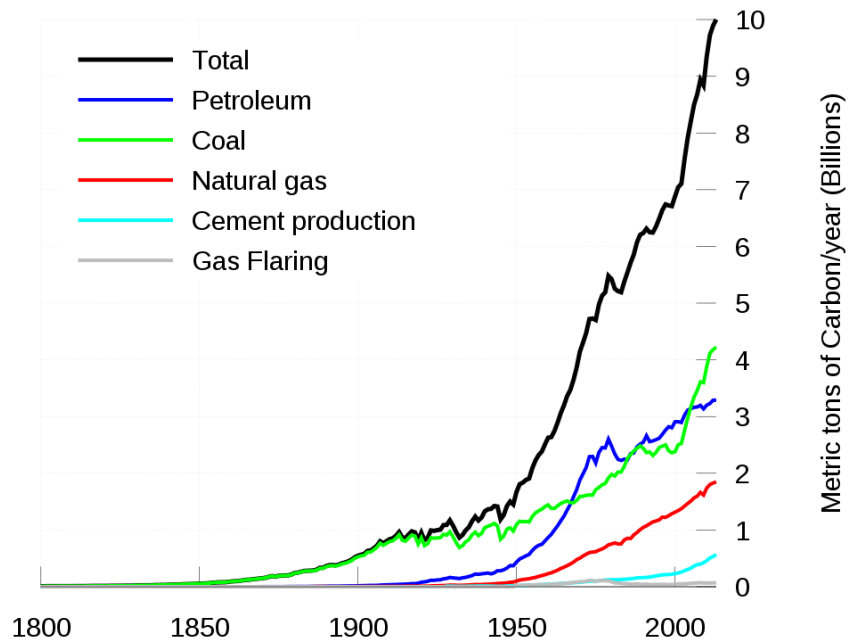
The wide scale use of fossil fuels, coal at first and petroleum later, to run [steam engines](#) enabled the [Industrial Revolution](#). The invention of the [internal combustion engine](#) and its use in [automobiles](#) and [trucks](#) greatly increased the demand for petroleum and diesel, both made from fossil fuels. Other forms of transportation, [railways](#) and [aircraft](#), also required fossil fuels. The other major use for fossil fuels is in generating electricity. [Tar](#), a leftover of petroleum extraction, is used in [construction of roads](#).

Environmental Concerns

The use of fossil fuels raises serious environmental concerns. The burning of fossil fuels produces around 21.3 billion tons of [carbon dioxide](#) (CO₂) per year, but it is estimated that natural processes can only absorb about half of that amount, so there is a net increase of 10.65 billion tons of atmospheric carbon dioxide per year. One ton of atmospheric carbon is equivalent to 44/12 or 3.7 tons of carbon dioxide. Carbon dioxide is one of the greenhouse gases that contributes to greenhouse effect and contributes to [global warming](#), causing the surface temperature of the Earth to rise in response, which [the vast majority of climate scientists](#) agree will cause major adverse affects on environment and various ecological processes. Combustion of fossil fuels generates Sulphuric, carbonic and nitric acids which fall to Earth as acid rain, affecting both natural areas and the buildings. Monuments and sculptures made from [marble](#) and [limestone](#) are particularly vulnerable, as the acids dissolve [calcium carbonate](#).

In economic terms, pollution from fossil fuels is considered as a negative [externality](#). Taxation is considered one way to make societal costs explicit, in order to 'internalize' the cost of pollution. This aims to make fossil fuels more

expensive, thereby reducing their use and the amount of pollution associated with them, along with raising the funds necessary to counteract these factors.



Graph Depicting Global Carbon Emissions (Source : Wikipedia.org)

Literature review

The following scholarly articles have been thoroughly read and reviewed by us:

1. Oxford journal by D. Pimentel, renewable energy : Bioscience
2. Institute forenergyresearch.org : Fossil Fuels
3. Daniel Zavala – Arazia, David T. Allen, Matthew Harrison, Fiji C.George , Gilbert R.Jersey : Natural Gas
4. Mark Maslin, Mathew Owen, Richard Betts, SimmonDay ,TomDunkly Jones, Andrew Ridgwell : Gas Hydrates (Clathrate).
5. Xin Wang, Haifeng Liu, ZunqingZheng, and Mingfa Yao:A Skeletal Mechanism of a Biodiesel Surrogate Fuel for Compression Ignition Engines.
6. M. C. Annesini, R. Augelletti, M. De Falco, S. Frattari, F. Gironi, M. A. Murmura :Production And Cleansing of Mixtures of Hydro-methane That are Used in Internal Combustion of Engines.
7. Chunde Yao, C.s. Cheung, C. H. Cheng : Decline in Production of Smoke and Nitrogen Oxides from Engines, Especially Diesel Engines Using Diesel/Methanol Compound Combustion System.
8. G.Tamizharasi, S.Kathiresan : Four Stroke Diesel Engine's Surface Ignition using Ethanol
9. MagínLapuerta', Octavio Armas, José Rodríguez-Fernández : Effect of Biofuel on Diesel Engine Emissions.

FOSSIL FUELS

RENEWABLE ENERGY : CURRENT AND POTENTIAL ISSUES - BIOSCIENCE

Oxford journal by D. Pimentel

- Coal,petroleum,natural gas provide 75% of U.S electricity and 93% of other energy needs
- Every year each American uses 93,000 kwh= 8000 litres of oil
- Cost of petroleum will rise
- U.S has consumed 82 to 88% of its oil reserves
- U.S imports 60% of its oil at cost of \$75 billion per year
- importing will increase to 90% within 20 years
- 3.6 trillion Kwh of energy is becoming insufficient for growing population of U.S
- Fossil fuels consumption is a key cause of global warming and climate change
- Global warming reduces agriculture production
- U.S with less than 4% of world population emit 22% of CO₂ from burning fossil fuels
- Diverse renewable energy sources provide only 8% of U.S needs and 14% of world
- Renewable resources: hydroelectric system biomass ,wind power,solar, thermal

Forms of energy	World(kwh X 10 ⁹)
Petroleum	43,271.7
Natural gas	24,414.9
Coal	27,295.8
Nuclear power	6984.0
Biomass	8439.0
Hydroelectric	7740.6

Production of energy from following resources worldwide

Source : Instituteeforenergyresearch.org

- 81% U.S energy demand fulfilled by fossil fuels
- Coal used since 1100 BC
- Concentrated organic compounds
- Inventing of fire bricks hiked use of coal
- Chinese refined crude oil for use in lamps
- Edwin drake extracted oil in 1859

- **Products of petroleum:**

Gasoline	45.3%
Heating oil and diesel	29.8%
Synthetic rubber and plastics	19.4%
Jet fuel	9.7%
Asphalt	2.1%

- Coal accounts for 30% of U.S electricity
- U.S is largest producer of natural gas

- **Energy consumption in U.S.A:**

Industrial	33%
Electric power	35%
Residential	17%
Commercial	12%
Transportation	3%

- 3.3% rise in fossil fuel demand by 2030
- Coal by 5.6% and natural gas by 13.4% increase in demand by 2030

Natural gas

Daniel Zavala- Araiza, David T. Allen, Matthew Harrison, Fiji C.George, Gilbert R.Jersey

- The natural gas supply chains originates from conventional, shale, coal bed, and other reservoirs.
- Important to allocate emissions to particular hydrocarbon products and reservoir types.
- Used life cycle allocation methods to assign methane emissions.
- Life cycle methods includes technique to assess environmental impacts associated with all the stages of a products life from cradle to grave (from raw material extraction, processing manufacture etc.).
- Emissions from production wells operating in shale formation to oil, condensate and gas products from wells.
- The emission allocations based on data set of 489 gas wells in routine operations and 19 well completion events.
- The methane emissions allocated to natural gas productions are approximately 85% of total emissions.
- Methane emissions allocated to salable natural gas production from shale formations, are a factor 2 to 7 lower than those reported in commonly life cycle data used life cycle data sets.
- Various life cycle allocation methods are used to assign methane emissions from production wells operating in shell formations to oil, gas products from the well.

GAS HYDRATES (CLATHRATE)

ROYAL SOCIETY BY Mark Maslin, Matthew , Owen, Richard Betts, Simon Day, Tom Dunkey Jones, Andrew Ridgwell

- Fossil fuel reservoirs can be used for almost a century. Hence we have to find some alternative source of energy which is called gas hydrate.
- Gas hydrates have ice-like structures having a mixture of water and gas under specific conditions i.e. pressure should be high and temperature should be low.
- Methane gas hydrate is the most common gas hydrate known on earth.
- The recent studies suggest that total amount of hydrate found on earth are in between 10000 to 11000 gig tonnes of carbon.
- Hydrates of hydrogen sulphide, Carbon dioxide and higher hydrocarbon hydrates usually exist at higher temperatures.
- Nitrogen hydrates and all the hydrates formed in dissolved salts require lower temperature.
- These are found below the oceans and in soils because they are covered with snow.
- About 1600–2000 Gig tonnes of Carbon is stored in ocean sediments and around 400 Gig tonnes of Carbon in Arctic soils because they are covered with snow.
- Production and use of these hydrates releases carbon dioxide, a major greenhouse gas contributor.
- Global warming prediction by intergovernmental panel on climate change, suggests that by the year 2100, temperature will rise between 1.1 °C to 6.4 °C and sea level will rise globally between 28-79 cm, which can even increase if the melting of Antarctica and Greenland accelerates.
- Due to global warming, the stability of these hydrate deposits decreases both under the oceans and in soil covered with snow leading to release in methane gas.
- As we know that methane is a very good greenhouse gas even 21 times more powerful than carbon dioxide, these hydrates have become one of the major concerns of global warming.
- Due to global warming, ice sheets start to melt. Increase in melting of ice sheets can also lead to tsunamis.
- Production technology that is cost-effective, environmentally friendly and safe has yet to be developed, for either marine or permafrost gas hydrate.

A Skeletal Mechanism of a Biodiesel Surrogate Fuel for Compression Ignition Engines

(Xin Wang, Haifeng Liu, ZunqingZheng, and Mingfa Yao)

- A reduced polycyclic aromatic hydrocarbon mechanism was merged into the skeletal combustion mechanism of MD to predict the soot emission.
- The skeletal mechanism was validated against the experimental data of ignition delays in a shock tube, as well as the mole fractions of the reactants and the intermediate species in a jet-stirred reactor.
- The skeletal mechanism maintains accuracy with its dramatically reduced size, compared with the detailed mechanism that consists of 2878 species and 8555 reactions.
- The skeletal mechanism was coupled with the KIVA code for 3-D biodiesel combustion simulation. Compared with the soot measurements in an optical constant volume combustion chamber, the simulation results showed similar soot location and occurrence during the combustion.
- Engine simulations were conducted with the EGR rate ranging from 0 to 65% at intake temperatures of 25 and 50 °C. The predictions profiles of the pressure and the heat release rate for various conditions agreed well with the experimental data.
- The skeletal mechanism predicted the emissions, including CO, HC, NO_x, and soot accurately.

Production And Purification Of Hydrogen-methane Mixtures Utilized In Internal Combustion Engines

Author(s)

M. C. Annesini , R. Augelletti, M. De Falco, S. Frattari, F. Gironi , M. A. Murmura

- Blends of hydrogen and methane (hydromethane) with 20–25% of H₂ can be used in internal combustion engines in order to reduce the CO₂ and unburned hydrocarbon emissions and greenhouse effect.
- Solar steam reforming of natural gas at 500–550°C is a suitable process to produce such a mixture, but the reformed gas must be purified to reduce the CO₂ concentration to less than 3%.
- Pressure Swing Adsorption (PSA) unit, which uses activated carbon as adsorbent material, is proposed to remove carbon dioxide, with H₂ and CH₄ recovery of about 99 and 43%, respectively.
- To enhance CH₄ recovery, a second PSA unit, using carbon molecular sieve (CMS) as adsorbent, can be introduced.
- The whole suggested process produces an enriched methane mixture with a hydrogen content of 25%, with an energy consumption of about 270 kJ/kg of hydro-methane, mainly due to the electrical energy required for gas compression and vacuum pumps.
- Environmental problems due to the extensive use of fossil-derived energy in our societies are leading to devote research and innovation efforts to the study of novel technologies for de-carbonizing the fuels, thus reducing the carbon dioxide (CO₂).

The reforming process :

The methane steam reforming (MSR) process is the most used massive hydrogen production route and is based on following reactions



which together yield



- The reactions are very fast on nickel based catalysts and conditions near to the equilibrium are easily reached. Since the global process is highly endothermic, operating temperature in the range 850–950°C have to be used to obtain high conversions.
- On the other hand, if the aim of the process is to produce EM blend, a low methane conversion is acceptable and the process can operate at a lower temperature, thus allowing the coupling of MSR with solar powered technologies, such as the molten salt based concentrating solar plant. Reforming process becomes environmentally friendly and requires only renewable energy.
- Required H₂/CH₄ ratio can be theoretically obtained even when operating at very low temperatures (near 400°C); in order to enhance the reaction kinetics, a higher temperature is suggested. We consider a temperature in the range 500–550°C: this temperature can be easily obtained with a concentrating solar plant.
- Furthermore efficient catalyst are suitable for the production a mixture with hydrogen content up to 30% even operating at high pressure in order to reduce the reactor size.

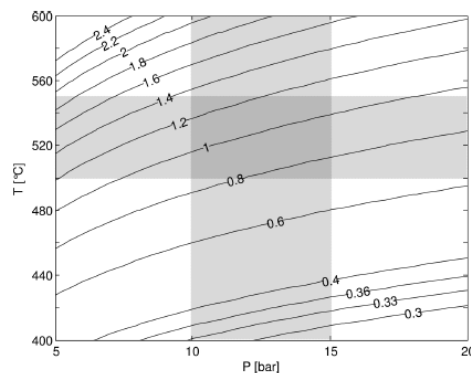


Figure 1: Hydrogen-to-methane ratio in the reformed gas as function of temperature and pressure. Feed: natural gas mixture (97% CH₄, 3% H₂) steam-to-carbon ratio 3.

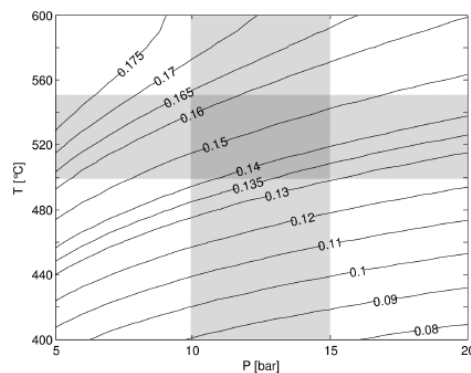


Figure 2: Carbon dioxide content in the reformed gas as function of temperature and pressure. Feed: natural gas mixture (97% CH₄, 3% H₂) steam-to-carbon ratio 3.

Pressure swing adsorption for reformed gas purification:

- This is the process to remove carbon dioxide by chemical absorption with amine solutions.
- Pressure Swing Adsorption (PSA) has attracted increasing interest because of its low energy Requirements and investment costs.
- In a PSA unit, an adsorbent material is subjected to pressure changes to selectively adsorb and desorb the undesired gas components; the process operates near ambient temperature, without any need of thermal regeneration.
- Solar driven steam reforming of natural gas with two PSA unit to remove carbon dioxide is a process to produce enriched methane mixture with 25% volume H₂ which can be efficiently used in NG internal combustion engine. The process can operate with an almost complete hydrogen recovery and a methane recovery greater than 97%. Using grid natural gas, the energy consumption is about 275 kJ per kg of produced hydro methane.

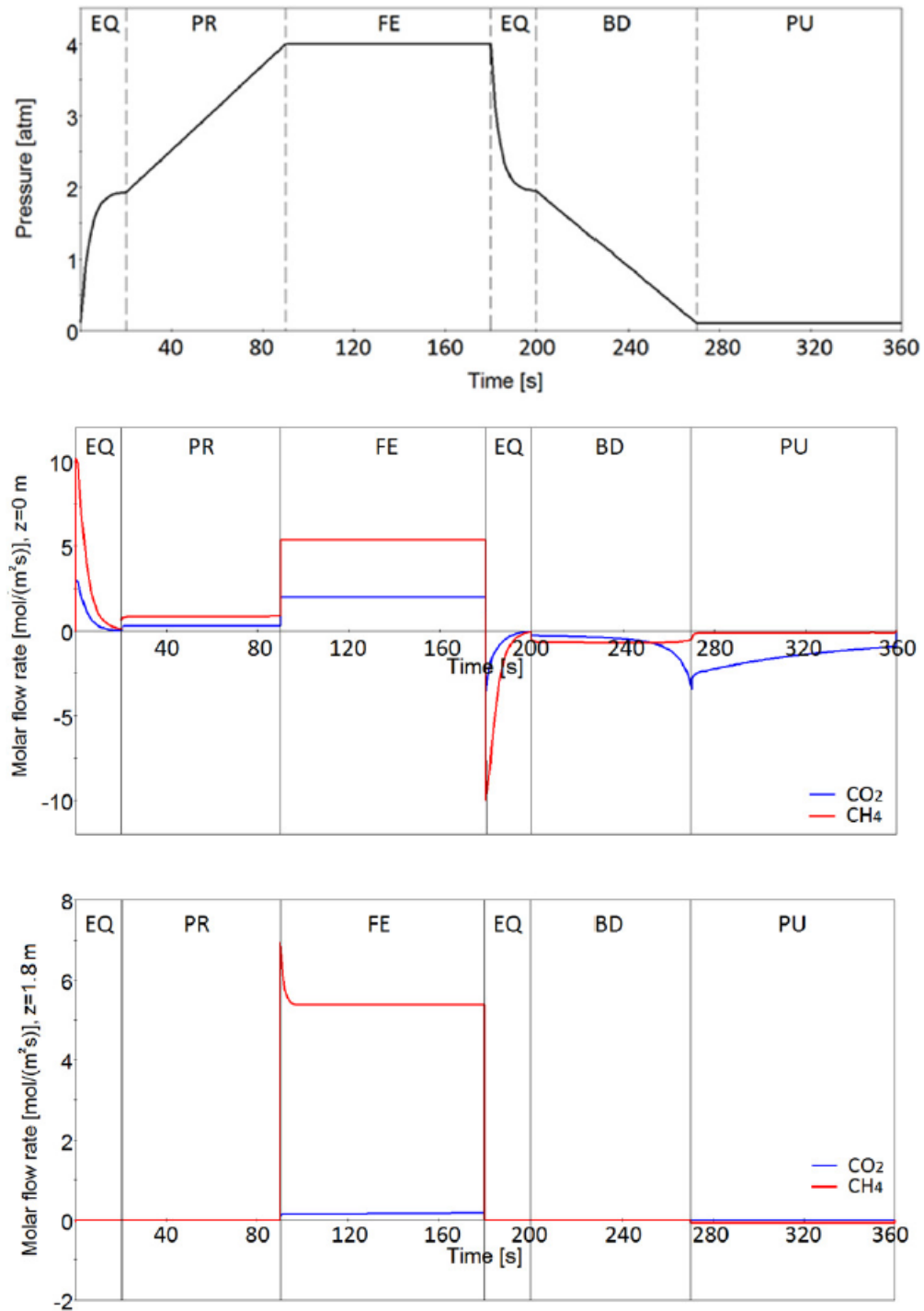
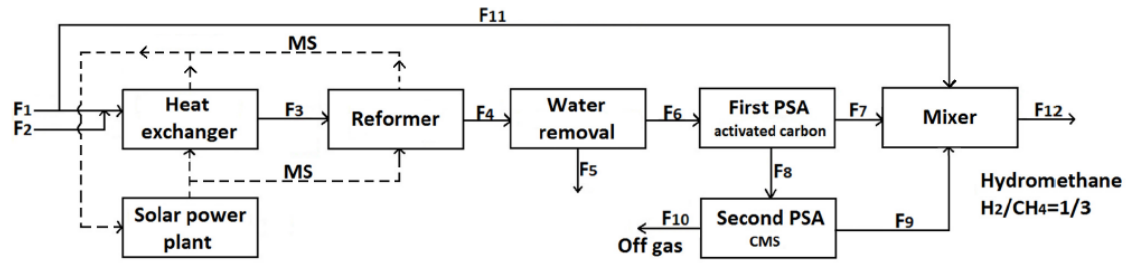


Figure 5: Pressure profile and flow rates in different steps of the PSA cycle for CH₄ recovery (column size in table 2).



	Flow rate		Composition, %				T	P
	kg/h	Nm ³ /h	CH ₄	CO ₂	H ₂	H ₂ O	°C	atm
F ₁	157.8	210	97	3	—	—	25	15
F ₂	490.7	611	—	—	—	100	25	15
F ₃	648.5	821.1	24.8	0.8	—	74.4	500	15
F ₄	648.5	891.6	18.9	4.6	15.6	60.9	514	14.5
F ₅	435.8	542.7	—	—	—	100	50	13
F ₆	212.7	348.9	48	12	40	—	25	13
F ₇	75.8	215.7	33.7	2.8	63.5	—	25	13
F ₈	136.8	133.2	71.9	26.6	1.5	—	25	1
F ₉	65.5	89.2	95.1	2.7	2.2	—	25	13
F ₁₀	72.7	42.1	25	75	—	—	25	1
F ₁₁	200.8	267.3	97	3	—	—	25	15
F ₁₂	342.2	570.3	73.1	2.9	24	—	25	13

Figure 6: Process of production and purification of EM mixture.

Reduction of Smoke and NO_x from Diesel Engines Using a Diesel / Methanol Compound Combustion System

By

Chunde Yao, C.s. Cheung, C. H. Cheng

- High particulate and nitrogen oxides emissions of diesel engines are major air pollution problems.
- Improvement of fuel properties can reduce pollutant emissions.
- Application of non-alcoholic oxygenates to diesel fuel is used for reducing pollutant emissions.
- The oxygenates used include esters, ethers, and carbonates. They are found to have a beneficial effect on reducing smoke and particulate emissions.
- The oxygen contents of the oxygenate helps in reducing particulate formation during the combustion process.

However, there are associated problems with the fuel additives including a probable increase in hydrocarbon and NO_x emissions.

- Alternative fuels such as alcohol fuels have also been applied to reduce emissions. Ethanol has been applied to spark ignition engines with success while its application to the diesel engine is also a current topic of research. Methanol has been extensively investigated as a transportation fuel because it is readily available from the conversion of biomass, coal.
- The low cetane number of methanol makes auto ignition difficult.
- Using methanol as a fuel show a reduction of particulate and NO_x emissions but an increase in CO and HC emissions from the methanol fuelled buses.
- Combined use of diesel and methanol is preferred over methanol.
- A decrease in PM and NO_x emissions but an increase in CO and HC emissions is found to occur.

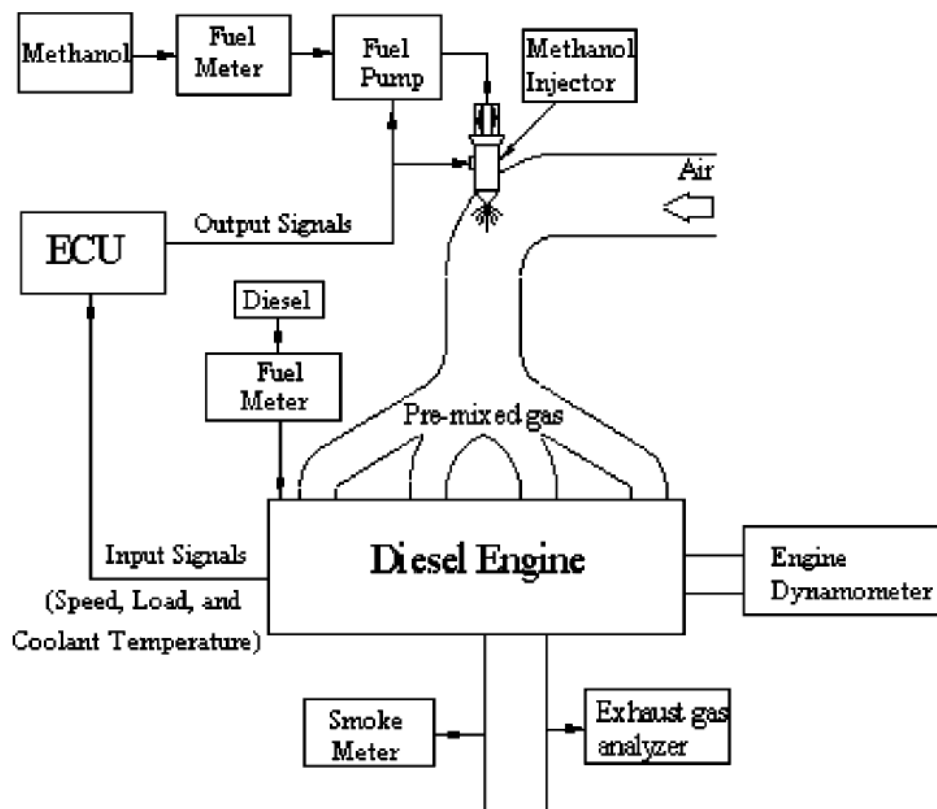
Table 1. Basic Properties of Diesel and Methanol Fuel

fuel type	diesel	methanol
cetane number	55	4
density (kg/m ³) @20°C	840	792
lower heating value (MJ/kg)	42.7	19.9
boiling point (°C)	195	64.5
latent heat of vaporization (MJ/kg)	0.28	1.09
fraction of oxygen/wt%	0	50
autoignition temp. (°C)	308	470
viscosity (MPa·S) @20 °C	2.8	0.61

Table 2. Specifications of Baseline Engines

Engine model	485QDI	4102BZQ
engine type	water-cooled, in-line, 4-stroke, 4-cylinder, DI, diesel engine	
bore/stroke (mm)	85/95	102/118
displacement (cc)	2156	3856
aspirated method	natural-aspirated	turbocharged
compression ratio	18	16.5
max. torque/speed (Nm/rpm)	110/2000	343/1600
max. power/speed (kW/rpm)	31/3000	88/2800
injection pressure (MPa)	20	19.5
injection nozzle	4-hole nozzle	4-hole nozzle
nozzle diameter (mm)	0.32	0.28

- Methanol is injected into the intake manifold through an electronically controlled fuel injection system.
- The quantity of methanol injected is controlled by the methanol injector operating time which is controlled by the engine control unit (ECU) based on the conditions.

**Figure 1.** Schematic of the experimental setup.

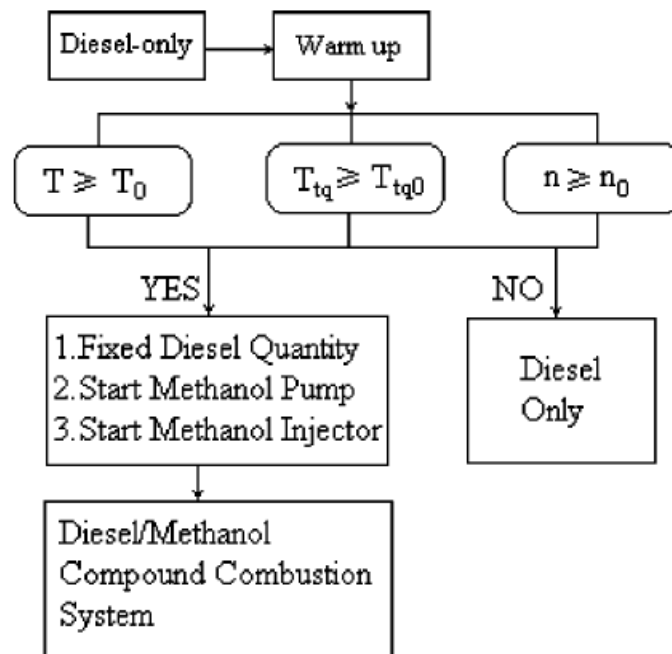


Figure 2. Flowchart of the DMCC control system.

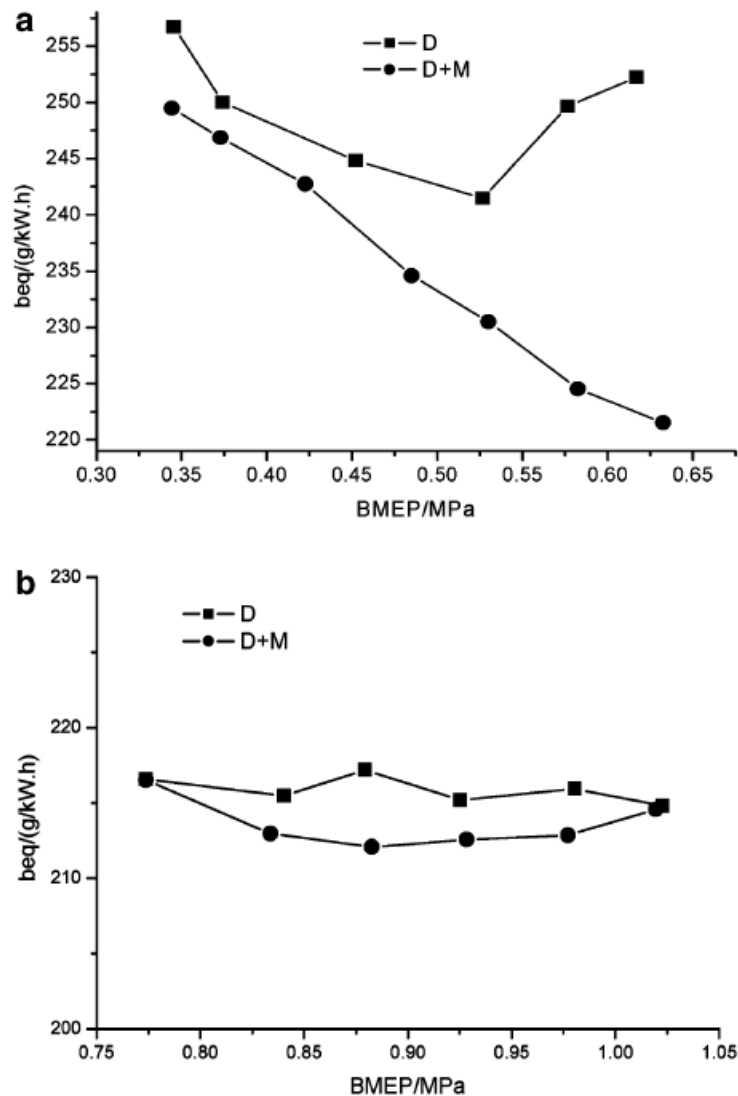


Figure 3. Comparison of brake specific equivalent fuel consumption (D for baseline engine, D+M for DMCC): (a) natural-aspirated engine; (b) turbocharged engine.

- The DMCC concept can be applied to both natural aspirated and turbocharged diesel engines with reduced brake specific equivalent fuel consumption.
- There is a significant reduction in smoke emissions from both engines using the DMCC system.
- There is a reduction of NO_x emission from both engines using the DMCC system due to the reduced intake air temperature and consequently the combustion temperature.
- There is an increase in CO and HC emissions due to the lower combustion temperature as well as the homogeneous methanol/air charge formed. However, an oxidation catalyst can be applied to reduce these pollutants.

Four Stroke Diesel Engine's Surface Ignition using Ethanol

G. Tamizharasi , S. Kathiresan

- Replacing diesel fuel entirely by alcohols is very difficult.
- Dual fuel engines could be best alternative to diesel engines.
- Ethanol can be produced from agricultural waste. The Ethanol Diesel emulsion technique is one of the techniques to use ethanol in Diesel engines. The most important profit of this technique is to use ethanol diesel as a dual fuel without any modification in diesel engine.
- Ethanol is an alternative to diesel fuel, it is renewable from biomass, it reduces carbon emissions and also a significant decrease in PM.
- Ethanol addition to Diesel reduces cetane number, viscosity and heating value.
- Ethanol is a promising oxygenated fuel. Pure ethanol with additives such as cetane number improver can sharply reduce particulates.

SCOPE OF ALCOHOLS

- Alcohols are the most plausible and abundant fuels of future. These type of alcohols can be made from non-petroleum sources.
- Methyl alcohol can be made from coal, ethyl alcohol can be produced by fermentation of carbohydrates which occur naturally and abundantly in some plants like sugarcane, potatoes, corn.
- Therefore these type of fuels can be made easily from these abundant and everlasting raw materials.
- These alcohols require high ignition temperature and therefore a high intensity spark is required to ignite these fuels.

Dual Fuel system

Fumigation

- Addition of secondary fuel to the intake air charge
- Displacing up to 50% of the diesel fuel demand

Dual injection

- Separate injection system with control for each fuel.
- Displacing up to 90% of diesel engine demand.

Blend Fuel

- Mixture of the fuel just prior to injection.
- Displacing up to 25% of diesel engine demand Fuel Emulsion.

- Mixture of the fuel by using emulsifier Displacing up to 25% of diesel engine demand.

Fuel Emulsion

- Mixture of the fuel by using emulsifier.
- Displacing up to 25% of diesel engine demand.

- **Ethanol Fuel**

Applications of Ethanol

- Gasoline blend (5 – 10%)
- Diesel blend (E-diesel)

Characteristic of Ethanol

- Lower volumetric energy content.
- High octane rating.
- Result in increased engine efficiency and performance.
- Environmental characteristics.
- Produced “renewably”.
- Reducing greenhouse gas emission.

Effect of Biofuels on diesel engine emissions

MagínLapuerta, Octavio Armas, José Rodríguez-Fernández

- In recent years, the reduction in sulphur content is the most notable restriction.
- Biofuel commonly refers to fatty acid methyl or ethyl esters made from vegetable oils or animal fats, whose properties are good enough to be used in diesel engines.
- Biofuel has around 9% less heating value in volume than conventional diesel fuel. Thus, if engine efficiency is the same, engine fuel consumption should be proportionally higher, and consequently vehicle autonomy proportionally lower, when using Biofuel.
- Biofuels have higher lubricity than other fuels, but they can contribute to creation of deposits, the degradation of materials or the plugging of filters, depending primarily on degradability, glycerol content, cold flow characteristics & on additional quality specifications.
- Biofuel is 100% renewable only when the alcohol used in the transesterification process is also renewable, but this proportion is reduced to around 90% (if the balance is made in mass) or 95% (if the balance is made in carbon mass) when fossil alcohol (usually methanol) is used.
- Biofuels also have an exciting potential to minimize chemical discharges.
- Oxides of nitrogen and particulate matter (PM) are the most significant in diesel engines due to the high flame temperature and diffusive combustion in the combustion chamber.

Engine performance

- Automotive engines are usually oversized and the power output when using Biofuel is usually the same as with diesel fuel, as the accelerator is not fully pressed down in most cases.
- The higher viscosity of Biofuel, which may affect the engine brake effective power, especially in full-load conditions.
- The advanced bulk modulus & sound velocity of Biofuel together with its advanced viscosity lead to a progressive start of injection. This, jointly with any cetane no. increase, may somewhat advance the beginning of combustion.
- Present diesel engine(s) must have delayed combustion to reduce pressure and temperature peaks in the combustion chamber, and thereby nitric oxide formation. If the start of injection, and thus that of combustion, is advanced, the combustion process is then re-centered and the power output increases.

- The higher lubricity of Biofuel could also reduce friction loss leading to an increased brake effective power.
- It is very unlikely that lubricity could contribute to the torque and power recovery.
- Full- load rotation curve was flatter and with highest at lower engine speeds when different Biofuel fuels (obtained with both methanol and ethanol) were used.

Brake-specific fuel consumption

- Brake specific fuel consumption is the ratio between mass fuel consumption and brake effective power, and for a given fuel, It is contrariwise proportional to thermal efficiency.
- Biofuel is going to increase by 14% in relative to the feeding with diesel fuel, conforming to the increase in heating value in mass basis.
- With respect to feeding of diesel fuel, a huge nos. of authors found increases in Biofuel fuel consumption in proportion to the Biofuel content in the blends & to loss of heating value.

Thermal efficiency

- Thermal efficiency is the ratio b/w the power output & energy presented over fuel injection.
- The opposite of thermal productivity is usually called as brake-specific energy consumption.
- Mostly it is established that thermal efficiency is similar to diesel fuel when using Biofuel or even with blends.
- Thus fuel consumption is not caused by any loss in efficiency but rather by the reduced heating value of Biofuel.
- Small developments in efficiency with Biofuel are observed, or even synergic blending effects, which can be caused by decrease in friction loss associated with higher lubricity.

Nitric oxides

Effect of Biofuel

- NO_x increases only in certain operating conditions.
- The rise in NO_x emissions obtained were in percentage to the concentration in Biofuel.
- There are even combustion models simulating the increase on NO_x emissions when using Biofuel fuels.

- The effect of Biofuel on NO_x emissions depends on the type of engine and its operating conditions.
- A slight decrease in NO_x emissions at low loads but increase at high loads is observed.
- The bigger cetane number of Biofuel fuel could explain the above mentioned different effect of Biofuel on NO_x emissions depending on the engine load.
- NO_x emissions were reduced at low load with enhanced cetane number. This effect could recompense any rise caused by the chemical composition of Biofuel.
- This advance was higher with diesel than with Biofuel fuel in a certain load range, leading to increased NO_x emissions with diesel fuel at these load conditions.

Reasons for the increase in NO_x emissions with Biofuel

- The combustion process is advanced as a consequence of the advanced injection derived from the physical properties of Biofuel (viscosity, density, compressibility, sound velocity).
- The main reasons for the increase of NO_x emissions with Biofuel are injection-related.
- The beginning of combustion was more progressive with Biofuel, leading to a high average temperature peak. The observed shift in the start of combustion increased with increasing loads.
- The consequence of the physical characteristics of Biofuel on the injection improvement (with respect to the start of injection with diesel fuel) has been widely proved in engines without shared rail injection system, but through pump-line-nozzle systems.
- When Biofuel is injected, the pressure increase created by the pump is faster because of its lower high bulk modulus & also propagates more speedily towards the injectors as a result of its higher sound velocity.
- The higher viscosity reduces leakages in the pump leading to an increase in the injection line pressure.
- A faster & earlier needle opening is detected in bio-fuel than the case of diesel fuel.
- The electric control unit also usually contributes to this advanced injection when using Biofuel, as a consequence of the accelerator over pressing needed to compensate the reduced heating value
- Higher cetane nos. could not only cause a combustion advance but a decrease in premixed combustion, the latter leading to softer pressure.
- The fuel spray properties like droplet size distribution, droplet moment of inertia, air entrainment, penetration, fuel evaporation, and heat dissipation are

all affected by the fuel properties: viscosity, surface tension & boiling temperature. All of these may have some influence on the delay time, on the premixed/diffusion combustion ratio and, in consequence, on the NO formation

- Nitric oxide is created by the prompt technique . The reactions governing the prompt mechanism are sensitive to the concentration of radicals, which could be higher during the combustion of Biofuel.
- The reduced soot formation, which could eliminate the reactions between carbon and nitric oxide. However, very little knowledge about these reactions has been developed as yet.

Measures to compensate the effect of Biofuel on NO_x emissions

- The injection cartographies are optimized by engine designers as a function of the NO_x-soot trade-off. Delaying injection has often been proposed to return the NO_x emissions level back to that observed with diesel fuel, although the advantage of lower soot or PM emissions is then reduced

Reasons for the reduction of PM emissions with Biofuel

- The oxygen content of the Biofuel molecule, which enables more complete combustion even in areas of the combustion compartment with fuel-enriched diffusion flames.
- The lower stoichiometric need of air in the case of Biofuel combustion and , which reduces the possibility of fuel-rich areas in the non-uniform fuel/air mixture.
- Absence of aromatics in Biofuel fuels, those being considered soot precursors. The decrease in aromatic content obtained, by unifying diesel fuel with octadecane (C₁₈H₃₈) provided a noteworthy decrease in PM emissions, which was even more noteworthy if soybean-oil Biofuel was also added in the blend.
- The combustion advance derived from the use of Biofuel. This effect, enlarges the residence time of soot particles in a high-temperature atmosphere, which in the presence of oxygen promotes further oxidation.
- The different structure of soot particles between Biofuel and diesel fuels, which may also favour the oxidation of soot from Biofuel.
- The nil sulphur content of most Biofuel fuels, which prevents sulphate formation, this being a significant component of typical diesel PM and , and the scrubbing effect, by which sulphur converts to an dynamic centre for hydrocarbon adsorption on the soot surface. However, the importance of this argument is currently fading as the standards of sulphur content in diesel fuels are also being sharply reduced.

- Often lower B.P of Biofuel, regardless of its higher mean distillation temp., provides lower possibility of tar being created from bulky hydrocarbon parts that is not able to vaporize.

Explanation for the reduction of total hydro carbon emissions with Biofuel

- Many explanations have been suggested to explain decline in total hydro carbon emissions after replacing conventional diesel with Biofuel:
- The oxygen content in the Biofuel molecule points to extra complete and cleaner combustion.
- The upper Cetane no. of Biofuel reduces the burning delay, and this type of reduction has been related to decreases in total hydro carbon emissions
- Although Biofuel is less volatile than diesel fuel, higher final distillation points have been reported for diesel fuel. This final fraction of the diesel may not be completely vaporized and burnt, thereby increasing It was resolved in to review that total hydro carbon emissions reduced as the O₂ in the combustion chamber improved, with oxygenated fuels or oxygen - riched air emissions.
- The advanced injection and combustion timing when using Biofuel. It is widely believed that injection improvement could contribute to slightly increased nitrogen oxide emissions with Biofuel, as explained in but Storey et al. Also observed that the more advanced the injection, the lower the Total Hydro Carbon emissions.
- Flame ionization detectors predictably used for calculating these emissions may have a lower sensitivity detecting oxygenated compounds, such as the ones that could be present in exhaust gas when consuming an oxygenated fuel similar to Biofuel.
- Since Biofuel is a less volatile fuel, hydrocarbons with high molecular weights and high boiling points could remain in the exhaust gas.

Reasons behind reduction in Carbon mono-oxide emissions

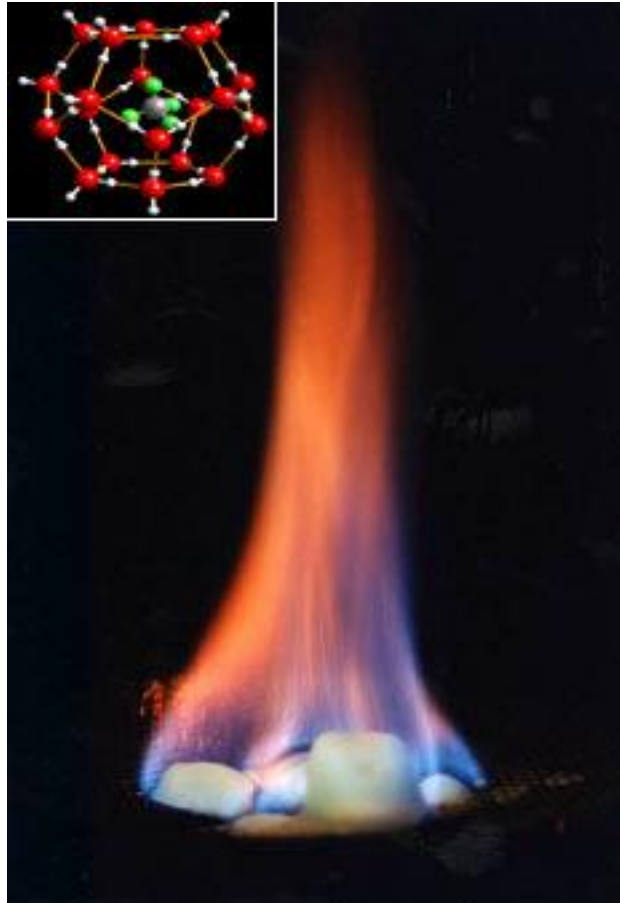
- Many reasons have been observed to explain Carbon mono-oxide decrease after replacing diesel by Biofuel:
- Further oxygen in fuel, which increases combustion of fuel, thus decreasing Carbon mono-oxide discharges. Lower Carbon mono-oxide concentration in exhaust line when O₂ in combustion chamber was enhanced with oxygenated fuels / oxygen enriched air.
- More the cetane no., lower the possibility of fuel-rich formation, often related to Carbon mono-oxide emissions.

- As stated in other sections, the increased injection & combustion while using Biofuel could justify the Carbon mono-oxide reduction with this fuel. Researches reported reductions in Carbon mono-oxide emissions when injection timing was increased.

Conclusion

- At less load process, no change in result is expected, since it increases in fuel used in case of biofuel will recompense its reduced heating value. In fully loaded condition, a certain fall in power is found with Biofuel, but the decrease is lower than that corresponding to the decrease in heating value, this means that a minor power retrieval is usually observed.
- An increase in Brake Specific Fuel Consumption is found when using Biofuel in most of studies. Such an increase is generally in proportion to the fall in heating value. Consequently, efficiency (thermal) of diesel engine is not greatly changed when replacing diesel by Biofuel either pure or blended.
- Majority of researches report small rise in Nitrogen oxide emission when using Biofuel fuels. Cause that is usually pointed out is that injection process is more advanced with bio diesel. The physical characteristics of bio diesel or the response of the electronic unit will cause such an increase. Some researchers prefer delaying injection as a mean to reduce the increase in Nitrogen oxide emissions, with less penalty in particulate emissions.
- A sudden decrease in particulate emission with Biofuel as compared to diesel is observed. This decrease is mainly caused by decreased soot creation & increased soot oxidation. The oxygen content & the absence of aromatic material in bio diesel have been reached out as the biggest reason. Under cold-start condition, the reduction could be reduced or even backed to cause sudden increase.
- A bulk of researchers have reported a fall in approximate diameter of the Particle size distribution obtained when Biofuel is used. While such a shift is largely caused by a sudden decline in number of big particles, some researchers have also found a sudden increase in number of the smallest ones.
- Other regulated emissions such as unburnt carbon particle and Carbon mono-oxide are found to significantly decrease with Biofuel. A Full combustion caused by increased oxygen in flame upcoming from the Biofuel molecules reached out as the main cause in every case.
- Emission of aromatic and poly aromatic compounds, and also their toxic effect, has been perceived to be minimised with Biofuel. However, no fixed trend is found regarding the emission of oxygenated compound like aldehyde and ketone. Further research shall be done in this field in future.

Hydromethane



Methane clathrate ($\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$) or ($4\text{CH}_4 \cdot 23\text{H}_2\text{O}$), also called **methane hydrate**, **hydromethane**, **methane ice**, **fire ice**, **natural gas hydrate**, or **gas hydrate**, is a solid clathrate compound (clathrate) in which a large amount of CH_4 is enclosed within a crystal structure of water, forming a solid resembling ice. Originally it was believed that it occurs only in the outer regions of the Solar System, where temperatures are low and water ice is common, high number of deposits of methane clathrate are found as sediments on the deepest ocean beds on Earth.

Methane clathrates are the common elements found in marine beds and occur in deep sedimentary structures and form visible rock-like structures on the ocean floor. Methane hydrates are believed to be formed by migration of gas deep along geological faults, followed by precipitation or crystallization, on contact of the rising gas with cold sea water (where temperatures range from 3 to 7 degree centigrade).

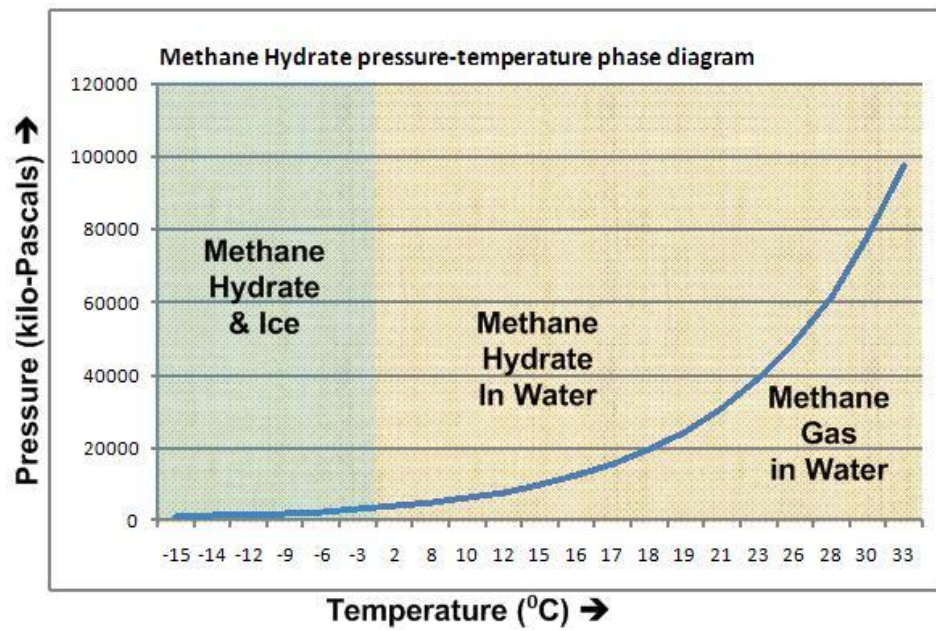
Methane clathrates are also found to be present in deep ocean waters along with other fossil based fuels.

Structure and composition

Methane clathrate hydrate consists of 1 mole of methane for every 5.75 moles of water, corresponding to 13.4% methane by mass, although the actual composition is dependent on how many methane molecules fit into the various cage structures of the water's crystal structure. The observed density is found to be around 0.9 g/cm^3 , which means that methane hydrate will float to the surface of the sea or of a lake unless it is bound in place by being formed in or anchored to sediment. One litre of fully saturated methane clathrate solid would contain about 120 grams of methane (or around 169 litres of methane gas at 0°C and 1 atm).

Methane forms a structure I hydrate with two dodecahedral (12 water molecules at 12 vertices) and six tetradecahedral (14 water molecules) water cages per unit cell. (Because of sharing of water molecules between cages, there are only 46 water molecules per unit cell.) This leads us to a coordination number of 20 for methane in aqueous solution. Recently, a clay-methane hydrate complex was synthesized in which a methane hydrate complex was synthesized at the interface of a sodium-rich montmorillonite clay. The upper temperature stability of this phase is similar to that of structure I hydrate.

Hydromethane



Phase Diagram of Methane Hydrate (Source : wikiwand.org)

Natural Deposits



Specific structure of a gas hydrate piece, found near Oregon

Methane clathrates are found exclusively in the shallow lithosphere (i.e. < 2,000 m depth). Necessary conditions are found only in continental [sedimentary rocks](#) in polar regions where average surface temperature is less than 0 °C, or at water depths greater than 300 m where the water temperature is around 2 °C. In addition, deep fresh water lakes may also have gas hydrates as well, e.g. the fresh water [Lake Baikal](#), Siberia. Continental deposits are located in [Siberia](#) and [Alaska](#) in [sandstone](#) and [siltstone](#) beds, less than 800 m depth. Oceanic deposits seem to be prevalent in the [continental shelf](#) and can occur at depth close to the sediment water bed. They may cover even larger excesses of gaseous methane.

Commercial use

Crystals of Methane Hydrate contain probably contains 2 to 10 times the currently known energy content of any conventional fossil fuel. This represents a potentially important future source of fossil fuels. However, in the majority of sites deposits are thought to be too dispersed for economic extraction. Other problems that persist for the commercial exploitation of methane clathrate are detection of feasible hydrate reserves and development of the technology for extracting methane gas from the hydrate deposits.

Synthesis of Hydromethane

As formation of Fossil fuels takes a lot of time and due to their non availability, they are considered as non renewable resource. Our idea of synthesis of Hydromethane was from formation of methane from biomass. Methane is created by a process termed anaerobic digestion, leaving behind a nutrient- rich liquid called in layman terms as a 'digestate'. Anaerobic digestion is carried out by methanogen bacteria, in the absence of oxygen. Initially carbon dioxide is produced aerobically by the decomposing organic matter until an anaerobic environment is created. After the initial digestion bacteria, convert the feedstock into methane and carbon dioxide.

Anaerobic digestion has a number of environmental benefits including production of 'green' energy and natural fertilizers, from biological wastes, thus helping in waste management also. The process of converting organic feedstock into methane can serve as a substitute for fossil fuels and artificially synthesized fertilizers, reducing a significant amount of greenhouse gases which are released into the atmosphere. The chemicals released once the manufacturing process for fertilizers has been completed leads to Eutrophication and thus, this process would significantly reduce water

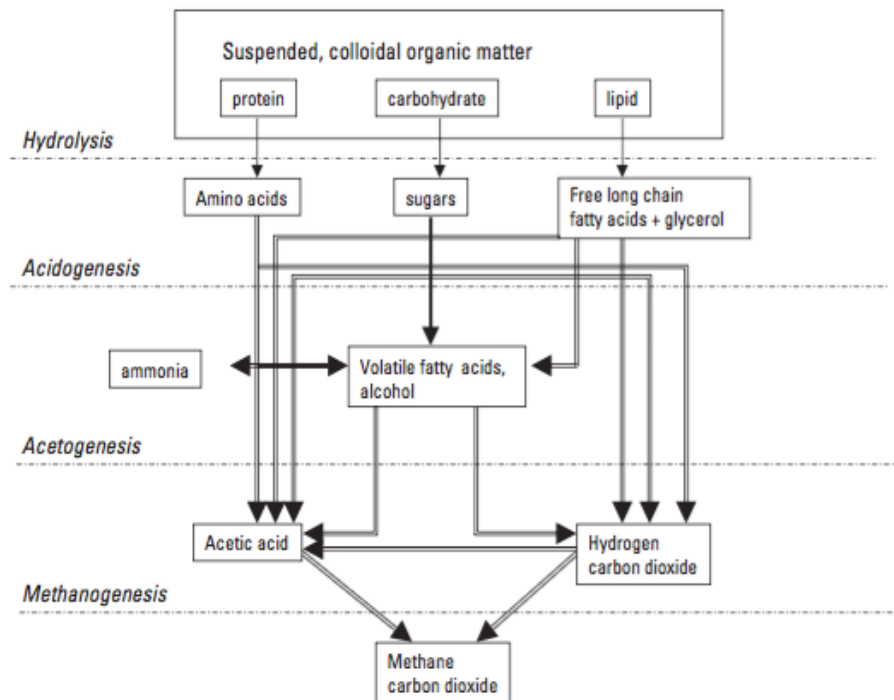
pollution also. The problems associated with waste disposal are also lessened by the production of useful products and reduced release of the potent greenhouse gases, methane, from landfill sites.

Methanogens are bacteria that respire anaerobically that cannot grow in the presence of oxygen. They use CO_2 as an electron acceptor and Hydrogen as a source of electrons. The reduction of CO_2 produces methane gas as a byproduct of cellular metabolism. Methanogens are abundant in swamps and sludge water. They play an important role in biomass degradation and CO_2 consumption.

Using food waste and garbage to produce methane appears to be an ideal way to use biology to solve various serious environmental concerns - to produce fuel while getting rid of garbage and producing sustainable energy from waste.

In this experiment food waste is incubated with sludge water in a tightly sealed container. Aerobic decomposition occurs first and CO_2 is produced while Oxygen is consumed. Once the oxygen has been depleted, the methanogenic bacteria, start growing and consume the CO_2 to produce methane. Therefore, an initial increase in CO_2 production followed by a decrease in CO_2 and a steady increase in methane production is observed clearly. The biogas obtained at the end of the reaction will be a mixture of CO_2 and CH_4 . The CO_2 can be monitored by using a CO_2 detection method. Methane can be identified by burning it. The methane thus synthesized will be collected in a balloon and burnt to check its consistency. The gas thus synthesized will be collected in a gas collector.

Process Diagram Depicting Synthesis Of Methane



Energy Content in Biomass

Type of waste	moisture %	volatile matter %	fixed carbon %	ash %	energy as collected (MJ/kg)	energy dry (MJ/kg)
fats	2	95.3	2.5	0.2	37.5	38.3
Mixed food	70	21.4	3.6	5	4.2	13.9
fruit waste	78.7	16.6	4	0.7	4.0	18.6
meat waste	38.8	56.4	1.8	3.1	17.7	29.0
cardboard	5.2	77.5	123	5	16.4	17.3
magazines	4.1	66.4	7	22.5	12.2	12.7
newsprint	6	81.1	11.5	1.4	18.6	19.7
mixed paper	10.2	75.9	8.4	5.4	15.8	17.6
waxed cartons	3.4	90.9	4.5	1.2	26.3	27.3

Energy content of some common solid wastes found

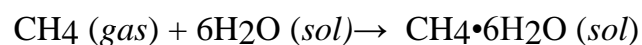
Effect of Particulate Size on Decomposition

The large size of pieces of MSW is believed to decrease the ability of microbes to decompose the material. Even, biogas production has been correlated with refuse particle size (Ferguson 1993). The effect of particle size reduction can be explained by the resultant increase in surface area available for microbial attack. Laboratory studies under saturated conditions, however, explain that size reduction, even down to a few microns or tens of microns has little effect on the rate of degradation. According

to Ferguson (1993), surface area increases only slightly with decreasing particle size for platy and fibrous particles such as paper. Thus the effect of size reduction on the methane production in landfills may be that relatively large pieces of plastic, paper, or other material shield the materials beneath them from infiltrating water. The shielded material may remain too dry for biodegradation. Pulverization, therefore, breaks down the impermeable layers and more of the waste is exposed to water and thus, to the degrading bacteria.

Processing Methane

Samples of polycrystalline methane hydrate can be efficiently synthesized by promoting the general reaction



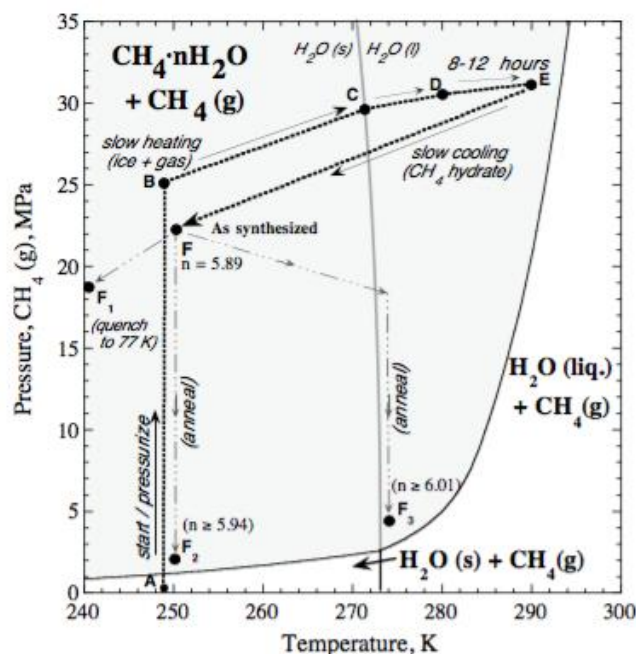
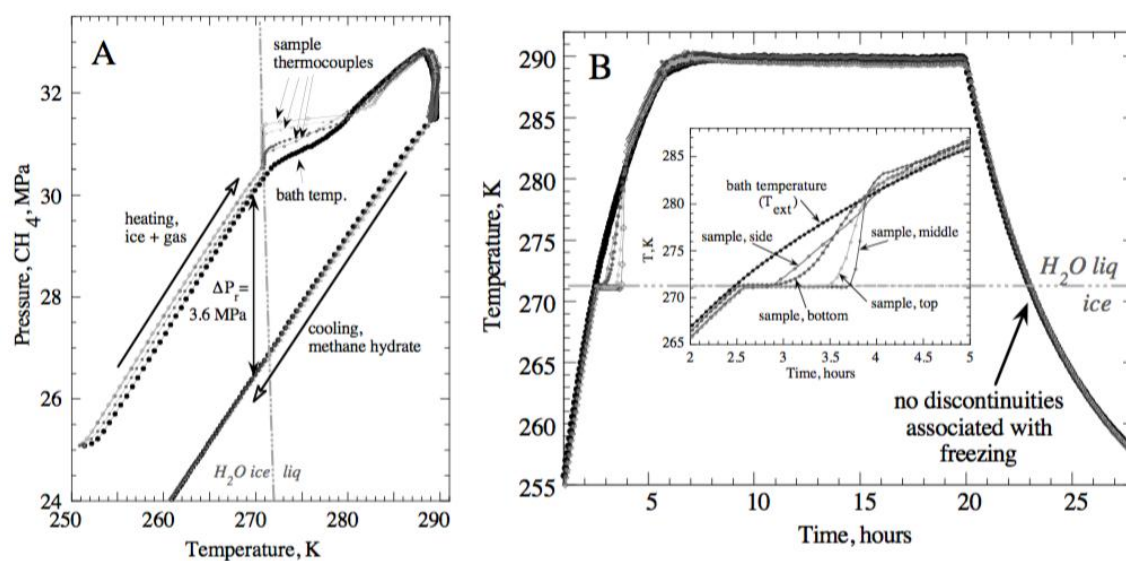


Figure 1: Methane hydrate synthesis and annealing conditions in relation to the CH_4 - H_2O phase diagram. Shaded region shows methane hydrate stability field. The metastable extension of the H_2O melting curve is shown by the solid grey curve. Black dotted lines trace the reaction path during methane hydrate synthesis from ice + gas mixtures. Points A-F indicate the P-T path during reaction. For synthesis, H_2O "seed" ice at 250 K (pt. A) is pressurized with CH_4 gas to 25 MPa (B). Heating the mixture through the H_2O melting point (C) and up to 290 K (C-D-E) promotes full and efficient conversion of the ice to gas hydrate. Samples are then cooled to 250 K (F), and can then be quenched (F_1) and removed from the apparatus, or annealed at conditions closer to the equilibrium curve (F_2 , F_3). The "n" numbers represent hydrate stoichiometry under various conditions.

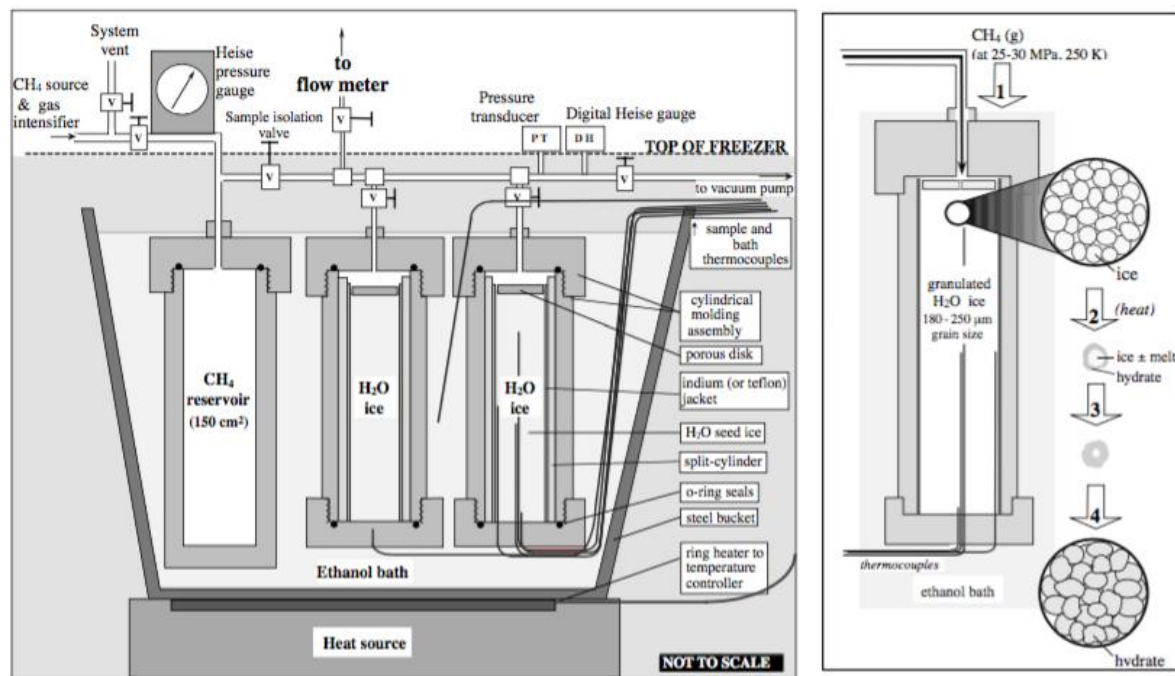
This product is achieved by the mixing and slow subsequent, regulated heating of sieved, granular, H_2O "seed" ice and cold, pressurized CH_4 gas in an approximately constant-volume reaction vessel. This seeding method for hydrate nucleation and growth permits successful synthesis of crystals with controlled and uniform grain size with no detectable preferred photometric orientation, which can be verified through sample light rotation properties.

Sample fabrication details are as follows: CH_4 gas from a sample source bottle is initially pressurized up to a high pressure (P) by a gas intensifier and routed into sample vessels placed in a conventional refrigerator freezer (or a blast freezer). The sample assembly (Fig. below) consists of four stainless steel vessels immersed in an ethyl alcohol bath initially held at freezer temperature of ~ 250 K. One vessel serves as a reservoir to store and chill pressurized CH_4 gas, and the others contain the sample sculpts. Each cylinder consists of a hollow split-tube that encases an indium sleeve filled with a measured mass of H_2O "seed" ice typically packed to 40% of the vessel capacity. Seed material is made from a gas-free and nearly single-crystal block of ice grown from triply distilled H_2O , crushed, ground, and sieved to a small size and evacuated of any physical impurities. A disk inserted on top of the packed ice grains prevents displacement of the ice during evacuation. Multiple thermocouples inserted into the base of either sample prior to loading of the ice permit careful monitoring of the sample's thermal history during synthesis and subsequent testing. A Heyse pressure gauge and pressure transducers monitor gas pressure of the sample gas.

The reservoir vessel is first filled with pressurized CH_4 gas and cooled to 250 K. When working on a single sample, the reservoir is opened to the pre-evacuated sample chamber and methane pressure (very high pressure of the order 25 MPa). For reaction of multiple samples, the reservoir charging, cooling, and opening procedures are repeated to bring the larger volume of the multiple-sample system to about 25 MPa at 250 K. These serve to fill the porosity between the ice grains to a molar ratio of CH_4 to H_2O well in excess of that required for complete hydrate reaction. The bath temperature can then be slowly raised by various methods such as by use of a ring immersion heater or a simple hot plate located beneath the alcohol bath. As the samples and gas reservoir warm, they self-pressurize by thermal expansion. Up to 271 K, methane gas pressure increases approximately linearly with increasing temperature, following a slope governed primarily by the equilibrium thermal expansion of free CH_4 in the system. Measurable reaction begins as temperature rises above 271.5 K (the approximate melting point of ice at our synthesis pressure), and consumption of CH_4 gas by hydrate formation slows the rate of increase in pressure of Methane. Progress of the hydrate-forming reaction is observed by plotting the deflection of P from the initially linear P-T curve. Completion of reaction is efficiently achieved by steady heating to $\sim 289 \pm 1$ K over a heating time interval of about 12 to 15 hours after the sample vessel crosses the 271.5 K isotherm monitors and records the P-T conditions throughout each run. The extent of reaction can be determined mid-run by the measured Pressure of Methane from the reversible CH_4 expansion curve.



Extent of reaction curve



Experimental Setup for the synthesis of Pure Methane Hydrate (Fig 2)

Key factors for successful synthesis of pure methane hydrate.

The synthesis procedures described here appear to be highly dependent on those aspects that influence the availability, transport, and concentration of gas-hydrate-forming species at the growth front. These factors include elevated P-T conditions, and a high surface-to-volume ratio of the reacting grains to minimize the thickness of the developing hydrate layer through which the reactants must pass.

In terms of the procedures described here, the following three experimental parameters are integral to the full and efficient conversion of ice to gas hydrate without measurable segregation of a bulk melt phase:

- (1) Maintenance of a very high methane pressure above the methane hydrate equilibrium curve (25-33 MPa)
- (2) Moderate thermal ramping (~ 5 -12 K/hr) and subsequent holding of temperature at very warm conditions (288-290 K for 8-12 hours)
- (3) Using a small initial grain size of seed material (< 300 pm). Synthesis tests conducted with larger grain sizes of seed ice (0.5-2 mm) or lower overpressures of CH₄ (4-11 MPa) resulted in only partial reaction, measurable bulk melting, and

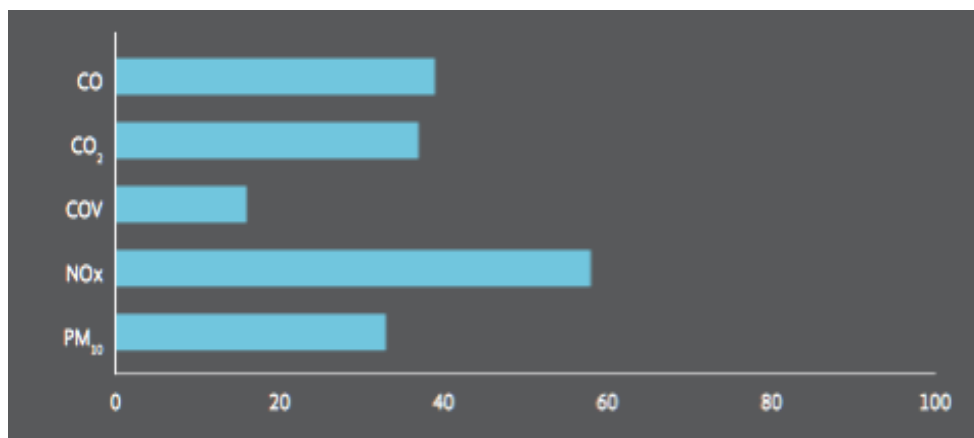
significant segregation and pooling of the melt into the lower region of the sample chamber.

Thermal ramping to lower temperatures ($< 285\text{ K}$) or with very slow ramping rates ($< 3\text{ K/hr}$) also reduced the efficiency of the reaction process, and commonly resulted in incomplete reaction and melt segregation.

For samples in which melt segregation occurs, it is troublesome and very inefficient way to convert the segregated melt phase to gas hydrate under static conditions. Multiple cycles through the ice point are required, but may still result in a substandard final material. Finally, we note that successful conversion of ice grains to hydrate grains may also be specific to our method for preparing the ice in order to minimize defects, impurities, or grain boundaries.

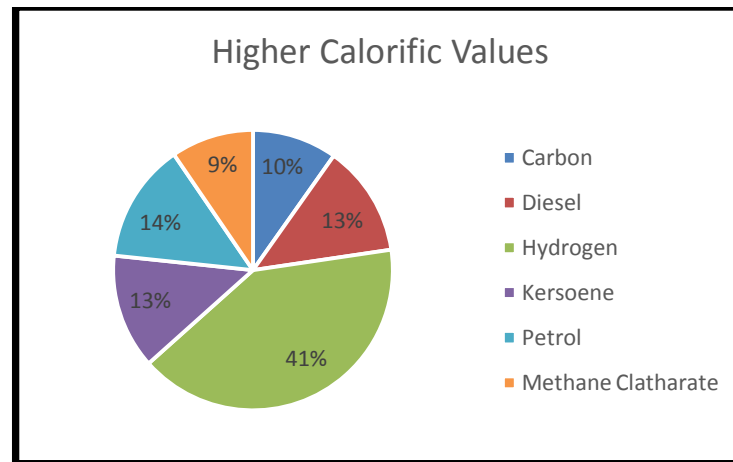
Advantages of Methane Clathrate over other conventional fuels :

- It is an eco-friendly, renewable energy source.
- Carbon Dioxide emissions are reduced to as low as 14.96% along with unburnt carbon particles that are reduced to 0.43%.



Contribution of Methane Clathrate in atmospheric emissions (Source : ARPA, 2013)

- Higher Calorific Values of some common fuels have been compared below :



Possible Uses of Hydromethane :

- It can be used as alternative to almost all of the conventional fossil fuels being used today.
- As the emissions are highly low, it poses as an excellent fuel for transportations.
- As the energy content is comparatively higher than all the fuels present today, it can be used in the generation of electricity.
- It can be used as a power fuel, for aircrafts and rockets.
- As the transportation of crystals is easy, it can effect the economy by lowering all direct and indirect costs.

Appendix

Actuator : Machine Unit responsible for controlling and moving mechanical system of a machine

Adsorbent:Material on which adsorbate gets concentrated.

Adsorption:Concentration of adsorbate on absorbent.

Break specific fuel consumption:Measure of fuel efficiency of any prime mover that burn fuels and produce rotational or shaft power.

Cetane number: Quality indicating the ignition properties of diesel fuel relative to cetane as standard.

Clathrate:Clathrate is a compound in which molecule of one component are physically trapped within the crystal structure of another.

Dual injection:It is an infusion method of putting fluid into the body.

Engine control unit: Type of electronic control unit that controls a series of actuators on an internal combustion engine to ensure optimal engine performance.

Fumigation:Method of pest control that completely fills an area with gaseous pesticides.

Gas flaring: Gas combustion device used in industrial plants.

Geological faults:Large fault within the earth crust that is due to action of plate tectonic forces, with largest forming the boundaries between the plates.

Injection line pressure: Fuel injection lines are required to deliver the fuel from the high pressure pump to the combustion engine without any loss of pressure.

Internal combustion engine: A heat engine where the combustion of fuel occur with an oxidiser in a combustion chamber.

Isotherm: A line on a map connecting points having the same temperature at a given time or an average over a given period.

Methanogens:Microorganisms that produce methane as a metabolic by product in anoxic conditions.

Montmorillonite: A very soft phyllosilicate group of minerals that form when they precipitate from water solution as microscopic crystals known as clay.

Naphtha: Number of flammable liquid mixture of hydrocarbons.

Oxygenates: Compounds enriched with oxygen.

Polypeptides: A linear organic polymer consisting of large number of amino acids residues bounded together in chain forming part of a protein molecule.

Polycrystalline: A solid consisting of many crystalline parts that are randomly oriented with respect to each other.

Pressure swing adsorption: It is the technology used to separate some gas species from the mixture of gases under pressure according to species.

Pulverisation: A solid substance in the form of tiny loose particles.

Silt stone: Fine grained sedimentary rock consisting of consolidated silt.

Soot: A deep black powder produced by the incomplete burning of organic matter.

Stroke engine: A four-stroke engine (also known as four cycle) is an internal combustion (IC) engine in which the piston completes four separate strokes while turning a crankshaft. A stroke refers to the full travel of the piston along the cylinder, in either direction.

Transesterification: Process of exchanging organic group of an ester with organic group of alcohol.