

Module 2: Sustainable Fuels

Fuels: Introduction, calorific value, determination of calorific value using bomb's calorimeter, numerical problems on GCV and NCV. Knocking in internal combustion (IC) engines - knocking mechanism in IC engines. Anti-knocking agents - methyl tertiary butyl ether (MTBE) and ethyl tert-butyl ether (ETBE). Importance of octane and cetane rating of fuel.

Green Fuels: Introduction, power alcohol – properties, applications and its limitations, biodiesel - synthesis by trans-esterification method, advantages and its applications. Production of green hydrogen by photocatalytic water splitting and its advantages, hydrogen storage – introduction, advantages and limitations of metal hydride and ammonia as chemical hydrogen carriers.

Introduction

Chemical fuel: is a naturally occurring or artificially made carbonaceous combustible substance, which on combustion liberates a large amount of energy in the form of heat or light.

Classification: Fuels are classified as primary and secondary fuels.

Primary fuels: Fuels that occur in nature and are directly used without processing are called primary fuels. They are raw fuels. Examples are wood, coal, petroleum, natural gas, animal dung, etc.

Secondary fuels: Fuels that are obtained by chemical processing and prepared from raw or primary fuels are called secondary fuels. Examples are charcoal, coke, coal gas, gobar gas, water gas. Based on the physical states both primary and secondary fuels are sub-classified as solid, liquid and gas.

	Primary	Secondary
Solid	Coal, Wood, Animal dung	Charcoal, Coke.
Liquid	Crude petroleum oil.	Petrol, Diesel, kerosene.
Gas	Natural gas.	Coal gas, gobar gas, water gas.

3.2 Calorific value of a fuel is defined as “*The amount of heat energy liberated when a unit quantity (volume or mass) of the fuel is burnt completely in presence of air or oxygen under standard condition.*”

The S.I unit of calorific values is

Solid and Liquid fuel = Jg^{-1} (J/g) or kJkg^{-1} (kJ/kg)

Gaseous fuel = Jcm^{-3} (J/cm³) or kJm^{-3} (kJ/m³)

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Calorific value of fuel is measured either as gross calorific value or net calorific value.

3.2.1 Gross calorific value (GCV, Higher calorific value HCV): “*The amount of heat energy liberated when the unit quantity of fuel is burnt in an isolated container in presence of air / oxygen and the products are cooled (condensed) to room temperature.*”

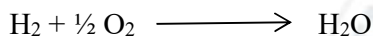
Usually CO_2 and H_2O is the major products of a fuel thus GCV is,

$$\text{GCV} = \text{NCV} + \text{heat associated with steam}$$

3.2.2 Net calorific value (NCV Low calorific value LCV): “*The amount of heat energy liberated when the unit quantity of fuel is burnt in presence of air / oxygen and the products are allowed to escape.*”

$$\text{NCV} = \text{GCV} - \text{heat associated with steam.}$$

3.2.2.1 Calculation of heat associated with steam



2 kg of hydrogen produces 18 kg of water, therefore

$$x \text{ kg of hydrogen produces} = \frac{18x}{2} \text{ kg of water}$$

$$\text{Water produced by 100 kg of fuel} = \frac{18}{2} \times \frac{x}{100} = 0.09 x \text{ kg of water}$$

$$\text{Heat associated with steam} = \text{weight of water produced} \times \text{latent heat of steam}$$

(Latent heat of steam = $587 \times 4.2 \text{ kJ/kg}$)

$$\text{LHV} = 0.09 x \times 587 \times 4.2 \text{ kJ/kg}$$

3.3 Determination of calorific value of a solid or liquid fuel using bomb calorimeter

A bomb calorimeter is a type of constant-volume calorimeter used in measuring the heat of combustion (calorific value) of a particular substance. Using electrical energy, the fuel is burnt in presence of excess of oxygen which heat up the surrounding air. This heated air while escaping through the tube heat up the water outside the tube. The change in temperature of the water is measured using sensitive thermometers. Using the change in temperature the calorific value of the fuel is calculated.

Apparatus

The bomb calorimeter is constructed as shown in figure 3.1. It consists of two units.

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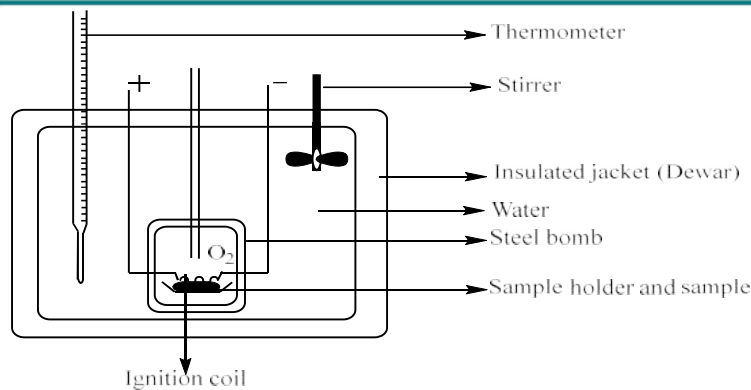


Figure 3.1 Schematic diagram of bomb calorimeter

Steel bomb

- Steel cylinder (steel bomb) which can withstand high pressure.
- A gas inlet tube to fill oxygen in steel bomb at 25 atm pressure.
- A platinum sample holder.
- An electric coil to ignite the fuel.

Dewar flask: This complete unit of steel bomb is placed inside a dewar (Insulated brass chamber) filled with water. A sensitive thermometer and a stirrer are provided to the dewar.

Working: A known quantity of fuel sample is taken in the sample holder and is placed in the steel bomb. The bomb is charged with oxygen at 25 atm pressure. Initial temperature of the water is noted. The sample is ignited using electric coil, the fuel starts burning liberating the heat which is absorbed by water in the calorimeter. The final temperature is noted.

Calculation of GCV

m = Mass of the fuel

W_1 = Mass of water

W_2 = Water equivalent mass of calorimeter and other accessories.

T_1 = Initial temperature

T_2 = Final temperature

S = specific heat of water

Heat loss by m kg of a fuel = heat gained by calorimeter + water

Heat associated with the fuel = mass X sp. Heat X change in temperature

$$= (W_1 + W_2) \times 4.187 \times (T_2 - T_1)$$

$\text{GCV} = \frac{(W_1 + W_2) \times 4.187 \times (T_2 - T_1)}{m} \quad (\text{kJ/kg})$

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Numerical Problems

Problem 4: Calculate HCV and LCV of the sample of 1.2 ml of liquid fuel C_2H_6 when subjected to combustion in a bomb calorimeter increased the temperature of 2000 ml water by $5^\circ C$. The water equivalent of calorimeter was 250g. Given that density of fuel = 0.8 g/cc and density of water = 0.998 g/cc, Specific heat of water was 4.187 kJ/kg/ $^\circ C$ and LHSV = 580×4.2 kJ/kg

$$\begin{aligned}
 M &= 1.2 \text{ ml} = \frac{m = d \times V}{m = 0.8 \times 1.2} = 0.96 \times 10^{-3} \text{ kg} \\
 W_1 &= \frac{2000 \text{ ml}}{2000 \times 0.998} = 1996 \times 10^{-3} \text{ kg} \\
 W_2 &= 250 \text{ g} = 250 \times 10^{-3} \text{ kg} \\
 W_1 + W_2 &= (1996 + 250) \times 10^{-3} = 2246 \times 10^{-3} \text{ kg} \\
 \Delta t &= 5^\circ C \\
 \text{HCV} &= \frac{(W_1 + W_2) \times 4.187 \times (T_2 - T_1)}{m} \text{ kJ/kg} \\
 &= \frac{2246 \times 10^{-3} \times 4.187 \times 5}{0.96 \times 10^{-3}} = 49,979.2 \text{ kJ/kg} \\
 \% H &= \frac{C_2H_6}{24 + 6} = \frac{12 \times 2 + 1 \times 6}{24 + 6} = 20\% \\
 \text{LHV} &= 580 \times 4.2 \\
 \text{HCV} &= ? \\
 \text{LCV} &= ?
 \end{aligned}$$

$\text{Wkt LCV} = \text{HCV} - \text{HAS}$
 $\text{HAS} = 0.09 \times 580 \times 4.2$
 $\text{LCV} = 49,979.2 - 0.09 \times 20 \times 580 \times 4.2 = 45,594.2 \text{ kJ/kg}$

Calculate HCV and LCV of the sample of 1.3g of Coal (C 90%, H₂ 5% and ash 5%) was subjected to combustion in a bomb calorimeter. Mass of water taken was 2500g and water equivalent of calorimeter was 550g. The rise in temperature was found to be $4.20^\circ C$. (Latent heat of Steam = 2457 kJ/kg and specific heat of water = $4.187 \text{ kJ/kg/}^\circ C$).

Converted Data

- $m = 1.3 \times 10^{-3} \text{ kg}$
- $W_1 = 2500 \times 10^{-3} \text{ kg}$
- $W_2 = 550 \times 10^{-3} \text{ kg}$
- $(T_2 - T_1) = 4.2^\circ C$
- $s = 4.187 \text{ kJ/kg/}^\circ C$
- $\% H = 5\%$
- $\text{LHV} = 2457 \text{ kJ/kg}$
- $\text{GCV} = ?$
- $\text{NCV} = ?$

Write down the formula

$$\text{GCV} = \frac{(W_1 + W_2) \times 4.187 \times (T_2 - T_1)}{m} \text{ kJ/kg}$$

Substitute all the converted data in the formula

$$\text{GCV} = \frac{(2500 + 550) \times 10^{-3} \times 4.187 \times (4.2)}{1.3 \times 10^{-3}} \text{ kJ/kg}$$

Calculate the GCV value

$$\text{GCV} = 41258.05 \text{ kJ/kg}$$

Write down the LCV formula and verify the data with you

$$\text{LCV} = \left[\frac{(W_1 + W_2) \times 4.187 \times (T_2 - T_1)}{m} \right] - \left[\frac{\% H_2}{100} \times \text{LHV} \right] \text{ (kJ/kg)}$$

$$\text{NCV} = 41258.05 - (0.09 \times 5 \times 2457)$$

$$\text{NCV} = 40152.05 \text{ kJ/kg}$$

Typical problems on calculation of GCV & LCV

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Problem 3: Calculate **HCV and LCV** of the sample of **1 g of solid fuel** with **8% H_2** when subjected to combustion in a bomb calorimeter increased the temperature of **2000 g** water from **25 °C** to **29 °C**. The **water equivalent of calorimeter was 250g**.

Hint for the problem 3, Specific Heat of water to be considered as **4.187 kJ/kg/ °C**, Heat associated with steam to be **587 * 4.187 kJ/kg**

Problem 4: Calculate **HCV and LCV** of the sample of **1.2 ml of liquid fuel** with **14% H_2** when subjected to combustion in a bomb calorimeter increased the temperature of **2000 ml** water by **5 °C**. The **water equivalent of calorimeter was 250g**. Given that density of fuel = **0.8 g/cc** and density of water = **0.998 g/cc**, Specific heat of water was **4.187 kJ/kg/ °C** and **HAS = 580 * 4.2 kJ/kg**

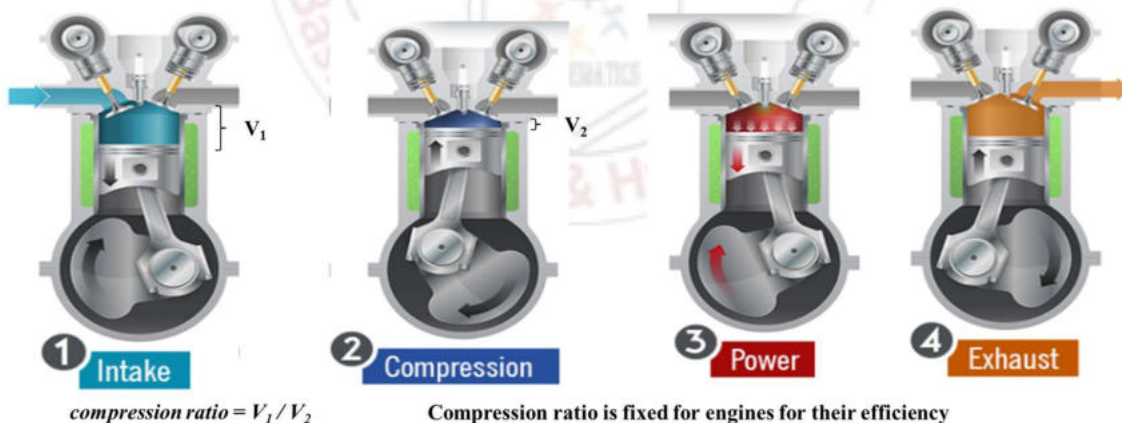
Hint for the problem 4, Initially the volume must be converted to mass by using the formula “density = Mass / Volume” or “Mass = Density * Volume”. Heat associated with steam is given as **580 * 4.2 kJ/kg**

Knocking and mechanism:

Explosive combustion of air-fuel mixture due to the variation in compression ratio produces shock waves which hit the cylinder wall and piston of engine, creating rattling sound known as knocking.

Mechanism

In petrol engine air and petrol are mixed, then compressed, ignited and allowed via Exhaust.

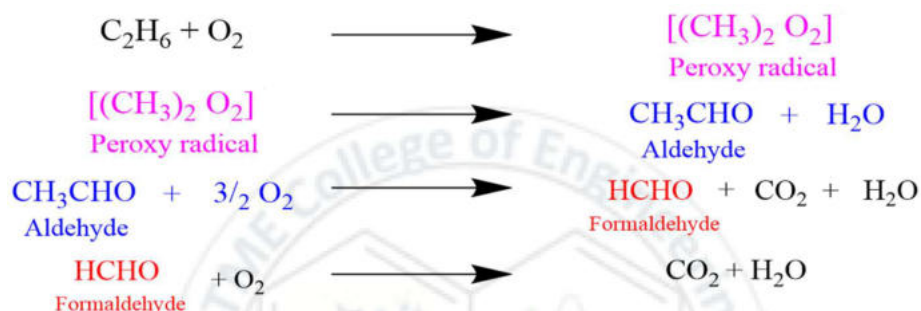


In an engine under normal compression ratio, the initiation of the combustion of petrol-air mixture occurs under normal conditions, and the rate of flame propagation is $20\text{--}25 \text{ ms}^{-1}$. However, beyond a particular compression ratio, the petrol-air mixture suddenly bursts into flames and propagates at 2500 ms^{-1} . A sharp knock in the engine accompanies this process due to explosive combustion, which produces a shock wave that loses its energy as it hits the cylinder wall and piston. As a result, a rattling sound is heard, referred to as knocking.

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The reaction mechanism of knocking is as follows:

Under normal conditions, the fuel-air mixture burns, forming unstable peroxides, and the reaction proceeds in multiple steps at a rapid rate. The unstable peroxide formed decomposes readily to give several gaseous compounds. This gives rise to pressure waves that knock against the engine walls. The reactions for normal and explosive combustion of fuel (for C_2H_6 as example) may be represented as follows:



Octane Number: *It is the ability of the fuel to resist knocking.* Higher the octane number lower is the tendency to knock and better is the quality of petrol.

Isooctane (2,2,4-trimethyl pentane) has the least knocking tendency and its octane number is arbitrarily (imaginary) fixed as 100.

n-Heptane, a straight chain hydrocarbon, has highest tendency to knock and is assigned an octane number zero.

The petrol whose octane number is to be determined is compared with reference mixtures of isooctane and n-heptane.

Definition: *The octane number of a petrol sample is defined as the percentage of isooctane in a mixture of isooctane and n-heptane which matches the fuel under test in knocking characteristics.*

For example, the octane number of automobile petrol is found to be equivalent to that of a mixture containing 70% isooctane and 30% n-heptane. Its octane number is said to be 70.

Cetane Number: The knocking tendency of a diesel fuel is expressed in terms of cetane number. Diesel engines works on the principle of compression ignition.

Cetane (n-cetane) or hexadecane $[CH_3-(CH_2)_{14}-CH_3]$ is a saturated hydrocarbon, its cetane number is arbitrarily fixed as 100.

Methyl naphthalene is an aromatic hydrocarbon; its cetane number is arbitrarily fixed as zero.

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Definition: Cetane number of diesel is defined as the percentage of hexadecane (*n*-cetane) present in a mixture of hexadecane and 2-methyl naphthalene, which matches the fuel under test in knocking characteristics.

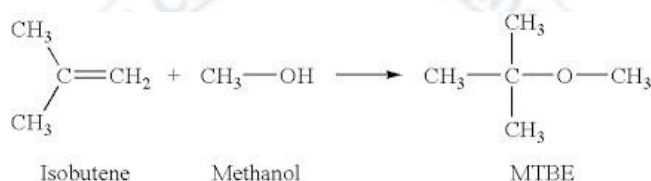
Antiknocking Agents: The additives added to petrol to control knocking are called antiknocking agents. Example: Tetra Ethyl Lead (TEL), Tetra Methyl Lead (TML), Oxygenates etc.,

Oxygenates are generally defined as any substances (usually ethers, such as MTBE, or alcohols, such as fuel ethanol) which, when added to gasoline, increase the amount of oxygen in that gasoline blend.

MTBE and ETBE are synthetic organic chemicals used primarily as an oxygenate.

Methyl tertiary butyl ether (MTBE):

MTBE is synthesized by reacting isobutylene with methanol in the presence of an acid catalyst.



Advantages

- **Increases octane rating:** MTBE boosts the octane rating of gasoline, which helps prevent engine knock and improves overall engine performance.
- **Reduces harmful emissions:** As an oxygenate, MTBE increases the oxygen content of gasoline, leading to more complete combustion and lower emissions of pollutants like carbon monoxide and volatile organic compounds (VOCs).
- **Replaces toxic components:** Its high blend octane number made it a suitable replacement for lead and other toxic additives like benzene, creating cleaner and safer fuel options.
- **Good blending properties:** MTBE mixes well with gasoline, has a low vapor pressure, and does not undergo phase separation, making it a reliable fuel additive.
- **Eco-friendly:** High water solubility and slow biodegradation make it a significant groundwater contaminant from leaking tanks, leading to its phase-out in many regions.

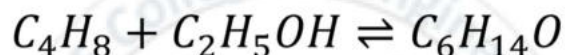
Disadvantages

- **Groundwater contamination:** MTBE's high solubility in water and low affinity for soil allow it to travel quickly through groundwater if spilled, contaminating drinking water sources. Once in the water, it is persistent and can lead to long-term environmental effects.

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- **Short-term exposure:** Inhalation can lead to headaches, dizziness, nausea, and irritation of the eyes, nose, and throat. Skin contact can cause dryness and redness.
- **Long-term exposure:** Animal studies have suggested a potential link to liver and kidney effects, and some studies have indicated reproductive toxicity in male rats.
- **Potential carcinogen:** The International Agency for Research on Cancer (IARC) classifies MTBE as a possible human carcinogen based on animal studies, although other agencies like the EPA and the DHHS have not classified its cancer-causing risk in humans

Ethyl tertiary butyl ether (ETBE): ETBE is manufactured industrially by the acidic etherification of isobutylene (IB) with ethanol.



Advantages

Increases octane rating: ETBE is a highly effective octane enhancer, which helps prevent engine knock and allows for engine downsizing.

Upgrades fuel: It can be used to upgrade lower-octane gasoline to higher grades to meet performance and environmental standards.

Reduces harmful emissions: Blending ETBE allows for more complete fuel combustion, leading to lower emissions of pollutants like carbon monoxide and nitrogen oxides.

Less evaporation: Unlike ethanol, ETBE has a lower vapor pressure and does not induce evaporation, which is a key component of smog formation.

Reduces greenhouse gases: The substitution of MTBE with ETBE can lead to a net reduction in greenhouse gas emissions.

Achieves lower aromatics: ETBE helps meet the EU's Fuel Quality Directive requirements for lower aromatic content in gasoline.

Disadvantages:

- **Higher cost:** The production of ETBE is generally more expensive than MTBE due to the cost of ethanol.
- **Production inefficiencies:** The synthesis of ETBE is an exothermic reversible reaction, meaning high temperatures can shift the equilibrium towards the reverse reaction, decreasing yield.
- **Byproduct formation:** The synthesis process can produce undesirable byproducts that may cause issues in separation units and later use.

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- **Groundwater contamination:** Like MTBE, ETBE can contaminate groundwater if spilled, with low taste and odor thresholds making affected water unusable for drinking purposes, even if the concentrations are not acutely toxic
- **Production impact:** The production of its precursor, ethanol, consumes agricultural land, water, and chemicals like fertilizers and pesticides, which can raise sustainability issues and compete with food production
- **Metabolite toxicity:** ETBE metabolizes into tert-butanol and acetaldehyde in the body. Chronic exposure to tert-butanol has been linked to non-cancer kidney effects in animal studies, while acetaldehyde is a known carcinogen that causes nasal and laryngeal cancers in rats and hamsters.

Green Fuels: Power alcohol:

Power alcohol is gasoline blends containing ethanol which can be used as a fuel in internal combustion engines. A blend containing up to 25% of alcohol with petrol is used. The main objective of the power alcohol was to reduce oil imports and provide an alternative to the non-renewable energy source, gasoline.

Ethyl alcohol can be synthesized by fermentation of carbohydrates (sugar material). Fermentation of molasses, which is the residue left after the crystallization of sugar, with yeast generates alcohol. This fermentation yields only about 20% alcohol.

Concentration of alcohol can be increased up to 97.6% by fractional distillation yields rectified spirit. The concentration of alcohol cannot be increased by distillation above 97.6%, because it forms a constant boiling mixture with water. The constant boiling mixture has a lower boiling point than alcohol. 100% alcohol (absolute alcohol) is prepared by removing last traces of water from rectified spirit. The following two methods can do it.

- (i) Alcohol, containing traces of water, is distilled with benzene. When benzene passes over with a portion of alcohol and water, it leaves behind absolute (power) alcohol.
- (ii) Alcohol is distilled in the presence of dehydrating agent, which holds the water.

Finally absolute alcohol is mixed with petrol at concentration of 5-10% to get power alcohols.

The importance of power alcohol as fuel is:

Properties

1. Power alcohol has a lower calorific values (7000 k.cal/kg).

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2. It has high octane number (90).
3. Its anti-knocking properties are good.
4. It generates 10% more power than the gasoline of same quantity.
5. Its compression ratio is also higher.

Advantages:	Disadvantages:
1. It is cheaper than petrol. 2. If any moisture is present, power alcohol absorbs it. 3. As ethyl alcohol contains oxygen atoms, complete combustion occurs, so emission of CO, hydrocarbon, particulates are reduced.	1. As the calorific value of power alcohol (7000 cal/gm) is lower than petrol (11,500 cal/gm), specially designed engine is required. 2. Output power is reduced upto 35%. 3. Due to its high surface tension, atomization of power alcohol is difficult, so it causes starting trouble. 4. It may under go oxidation to give acetic acid, which corrodes engine part. 5. As it contains oxygen atoms, the amount of air required for combustion is less therefore, the engine and carburetor need to be modified.

Biodiesel

Biodiesel is a renewable fuel substitute for conventional diesel, made from sources like vegetable oils, animal fats, and recycled cooking oil through a process called transesterification.

It is a biodegradable and less toxic fuel that can be blended with petroleum diesel in any percentage. Biodiesel is produced through a process called transesterification, which chemically reacts vegetable oils or animal fats with a short-chain alcohol (like methanol or ethanol) to create biodiesel and glycerin.

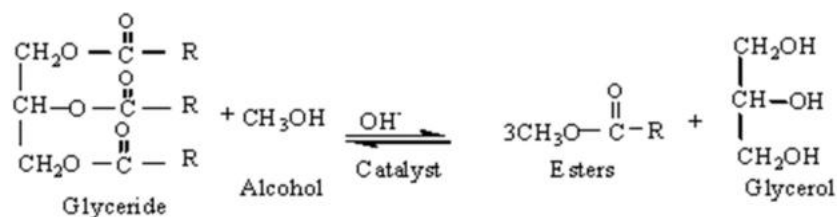
The process begins with a source of oil, such as vegetable oil, waste cooking oil, or animal fat. This oil is typically heated to make it more fluid, with an ideal temperature range of 50-65 degree.

The oil is reacted with a short-chain alcohol (most commonly methanol) in the presence of a catalyst (like sodium or potassium hydroxide). This chemical reaction converts the triglycerides in the oil into fatty acid methyl esters (FAME), or biodiesel, and glycerin.

After the reaction, the mixture separates into two layers: the lighter layer of biodiesel and the heavier layer of glycerin.

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The glycerin is drained off. The raw biodiesel is then washed with water to remove any residual catalyst and other impurities. The fuel is then dried and may have additives, such as antioxidants, added to it to meet quality standards.



Advantages:

1. **Renewable and Sustainable:** It helps reduce reliance on fossil fuels and contributes to diversifying the energy mix.
2. **Lower Greenhouse Gas Emissions:** Biodiesel has lower carbon dioxide (CO₂).
3. **Reduced Air Pollutants:** Biodiesel produces fewer air pollutants such as sulfur oxides (SO_x), particulate matter (PM), and aromatic hydrocarbons. It contributes to better air quality and reduces the negative impacts of diesel combustion on human health.
4. **Compatibility with Existing Infrastructure:** Biodiesel can be blended with petroleum diesel, allowing its use in existing diesel engines, vehicles, and infrastructure without any modifications.
5. **Energy Security and Domestic Production:** Biodiesel production promotes domestic energy production, reducing dependence on imported fossil fuels.
6. **Economic Benefits:** Biodiesel production creates opportunities for rural development and job creation in the agriculture and biofuel sectors. It can stimulate local economies and provide income for farmers and feedstock suppliers.

Disadvantages:

1. **Feedstock Availability and Competition with Food Production:** The availability and cost of biodiesel feedstocks can be influenced by factors such as land availability, competition with food crops, and seasonal variations.
2. **Limited Production Capacity:** Biodiesel production capacity is currently limited compared to petroleum diesel. Scaling up production to meet the growing demand requires significant investment in production facilities and infrastructure.

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3. **Land Use and Environmental Concerns:** The expansion of feedstock cultivation for biodiesel production can lead to land use change, deforestation, and habitat destruction if not managed sustainably.
4. **Cold Weather Performance:** Biodiesel can have higher cloud point and pour point temperatures compared to petroleum diesel, which may affect its flow and performance in cold weather conditions. Blending with petroleum diesel or using additives can help address this issue.
5. **Oxidative Stability and Storage Concerns:** Biodiesel has lower oxidative stability than petroleum diesel, making it more prone to degradation and the formation of sediments over time.
6. **Infrastructure Compatibility:** While biodiesel can be blended with petroleum diesel, higher blends may require modifications to storage tanks, fuel lines, and engine components to ensure compatibility and prevent potential issues such as clogged filters.

High energy Fuels: Hydrogen

Hydrogen is the lightest, simplest, and most abundant chemical element in the universe. On earth, it occurs in almost limitless quantities as a constituent of water (H_2O) and in fossil fuels such as natural gas (CH_4) and in other organic matter. In its molecular form (H_2), it is a colorless, odorless, non-toxic, highly combustible gas.

Need For Hydrogen

- Water and solar light are renewable energy resources which on splitting produce hydrogen and oxygen
- Hydrogen is highest energy yield per unit mass among the various fuels: 122kj/g that of fossil fuel is 40kj/g
- Hydrogen is environment friendly and has zero negative impact on environment
- Major outcome of hydrogen consumption is water which does not harm environment and also contains hydrogen

Principle of Photocatalytic water splitting

A photocatalyst is a substance that absorbs photon of light having energy equal or greater than its band gap to excite its electrons from valance band(VB) to conduction band(CB). This excitation produce positive charge (hole) in valance band that of negative charge due to electron in conduction as charge carriers. Photogenerated charges are then transferred to surface of photocatalyst over which water is adsorbed The holes are then used to oxidize the water to produce oxygen and the

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electrons are used to reduce the hydrogen ions to hydrogen molecule. Hydrogen is then captured as a gas and can be used for beneficial purposes.

Hydrogen-production by photo catalytic water splitting

Here photocatalyst is immersed as tiny particles in water-based electrolyte. When the system interacts with solar light than absorption of light occur followed by the charge carrier generation. Charges are moved to surface of photocatalyst to start the surface catalyzed chemical reaction with water. Holes (h^+) are oxidizing the water. The Electrons reduce the hydrogen ions to hydrogen gas. The reaction is as follows,

