Introduction

Discovery of petrol, in the nineteenth century, led to increased interest in fossil energy sources. Inexpensive fossil fuels improved the quality of life and ushered in rapid industrialization. Geophysicist, M.K. Hubbert [1], was one of the first to point out problems facing increased demand for fossil fuel. In 1956, at a meeting of the American Petroleum Institute, he presented a model of petroleum production, called the “peak of oil”. This model had predicted oil production to peak in the year 2000. Significant decrease of fossil fuels resources and lack of new ones becomes the basis for the Olduvai theory, published by R.C. Duncana in 1989 [3]. The theory postulated that in the years 2012-2030, as a result of shortage of energy, the world would go through an economic crisis. This crisis would lead to collapse of industrial civilization. Hence, there is a need to look for alternative, renewable sources of raw materials. Biomass is one of them.

It is very difficult to estimate earth’s potential to supply biomass for production of renewable energy. The literature data on this subject are not unambiguous. They depend on considered sources of biomass (e.g. whether total biomass was used in the estimation or only biomass not provided for food production, whether waste from agriculture and forestry is included, etc). According to the authors of [4], energy potential obtained from biomass on surplus agricultural land (i.e. land not needed for production of food and feed) would be 215–1272 EJ/yr, depending on the level of advancement of agricultural technology, by the year 2050. Global potential of bioenergy production from agricultural and forestry residues and wastes was calculated at 76–96 EJ/yr, but from surplus forest growth (forest growth not required for the production of industrial roundwood and traditional woodfuel) was calculated at 74EJ/yr, by the year 2050. Consequently, the authors of [5] estimated the energy potential of biomass obtained from abandoned land, land with low productivity and other land not used in agricultural production, to reach between 130 and 410 EJ/year by the year 2050. However, as described in [6], Shell International Petroleum Company analysis estimated the total consumption of biomass energy to reach 221 EJ by the year 2060. As can be seen from these data, theoretically energy obtained from biomass can meet all energy demand. Currently this demand is above 400 EJ/year [7].

Researches connected with the use of biomass as an energy source are being conducted by many research centres as well as chemical and petrochemical companies, among them are: Neste [8], UOP and ENI [9], Conoco-Philips and Petrobras [10].

Biomass has two advantages: it is a potential source of feedstock for chemical and petrochemical industry and it is readily available. Because of these, an intensive search for low-cost processing technology to convert these raw materials into cheap fuel and chemicals has already begun.

The aim of this paper is to outline the most common methods of obtaining of synthetic hydrocarbons from biomass. Discussed methods are an example of potential technologies of biomass conversion into fuels.

The biomass liquefaction

The biomass is all biodegradable substances obtained from plants or animals. Biomass includes, inter alia, residue from agricultural production, forestry residues, industrial and municipal waste and plants from energy crops. Due to wide range of biomass resources and materials, there are many ways of converting biomass into fuel [11, 12]. The final state of the product could be gaseous (biogas, hydrogen), liquid (alcohols, hydrocarbons, esters) or solid (biocarbon). The chemical composition of biomass is different from that of coal and petroleum. It consists of O-containing organic polymers. The main structural components of biomass are high-molecular compounds such as: cellulose (polymers of glucose), polyose (hemicelluloses) and lignin [13]. It also contains a small amount of organic and inorganic low-molecular compounds [14]. The content of particular components is different in different plant materials. The chemical composition of plant biomass is presented in Figure 1.

Due to biomass' chemical composition and various processes involved in its processing (Gasification [15, 16], combustion [17, 18], pyrolysis [19, 20], fermentation [21, 22]), it is possible to obtain a wide range of products [11, 23], these products could include crude oil substitutes and petroleum products.

At present there is no technology capable for obtaining liquid fuel from biomass in one-step process. Figure 2 [24] presents an example of paths in the processing of cellulosic biomass.

In addition to the three paths of processing biomass presented in Figure 2, it is worth mentioning a fourth one - hydroconversion of fats into hydrocarbons [25, 26]. This method can be used to process both animal fats as well as vegetable oils.

By their chemical structure and properties, synthetic hydrocarbons are very similar to conventional crude oil based liquid fuel. For this reason, they have aroused widespread interest. At present the best-known and most technologically advanced process is to obtain synthetic hydrocarbons from synthesis gas [27, 28] via Fischer-Tropsch synthesis (FT). Operating Industrial installations run by the companies: Choren [29] and Enerchem [30] are a confirmation of this.
The process of hydrocarbons synthesis by gasification of biomass and FT synthesis, takes place in four basic stages. Preparation of raw material, namely sorting, cutting and drying takes place in the first stage. In the next stage, gasification of raw materials takes place at very high temperatures of around 1400°C. In most cases gasification stage is implemented in several sub-stages. The resulting gas is then subjected to purification into synthesis gas (CO and H₂), the process next moves to the fourth stage - conversion to liquid fuel. Fischer-Tropsch synthesis (FT) is employed at this stage. This process is carried out at around 200°C, under increased pressure, in the presence of a catalyst. Reactive components of synthesis gas react with each other to give hydrocarbons as shown by the following reaction equation:

\[(2n+1)H_2 + n CO \rightarrow C_{2n+2}H_{4n+2} + nH_2O (1)\]

FT synthesis products are straight-chain alkanes containing from one to fifty carbon atoms in the chain. It is a mixture of gas products with gasoline fractions and gas oil fractions [11]. However, it is possible, through appropriate choice of catalysts, to selectivity conduct a reaction in order to obtain target product, for example, premium petrol [31].

Another method of synthesis of liquid alkanes is the process of converting liquid phase from biomass. The first stage in this method involves conversion of solid biomass into liquid O-containing organic compounds with a lower molecular weight, such as C₆ sugars and glucose. This is accomplished mainly via acid hydrolysis [32] or enzymatic hydrolysis [33]. The disadvantage of hydrolysis processes accomplished by using mineral acids is the use of acids themselves; they cause strong corrosion, and problems with stopping progressive degradation of monomers and disposal of waste after neutralization. Enzymatic conversion of biomass entails significant costs of enzymes and pH buffers, which maintain adequate working conditions for the enzymes, but also involves problems with separation of product from reaction mixture [23]. The next stage is the catalytic conversion of sugars into hydrocarbons [34].

The conversion of biomass into fuel with the use of alcohols may be carried out on a principle similar to methanol-to-gasoline progress (MTG). A mixture of hydrocarbons of a composition similar to petrol is obtained as a result. Although knowledge of this process has been around for some time [35], the process itself is still at research stage [36] and only laboratory or pilot installations exist.

Liquid state biomass may also be obtained through thermal methods such as depolymerization or pyrolysis. During depolymerization, biomass is subjected to single-stage thermal decomposition, during which it has contact with contact oil. This process is carried out at around 350-450°C, under atmospheric pressure and optionally in the presence of a catalyst (depending on technology). Thermal conversion of appropriately prepared biomass (dried and ground) takes places within seconds. Reaction mixture is divided into fractions, high and low boiling-point constituents; water is next extracted from these constituents. Resultant hydrocarbons may be used as diesel fuel. However, there is little literature data on this process [37, 38].

Pyrolysis constitutes the second of these methods of thermal decomposition of biomass. It is a process of thermal conversion of organic matter in the absence of oxygen. The percentage of different individual components (solid, liquid and gas) in the final product varies; it depends on how pyrolysis is conducted. Two fundamental [39] approaches to this conversion technique have been put forward. The first, referred to as traditional or conventional pyrolysis, leads to maximum efficiency of gaseous phase (high temperature, low rate of temperature rise, long time) [40, 42], or maximum efficiency of solid phase - coke (low temperature, low rate of temperature rise) [43, 44]. The second approach known as flash or fast pyrolysis leads to maximum efficiency of liquid phase [45, 47]. Pyrolytic oil (biodiesel) obtained by this process is a complex mixture, containing about one hundred O-containing organic compounds. The main components include: acids, phenols, ketones, aldehydes, ethers and aromatic compounds [39, 48]. Due to high oxygen content, as high as up to 50% [49], its chemical properties are different from those of crude oil. Because of the very complex composition of raw bio-oils, it doesn't have wide application, however, it is regarded as a product to be subjected to further processing. Some properties of pyrolytic oils (such as alkali content, acidity) are not compatible with typical refinery processes, hence often require further refinery processes. Conversion of pyrolysis oil into hydrocarbons usually takes place in two stages: in the first approach, the amount of oxygen and acid number is reduced; next the deoxidized oil is processed in the presence of hydrogen [49]. Ensyn Technologies Inc., a Canadian Company, is one of the leading producers of pyrolytic oil from biomass [50]. This company, together with UOP LLC company, through a process referred to as UOP/Eni Ecofining™, converts biooil into hydrocarbons of composition comparable to diesel. The resulting fuel is called Green Diesel [51].

Fats constitute yet another raw material for obtaining synthetic hydrocarbons. They can be waste animal and vegetable fats or vegetable oils, including non-food (for example, jatropha oil [52] or oil from algae [53]). The following leading petrochemical companies are involved in catalytic hydrodeoxygenation technologies: Conoco-Phillips, Petrobras and Neste Oil. With this that Conoco-Phillips and Petrobras processe fats together with petroleum fractions while Neste Oil processes only fats. In the process developed by Neste, vegetable oils are processed using processes used in refining of crude oil [54, 55]. The end product of the process is diesel fuel called NExBTL, it complies with all applicable regulatory requirements for diesel fuel. This technology was commercialized in 2007 in the petroleum refinery works in Porvoo, Finland.

Summary

Escalating prices of conventional fuels have led to intensive search for petroleum substitutes. This has become the main engine of development of biofuel technology. The main aim of this technologies is to obtain a product enjoying high demand, starting with a cheap (preferably waste) raw material, and using of the simplest and cheapest available technology. Replacements of conventional fuels would constitute an ideal solution. Synthetic hydrocarbons offer such opportunity. Unlike other biofuel such as fatty acid esters or alcohols, these hydrocarbons may be mixed with petroleum fuels in any ratio or may they could be used as stand-alone fuel without the need for costly changes in engine construction or fuel system. At present, technologies for obtaining synthetic hydrocarbons from biomass are not in a position to compete, price-wise, with fossil fuels, hence the small number of commercial installations. But immediate future may change all these.

English translation by the author

Bibliography
