Chapter

Syngas Production, Properties, and Its Importance

Raghda Ahmed El-Nagar and Alaa Ali Ghanem

Abstract

Much attention has been focused on reducing the use of petroleum products as fuels, so synthetic gas (Syngas) introduces a great opportunity for energy sustainable developments. Syngas is created either by gasification of plants biomass or waste products (carbon-based) pyrolysis. In principle, Syngas can be produced from any hydrocarbon feedstock. It mainly affects the combustion process in internal combustion engines. The most important is flammability limit, which is very important in the safety and the laminar flame velocity or burning velocity, which is an essential parameter for the investigation of combustion chamber operation and emission performance. This chapter generally reviewed the syngas sources, production, properties, and its importance in the sustainable development for energy.

Keywords: synthetic gas (syngas), petroleum products, pyrolysis, gasification, thermo-chemical process, partially combustion, flammability

1. Introduction

The synthesis gas is defined as a gas with H_2 and CO as the main components of fuel. Row syngas contains mainly significant amounts of CO_2 and H_2O as well. Since syngas is usually used at higher pressures for synthesizing chemicals and fuels (**Figure 1**), the N_2 contents must usually be minimized in syngas. Bio-syngas, however, are biomass produced, chemically identical to syngas. This definition is in accordance with the SYNBIOS-conference definition.

Syngas differ chemically from gasses normally generated by gasification processes at low temperatures, including fluidized bed reactors [1]. To be clear, the gas produced by such reactors is referred to in this report as "product gas." Product gas is defined as a fuel gas with H_2 and CO as well as with substantial amounts of hydrocarbons, such as methane. Product gas contains CO_2 and H_2O, and often N_2, also inevitably.

Throughout the chemical industry, syngas is a substantial intermediate product. Each year, around 6 EJ of syngas are manufactured globally, which is almost 2% of the world's current primary energy consumption. The ammonia industry dominates the global market for syngas (mainly from fossil fuels like coal, natural gas, and oil/residues) [2]. The production of hydrogen for use in refineries, for instance, the processing of hydrogen, and methanol are other major applications. The current market distribution of syngas is shown in **Figure 1**.

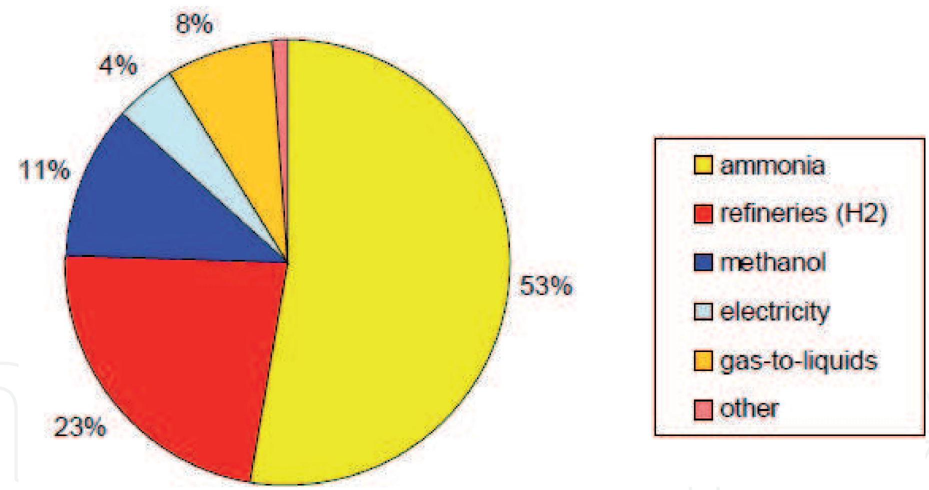

Figure 1.
Present world syngas market, totally ~6 EJ/y.

2. Major properties of syngas

Different characteristics of syngas can affect the process of combustion in internal combustion (IC) motors. The flammability limit of the syngas is one of the most important properties in IC engine safety and fuel. Also, the laminar flame velocity [3] (burning velocity) is an essential parameter to investigate the operation of the combustion chamber and its emission performance.

2.1 Syngas flammability limits

The limit of flammability is usually used as an index for the flammability of the gas. This describes the range of the fuel concentrations in the fuel/air mixture at certain temperature and pressure, which allow the ignition of the flame to propagate and sustain the flammability limits [4] are known in line with generally accepted usages as those fuel-air areas where flame propagation can take place and where fire cannot propagate. The fuel, the spread direction, the size and the form of the combustion chamber, the temperature, and the pressure are primarily affected [4]. And for the fuel-air blend, there are two distinct flammability limits, namely the smallest fuel boundary the flames can propagate is called the lower flammability boundary (LFL), while the richest one is called the upper flammability boundary (UFL). The fact that H_2 and CO are the principal flame-retardant components of syngas inherits the characteristics of these gasses. The presence of inert gasses such as nitrogen and carbon dioxide in the gas mixtures reduces the flammability limit.

2.2 Laminar flame velocity

The laminar flash speed is the speed at which the flame propagates in the direction of expansion wave surfaces under a laminar flow condition via quiet unbranded fuel-oxidant mixes [5]. Because LFV is highly sensitive to combustion chamber operations and emission performance, it is very important for the investigation of combustion chamber operations. The composition of the fuel, mixture equivalence ratio, temperature, and pressure affects it.

2.3 Syngas composition and its calorific value

The composition of the manufacturer's gas depends on feedstock, particulate size, gas flow rate and feedstock flow, chemical reactor configurations, operating conditions or process of gasification, gasificator and catalyst, and gas residence time. But the temperature of the reactor, which in turn is affected by the ER value, mainly influences it. Furthermore, CO, H_2, and CH_4 concentrations in producer gas are also controlled by chemical reactions in the process of gasification.

There is, therefore, a considerable influence on the calorific value of the producer gas on the type of oxidizing agent used for gasification. As ER increases and then the concentrations of these useful components decreases because of the intensification of combustion at higher ER values, the concentrations of CO and H_2 reach the maximum value. As ER increases, the concentrations of CO_2 and N_2 in the producer gas are also increased [4]. Air as an oxidant produces syngas with relatively high levels of nitrogen and thus a lower heat value, which does not normally exceed 6 MJ/Nm^3.

The producer's gas is classified as fuel gas of low quality. The typical biomass gasification composition of an air-borne downdraft reactor with the oxidizer is as follows: 15–20% of H_2, 15–20% of CO, 0.5–2% of CH_4, 10–15% of CO_2, and the rest of the component of N_2, O_2, and CXHY. If the concentration of fuel components is considerately increased and the gas is called a medium heat value, up to 16 MJ/Nm^3 [6], where oxygen or water steam or the mixture of both are used.

3. Production of synthesis gas

Synthesis gas or syngas is called carbon monoxide (CO)-hydrogen (H_2)-containing gas mixture. Carbon dioxide (CO_2) and other components such as water (H_2O) may also be present in syngas.

The chemical synthesis can be used as a building block in all products normally produced from crude oil or natural gas. Petrol and diesel are fuels with definitions, which are not based on the chemistry but on their physical qualities such as boiling and flashing.

The octane rating of gasoline in an internal combustion (IC) engine is empirical and based on its actual performance. This means that at least low-grade blending is possible as long as synthetic fuel matches the characteristics of petrol- or diesel-based crude oil.

3.1 Production of fuels and chemicals from gasification of biomass/coal or reforming of natural gas

The feedstock must be gasified when beginning with a solid feedstock, such as biomass or coal. It may be necessary to ground or pulverize the feedstock before gasification (usually carbon). The particle fineness depends on the gasification type. For most biomass gasification plants, drying is required as the next step. The drying is integrated into a gasifier reactor vessel by certain gasifiers [7].

Following gasification, the product is a gas, known as producer gas, filled with impurities that must be removed. Prior to synthesis, the producer of gas usually also needs the ratio from H_2 to CO. H_2:CO Both.

3.2 Gasification

All hydrocarbon feed resources like coal, heavy oils, or combustible biomass can be gasified as synthesis gas. Several reactions occur in the gasificator, but the total reaction can be summarized by Eqs. (1) and (2).

$$\text{Biomass} + O_2 \rightarrow CO + H_2 + CO_2 + H_2O + CH_4 \tag{1}$$

Composition	Updraft Gasifier (% by Volume)	Downdraft Gasifier (% by Volume)
Carbon monoxide	24	21
Hydrogen	11	17
Methane	3	2
Hydrocarbon	0.2	0.3
Nitrogen	53	48
Water vapor	3	4

Table 1.
Composition of producer gas [8].

By-products: tar, char, ashes.
Reaction conditions:

- High temperature (800–1000°C) and low pressure (1–20 bar)
- H_2/CO ratio within 0.5 and 1.8, depending on the technologies

The reaction also can be expressed as:

$$\text{CaHbOcNd} + O_2/H_2O/N_2 \rightarrow CO + H_2 + \text{CxHyOz} + CO_2 + H_2O + NH_3 + N_2 \quad (2)$$

The solid carbon is partially oxidized with oxygen (O_2), air, steam (H_2O), or a combination of all gasification agents. CxHyOz is mostly made of methane with a few low percent of hydrocarbon, including ethane and ethylene (**Table 1**). For most gasifiers, gas may also contain heavier hydrocarbons such as benzene, toluene, and naphthalenes, depending on the feedstock and the operational parameters. Hydrocarbons, which are heavier than benzene, are often known as tars (**Figure 2**).

This is an important factor in determining the technical mechanism and the economic feasibility of the gasification system. Efficiencies in gasification are based on the biomass type used, its particle size, its ER value, and the reactor design [8].

The gasification efficiency is usually determined on the lower heating value basis. The efficiency is calculated as the ratio of the total energy in the producer gas (sensible and chemical) and the chemical energy in the feedstock (the heating value). Depending on type and design of the gasifier as well as on the characteristics of the fuel, mechanical gasifier efficiency may vary between 60 and 75%. A useful definition of the gasification efficiency (%) used for engine applications is as follows:

$$\eta_m = \frac{H_g \times Q_g}{H_s \times M_s} \times 100$$

where ηm is the gasification efficiency (%) (mechanical), Hg is the heating value of the gas (kJ/m^3), Qg is the volume flow of gas (m^3/s), Hs is the lower heating value of gasifier fuel (kJ/kg), and Ms is the gasifier solid fuel consumption (kg/s).

3.3 The yield of syngas

The syngas yield is measured by the mass of the produced in cubic meters per the mass of the feedstock provided to the system The yield is directly commensurate with the difference in ER and with the gas residence time in the reduction area [9]. The biomass ash content also has a considerable impact and limits the yield of the gas producer.

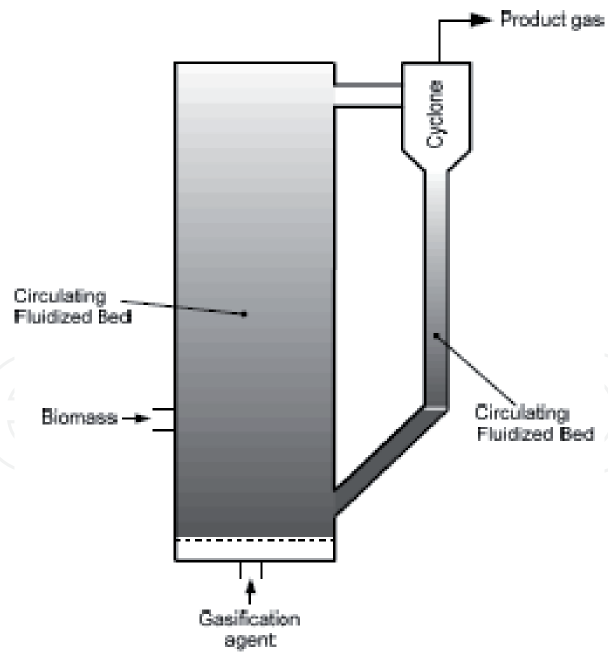

Figure 2.
The gasificator [8].

3.4 Cleaning and cooling of producer gas

The combustible gas can be used as a feedstock for the production of chemicals like methanol or in internal combustion engines for direct heat uses.

4. Fischer-Tropsch diesel production

One of the commercially accessible methods of manufacturing clean synthetic fuel from syngas is Fischer-Tropsch technique. Industrially speaking, coal/pet-coke/biomass emits huge quantities of carbon dioxide that can be used to enhance the fuel production.

Because of the increased level of carbon dioxide in atmosphere and also the depletion of conventional fuels, scientific researches recommend the chemical recycling of carbon dioxide into renewable fuel and more added-value chemicals [8].

The production of synthetic fuel from syngas is favorable process owing to its portability as well as to its large quantity of chemical energy, saved without further processing and easy to use.

The raw syngas undergoes multiple energy intensive processes to fulfill the stoichiometric requirements ($2.05 < H_2/CO < 2.15$) for Fischer-Tropsch, including removal of carbon dioxide for subsequent sequestrating, to mitigate negative carbon dioxide emission impacts. Absorption techniques with mono- and diethyl amines are the most popular technology for the removal of carbonic gases from syngas. These procedures are energy intensive owing to the intermediate steps of absorption, desorption, and compression.

The main Fischer-Tropsch reaction is to produce aliphatic long-chain saturated hydrocarbons from syngas (Eq. (3)). There are a lot of side reactions that occur on active sites accompanying the main reaction (Eq. (4)).

Original FT reaction:

$$nCO + 2nH_2 \rightarrow (CH_2)n + nH_2O; \Delta H298\ K = -152\ kJmol^{-1} \tag{3}$$

Carbon dioxide is also a Fischer-Tropsch waste product and considered to effect the targeted yield of the produced liquid hydrocarbons, and also the presence of carbon dioxide can lead to a substantial reduction in the catalytic reaction activity [10]. This is due to the water-gas-shift (WGS) reaction (Eq. (4)) by which the hydrogen lack is overcome and releases a large quantity of carbon dioxide during the reaction.

Water-gas-shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2; \Delta H298\ K = -41.2\ kJmol^{-1} \tag{4}$$

It was reported that the carbon dioxide found in syngas plays the role of an oxidizing agent on reduced Co/γ-Al_2O_3, which effects the conversion of carbon monoxide and C5+ hydrocarbons selectivity. Another role for the carbon dioxide was proposed as an inert gas in cobalt-based catalysts [10]. Another approach described the formation of dioxide during the Fischer-Tropsch reaction that will reduce with the using of syngas-containing carbon dioxide as the equilibrium tends to be directed in the inverse direction without affecting the Fischer-Tropsch process.

The change in equilibrium of carbon dioxide is the first step in Fischer-Tropsch (Eq. (6)), resulting in an enhanced proportion of oxygen atoms in carbon monoxide, which is retrieved by water over iron-based carboxylic catalysts comprising syngas. The produced carbon monoxide from this shift is further processed in the Fischer-Tropsch technique.

Boudouard reaction:

$$2CO \rightleftharpoons CO_2 + C(s); \Delta H298\ K = -172.5\ kJmol^{-1} \tag{5}$$

Modified CO_2-FT reaction:

$$CO_2 + H_2 \rightleftharpoons CO \rightarrow 2nH_2 \rightarrow (CH_2)n + nH_2O + H_2O \tag{6}$$

Direct CO_2 hydrogenation:

$$nCO_2 + 2nH_2 \rightarrow (CnH_2n)n = 2\text{–}4 + nH_2O \tag{7}$$

The low selectiveness of 10Co5Fe supported on carbon nanofiber catalyst to produce methane during Fischer-Tropsch reaction. The increase in carbon dioxide levels in syngas produces only 22% of C5+ hydrocarbons.

Fe_3O_4 catalyzes the transformation of carbon dioxide into carbon monoxide through the inverse response of the water-gas-shift system, while χ-Fe_5C_2 is involved in hydrocarbon production.

Catalytic transformation of syngas was demonstrated with the use of bifunctional Fe-Co, backed on hierarchical HZSM-5, of 16% (mol%) carbon dioxide in hydrogen deficiencies. 1Fe:2Co (wt%) is the most effective bimetallic mixture of several combinations of iron and cobalt.

5. Conclusion

- The synthesis gas is defined as a gas with H_2 and CO as the main components of fuel.

- The flammability limit of the syngas and the laminar flame velocity are the major syngas properties.

- Syngas can be produced from gasification of biomass/coal or reforming of natural gas, and the yield is measured by the mass of the produced in cubic meters per the mass of the feedstock.

- Fischer-Tropsch technique is one of the commercially accessible methods of manufacturing clean synthetic fuel from syngas.

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