Lecture 39:Alternative Fuels

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ALTERNATE FUELS

Most important alternative fuel candidates are: ethanol, methanol, natural gas, liquefied petroleum gas (LPG), vegetable oil esters commonly called as 'biodiesel' and hydrogen High petroleum prices during 1980's provided motivation for development programmes for use of ethyl alcohol produced from agricultural products as motor fuel in countries like Brazil. During the same period, clean burning properties of methanol and its easy production from natural gas led to technological development activities on methanol in the USA. Methanol being liquid it is better suited than natural gas for storage on-board of vehicles. However, due to its toxicity and its corrosive nature towards fuel system materials, interest in methanol as automotive fuel has gone down although a number of demonstration fuel cell vehicles (FCV) using methanol have been developed. Presently, natural gas and biodiesel have attracted maximum attention of the governments, vehicle manufacturers and fuel suppliers. Hydrogen is considered as an alternative transport fuel in the long term especially for the fuel cell powered vehicles. .

Properties of Alternative Fuels

Some of the key properties of the main alternative fuel candidates are compared in Table 8.13 with those of conventional petroleum fuels. Key properties to be considered for :

- *Combustion and Performance*: Heat of combustion, heat content of stoichiometric mixture, octane number (SI engine) , cetane number (CI engine), boiling point (esp., cold start), flammability limits
- *Emissions*: Chemical composition and nature, adiabatic flame temperature
- *Storage and Handling:* Boiling point, volumetric energy density, vapour pressure, flammability limits

Keeping the above in view the main alternative fuels are being discussed below

Table 8.13

Properties of Various Fuels for Vehicles

Property	Gasoline	Diesel	Methanol	Ethanol	Natural gas	Propane	DME	RME	Hydrogen
Mol.wt.	˜110	˜195	32.04	46.07	˜18.7	44.10	46.1	˜ 300	2.015
Specific gravity	0.72-0.78	0.82-0.88	0.796	0.794	0.72	0.51 liquefied	0.67 liquid	0.882	0.090
LHV, MJ/kg	44.0	42.5	19.9	26.8	50.0	46.3	28.4	37.7	120
Heat of vaporization ,kJ/kg	305	250	1110	904	509	426	410 at 20^o C		
Boiling point, ^{o}C	30-215	180-370	65	78	-160	-43	-24.9	330-340	-253
RON (MON)	90-98 (80-90)	-	112 (91)	111 (92)	120-130 (120-130)	112 (97)	-	-	106
Cetane number	-	45-55	-	-	-	-	>55	51-52	-

Stoichiometric A/F ratio, mass	14.7	15.0	6.43	8.94	17.12	15.58	9.0	11.2	34.13
LHV of stoich. mixture, MJ/m3	3.50	-	3.14	3.28	3.10	3.38			2.88
Adiabatic flame temperature (K)	2266		2151	2197	2227	2268			2383
Stoichiometric CO2 emissions, g/MJ fuel	71.9	75.4	69.0	71.2	54.9	64.5	69.0	75.5	0

LHV= Lower heating value

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Example 8.1:

Calculate energy content of 1 m^3 of stoichiometric mixture of methane with air at 1 atmosphere pressure (101 kPa) and 298 K. LHV of methane is 50 Mj/kg.

Solution:

Stoichiometric mixture composition of methane is given by

$$CH_4 + \left(1 + \frac{4}{4}\right)(O_2 + 3.76N_2) = CO_2 + 2H_2O + 7.52N_2$$

Total moles of fuel-air mixture = 1 + 2 x 4.76 = 10.52

Energy content of mixture consisting of 1 kmol of methane:
= mol wt x LHV
= 16 x 50 = 800 MJ
Volume of stoichiometric mixture consisting 1 kmol of methane

$$V = n\frac{RT}{P} = 10.52\frac{8314.3 \times 298}{101 \times 10^3} = 258.07m^3$$

Energy content per unit volume of stoichiometric mixture = 800/258.07 = 3.10 MJ/m^3

Ans.

Alcohols: Methanol and Ethanol

Methanol at present is produced mostly from natural gas although both methanol and ethanol can be produced from renewable sources. Methanol may be produced near the natural gas field and it being liquid can be more easily handled and transported over long distances compared to natural gas. Ethanol is produced almost entirely from the renewable agriculture sources by fermentation of sugar, grains, tapioca etc.

Alcohols in engines may be used as:

- Low concentration (5 to 10% by volume) blends in gasoline
- Neat alcohol or high level (85% by volume) blends

Neat ethanol (95% ethanol + 5% water) and anhydrous ethanol blended up to 20% in gasoline have been widely used in Brazil during 1980's. In the USA, use of ethanol was promoted due to agricultural surplus for blending in the reformulated gasoline as oxygenate. Use of 5 to 10% ethanol as a blending component in gasoline is permitted in Europe and India. Now, ethanol is the preferred oxygenate replacing MTBE. As mentioned earlier, methanol due to its toxicity is not permitted any more for blending into gasoline. The 10 percent ethanol-gasoline blends used in the USA are commonly referred as 'Gasohol'. Key features of alcohols as motor fuel are;

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- Alcohols are a preferred alternative for SI engines only due to their high octane number. A higher engine compression ratio could be used to obtain a higher engine thermal efficiency.
- Cetane number of methanol and ethanol are close to 5 and 8, respectively.
- Direct injection alcohol engine prototypes operating similar to diesel/CI engines have also been developed using either a positive source of ignition or high dosage of ignition quality improvers (3 to 7% by volume).
- Alcohols are not easily miscible in the diesel fuels. To prepare alcohol-diesel blends high amounts of emulsifiers or solublizers are required.
- Heating value of ethanol is approximately 60 percent and that of methanol is only 45 % of gasoline.
- The stoichiometric air-fuel ratio due to presence of oxygen in the molecule is much lower than the gasoline.
- The volumetric energy content of stoichiometric mixture (gaseous state) of alcohols and gasoline however, are not very different. Thus, engine specific power output that may be obtained with alcohols and gasoline is nearly the same.
- The latent heat of vaporization of methanol and ethanol is nearly 4 and 2.7 times, respectively compared to gasoline. Cold starting performance with neat alcohol is therefore, poor compared to gasoline.
- Flames of neat alcohols in air are not easily visible to the naked eye. Hence, 15% gasoline is mixed to alcohol for making the flame visible in case of an accidental fire.

A large number of investigations have been carried out with alcohols as engine fuel. Emissions with low level alcohol blends as well as with neat alcohols have been studied. CO and NO_X emissions show no clear trend although lower flame temperatures with alcohol may result in lower NO_X emissions. With neat alcohol operation, as the emissions of most of the volatile organic compounds in the exhaust would consist of alcohols or aldehydes only, the photo-chemical reactivity and the ozone forming potential is lower with alcohol fuel operation.
The main advantages and disadvantages of alcohols with respect to conventional gasoline and diesel fuels are summarized in Table 8.14.

Table 8.14

Advantages and Disadvantages of Alcohol Motor Fuels Compared to Gasoline and Diesel

Performance Parameter	Compared to gasoline and diesel fuels	Advantages/Disadvantages
Flame temperature	Lower	Potentially lower NOx emissions and lower heat losses
Vapour pressure	Lower	Poor cold starting and warm up performance, higher unburned fuel emissions during starting/warm up phase
PM emissions	Lower	Due to clean burning characteristics PM emissions are even lower than the gasoline engines

Air Toxic Emissions	Lower	Lower benzene and 1,3 butadiene emissions
CO and NOx Emissions	Similar	No definite trend is observed, So, no advantage over petroleum fuels have been noted
Aldehyde emissions	Higher	Formaldehyde and acetaldehyde emissions are higher
Nature of sources	Renewable esp. of ethanol	Sources more widespread around the world, hence better energy security. Lower net CO_2 emissions.

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Natural Gas

Natural gas has been used now for more than 50 years as fuel for stationary engines for power generation, and agricultural machinery. Several million natural gas vehicles are in operation in Argentina, Brazil, Australia, Italy, India and Pakistan, besides other countries. In the USA, stringent particulate emission standards for the urban buses implemented from the year 1994 was the motivation for development of natural gas operated urban buses.

The principal constituent of natural gas is methane (80 to 95% by volume). The balance is composed of small amounts of other hydrocarbons such as ethane, propane and other gases like nitrogen, carbon dioxide, water, hydrogen sulphide and some trace gases. Composition of natural gas varies from source to source. Composition of natural gas from two different sources is given in Table 8.15.

Large variations in gas composition can have significant effects on engine performance and emissions, especially if the engine performance and emissions are optimized on a fixed gas composition. The natural gas before transportation or use is upgraded by removing water, hydrogen sulphide and condensable higher hydrocarbons.

To minimize variations in engine emissions and performance, and to ensure a minimum heating value to customers, specifications for natural gas sold commercially as fuel have been established.

Table 8.15

Typical Composition of Natural Gas from Two Different Sources

Constituent, mole%	Natural gas 1	Natural gas 2
Methane	94.8	84.8
Ethane	2.9	7.7
Propane	0.8	1.7
C4 and higher	0.2	0.5
Carbon dioxide	0.1	5.2
Nitrogen	1.2	0.1

Natural gas liquefies at -161º C at atmospheric pressure. To use liquefied natural gas (LNG) as automotive fuel, cryogenic systems are required. Therefore, natural gas is stored on board in high-pressure cylinders at pressure of 200 to 300 bars as compressed natural gas (CNG). Storage of natural gas at high pressure on board provides an acceptable range of vehicle operation.

High antiknock quality of natural gas makes it a fuel that is better suited for spark- ignition engines. The following types of natural gas engines have been developed:

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Bi-fuel Operation: The conventional gasoline vehicles are converted to operate either on gasoline or natural gas.

Dedicated NG Operation: Vehicle operating only on natural gas using spark ignition.

Dual-fuel CI engine Operation: Natural gas usually is carburetted/ inducted along with intake air and gaseous fuel is ignited by diesel injection spray. The amount of diesel used may be as low as 10%.

As natural gas has very high octane number, dedicated natural gas engines can be built with a high compression ratio of around 11:1, which results in significant improvements in fuel efficiency and lower carbon dioxide emissions. Lean burn spark ignited, high compression ratio heavy duty engines can be built to give very low particulate emissions compared to diesel engines and a high-energy efficiency similar to IDI engines. The stoichiometric SI engines can utilize three-way catalysts and therefore, it provides the greatest emission reduction potential.

Effect of Natural Gas on Emissions

Light-duty SI, natural gas engines run at stoichiometric conditions and use 3 Way catalysts. With natural gas, mixture enrichment during cold starting which is needed with gasoline operation is not required as the fuel is already in gas phase. Hence, with natural gas operation lower unburned fuel emissions during cold starting and warm-up phase are obtained. Similarly, as very little mixture enrichment is necessary during warm-up and transient engine operation, CO emissions are also lower. With the use of electronic engine and fuel management and emission control technology, natural gas vehicles complying with the US Tier 2 and ULEV standards can be built more easily compared to gasoline vehicles. Emission results for two vehicles operating on gasoline and natural gas vehicles are compared in Table 8.16. Natural gas cars gave more than 50% lower non-methane hydrocarbons, 10 to 50% lower CO and 10 to 80% lower NO_x.

Table 8.16

Emissions and Performance of a SI Natural gas Heavy-duty Engine with 3-Way Converter, European Transient Test Cycles, g/kWh

Test Cycle – Fuel	CO	NMHC	CH_4	NO_x	PM
ETC limits	3.0	0.40	0.65	2.0	0.020
NG Engine	1.10	0.04	0.15	0.57	0.008

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Liquefied Petroleum Gas

Liquefied petroleum gas (LPG) is a mixture of commercial propane and butane. It is obtained either from the natural gas processing or during petroleum refining. Composition of LPG varies very widely from country to country depending on the use and demand of butane. LPG is a gas at normal ambient temperatures and pressures (the boiling point of propane and butane at atmospheric pressure is about - 45° C and -2° C, respectively). When subjected to pressure of 4 to 20 bars mixture of propane and butane becomes liquid. The pressure at which it becomes liquid at room temperature depends upon propane to butane ratio. The LPG is usually fed to the engine in gas phase.

- Most LPG vehicles operate on bi-fuel systems for operation either on gasoline or LPG. It is important as the number of LPG filling stations is usually small.
- One drawback with a bi-fuel system is that the engine is neither optimised on LPG nor on gasoline.
- Better cold start and warm-up characteristics due to its gaseous state compared to gasoline hence lower HC emissions.
- HC emissions from LPG vehicles have significantly lower potential of smog formation compared to gasoline and diesel fuels.
- Negligible PM emissions compared to diesel.
- Small reductions in CO compared to gasoline as no enrichment of mixtures during warm up or acceleration phase is required.
- No significant difference in NO_x emissions.
- Variation in propane/butane ratio in LPG poses problem as the octane number of the two main constituents; propane (RON is 112) and butane (RON is 94) is quite different.
- For bi-fuel vehicles specific technological development will be necessary to ensure compliance with the stringent emission standards.

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