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Analysis of biofuels from waste lignocellulosic materials by gas chromatography

Master's Thesis

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Conservation and Use of Natural Resources

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Declaration

I declare that I have worked on my master's thesis titled „*Analysis of biofuels from waste lignocellulosic materials by gas chromatography*" by myself under the guidance of the thesis supervisor and using only professional literature and other information sources, cited and mentioned at the end of the thesis. As the author of the master's thesis, I further declare that the thesis does not break any copyrights.

In Prague on 13.04.2023 ______________________________

Acknowledgement

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Summary

In recent years, there has been a massive increase in demand for renewable energy and biofuels. This is mainly to minimise the environmental impact of greenhouse gas emissions and to improve competitiveness by reducing dependence on oil imports. Considering their renewability and sustainability, biofuels are increasingly perceived as an environmentally friendly and economically viable alternative to conventional fossil fuels. The development of new technologies in the field of biofuel production is also leading to the possibility of using various renewable resources such as vegetable oils, algae and also waste lignocellulosic biomass (LIBS), which is increasingly becoming a focus of interest. There are several methods to use waste LIBS to produce motor fuels. One of these is the Fischer-Tropsch synthesis (FTS), which allows the synthesis of hydrocarbon fractions from these waste materials with the catalyst presence, having the potential to produce motor fuels. FTS technology is becoming an important alternative to traditional fuel production from fossil sources.

Prior to the actual use of the fuels produced in this way, it is necessary to analyse their chemical composition and physical properties and verify whether they meet the legislative requirements for motor fuels. The analysis of *n*-alkanes is a common method for characterising the chemical composition of fuels and also provides information on their quality. In this diploma thesis, realized with the collaboration of the research organization ORLEN UniCRE, gas chromatography with a flame ionization detector was used to identify and quantify linear hydrocarbon chains for individual petrol and diesel fractions obtained by FTS based on their retention times compared to reference substances. For the most suitable diesel fraction, some other properties such as density, viscosity, flash point and laboratory cetane number were evaluated.

In the context of this diploma thesis, it has been shown that the synthesised hydrocarbon fractions contain different *n*-alkane compositions compared to commercial petrol and diesel fuels and that not all of them can be used purely as motor fuel without additional treatment. FTS petrol fractions are only suitable as additives to fossil petrol after further chemical processing. In contrast, diesel fractions can be an equivalent substitute to fossil diesel entirely. In particular, the assessment of the diesel fraction produced by hydrocracking of waxes has confirmed that this fraction can be successfully used to produce a high-quality biofuel that even overcomes fossil diesel in purity and properties. The obtained data contributes towards raising awareness that Fischer-Tropsch synthesis represents an efficient method to produce biofuels from waste lignocellulosic materials and the possibility of publishing these data in a peer-reviewed journal is predicted.

Keywords: waste materials; lignocellulose; Fischer-Tropsch synthesis; biofuels; gas chromatography

Analýza biopaliv z odpadních lignocelulózových materiálů pomocí plynové chromatografie

Souhrn

V posledních letech se masivně zvyšuje poptávka po obnovitelných zdrojích energie a po biopalivech. Důvodem je zejména minimalizace dopadu na životní prostředí vlivem emisí skleníkových plynů a zlepšení konkurenceschopnosti díky omezení závislosti na dovozu ropy. Vzhledem k obnovitelnosti a udržitelnosti jsou biopaliva stále více považována za ekologickou a hospodářsky výhodnou alternativu ke klasickým fosilním palivům. Vývoj nových technologií v oblasti výroby biopaliv také vede k možnosti využití různých obnovitelných zdrojů, jako jsou rostlinné oleje, řasy nebo také odpadní biomasa na bázi lignocelulózy (LIBS), která se stává stále více středem zájmu. Existuje celá řada metod, jak využít odpadní LIBS k výrobě motorových paliv. Mezi ně patří také Fischer-Tropschova syntéza (FTS), která umožňuje z těchto odpadních materiálů syntetizovat za účasti katalyzátorů uhlovodíkové frakce s potenciálem pro výrobu motorových paliv. Technologie FTS se stává důležitou alternativou k tradičnímu získávání paliv z fosilních zdrojů.

Před samotným použitím takto vyrobených paliv je nezbytné provést analýzu jejich chemického složení a fyzikálních vlastností a ověřit, zda splňují legislativní požadavky na motorová paliva. Analýza *n*-alkanů je běžnou metodou pro charakterizaci chemického složení paliv a zároveň poskytuje informace o jejich kvalitě. V rámci této diplomové práce realizované ve spolupráci s výzkumnou organizací ORLEN UniCRE byla použita plynová chromatografie s plamenovým ionizačním detektorem s cílem identifikovat a kvantifikovat lineární uhlovodíkové řetězce pro jednotlivé benzinové a dieselové frakce získané pomocí FTS na základě jejich retenčních časů v porovnání s referenčními látkami. U nejlépe vyhovující dieselové frakce byly vyhodnoceny některé další vlastnosti jako je např. hustota, viskozita, bod vzplanutí a laboratorní cetanové číslo.

V rámci této diplomové práce bylo prokázáno, že syntetizované uhlovodíkové frakce v porovnání s komerčním benzínem a motorovou naftou obsahují rozdílné složení *n*-alkanů a že ne všechny mohou být bez úpravy použity jako motorové palivo. Benzinové frakce FTS jsou vhodné jako příměsi k fosilnímu benzinu teprve po dalších chemických úpravách. Naopak dieselové frakce mohou být rovnocennou náhradou pro fosilní dieselová paliva. Zejména vyhodnocení dieselové frakce vyrobené hydrokrakováním vosků potvrdilo, že může být tato frakce úspěšně využita pro výrobu biopaliva, které čistotou a vlastnostmi fosilní diesel dokonce překonává. Získaná data přispívají k rozšíření informací o tom, že Fischer-Tropschova syntéza představuje účinnou metodu pro výrobu biopaliv z odpadních lignocelulózových materiálů a předpokládá se možnost publikování těchto dat v odborné literatuře.

Klíčová slova: odpadní materiály; lignocelulóza; Fischer-Tropschova syntéza; biopaliva; plynová chromatografie

Table of Content

1 Introduction

Fuels, as a generally accepted fact, are conceptually perceived as a source of energy, providing post-consumer energy services such as heating, transportation, and electrical generation not only for household use. However, evolution does not accompany the development of only humankind, but also influences everything around us, including technological progress - these sources of energy, specifically. Current fuels are therefore increasingly being replaced under the guise of better cleanliness and greater efficiency and therefore receive a new label - biofuels. Today biofuel research is performed globally because of the major four fundamental properties, (1) substitutability, (2) protection, (3) recyclability and (4) sustainability.

1.1 Substitutability

Fossil fuels (FF) consumption is constantly rising, and their stock is dwindling. The world's energy demand is constantly increasing in correlation, with FF - coal, natural gas, and crude oil continuing to be the major sources (Dai *et al.* 2015). According to Biernat *et al.* (2013) FF from crude oil supply about 96 % of the worldwide energy demand for transport. The aggregating usage of FF, rising demand for energy, fluctuating FF prices, and increasing emissions of greenhouse gases are some of the concerning factors contributing to a shift in the interest from FF to biofuels (Nanda *et al.* 2018). Rapid industrialization at a global scale is the leading cause of the momentous consumption of FF and the worldwide economy is drastically driven by FF.

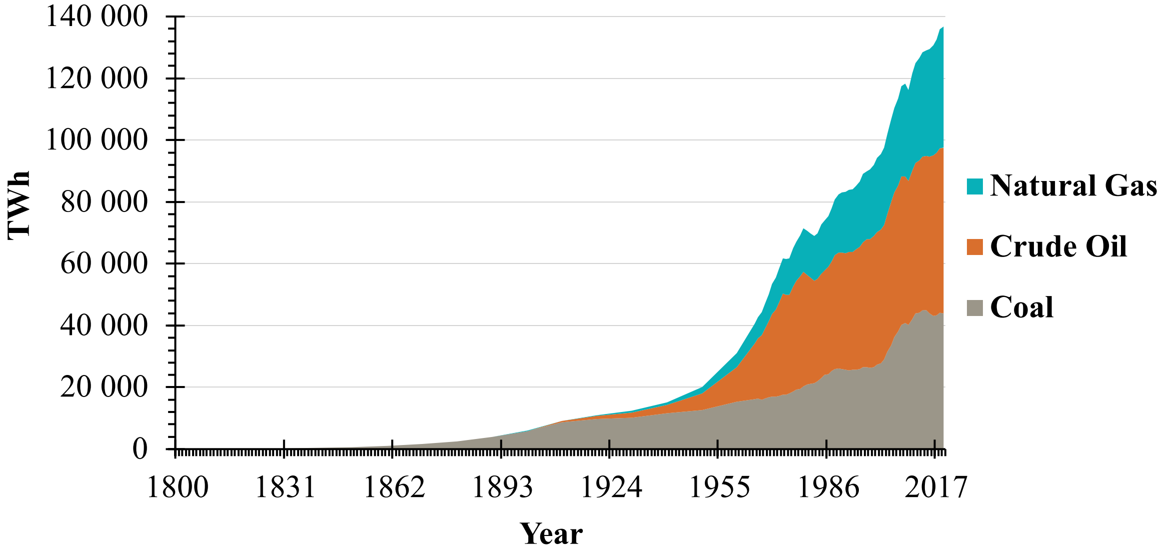

Figure 1 - Global fossil fuel consumption (data from Ritchie *et al.* 2020b).

The burning of FF for energy began around the onset of the Industrial Revolution, but consumption has changed significantly over the past few centuries (Ritchie *et al.* 2020b). Figure 1 shows global FF consumption broken down by coal, crude oil, and natural gas since 1800. The demanding energy is expressed in Terawatt-hours (TWh). The consumption of FF has increased significantly over the past half-century since 1950, and since 1980 it is doubling. But the types of FF humankind rely on have also shifted, from sole coal to a combination of oil, and then gas (Ritchie *et al.* 2020b). Today, coal consumption is falling in many parts of the world, but oil and gas are still growing quickly. The world's energy consumption has steadily been increasing and this trend is likely to continue at a higher rate in the future (Mencigar 2020).

Considering the economic development, and therefore high consumption and the constantly increasing number of people in the world, it is estimated by Biernat *et al.* (2013) that energy demand in 2050 will be around 28 - 30 TW/y. Many countries in the world are facing the demand for non-renewable FF because of overpopulation and the economic boom (Saravanan *et al.* 2022). In recent years, global economic development has raised energy demand more than consumption. Extensive investigations have been carried out worldwide to enhance biomass use by substituting FF for energy conversion (Vassilev *et al.* 2012). Biofuels are promoted on a wide scale as a means of achieving energy security. (Nanda *et al.* 2015).

On the other hand, known FF reserves are limited and will eventually run out (Biernat *et al.* 2013). The number of years shown in Figure 2 is production left based on known reserves and annual production levels (estimated in 2022).

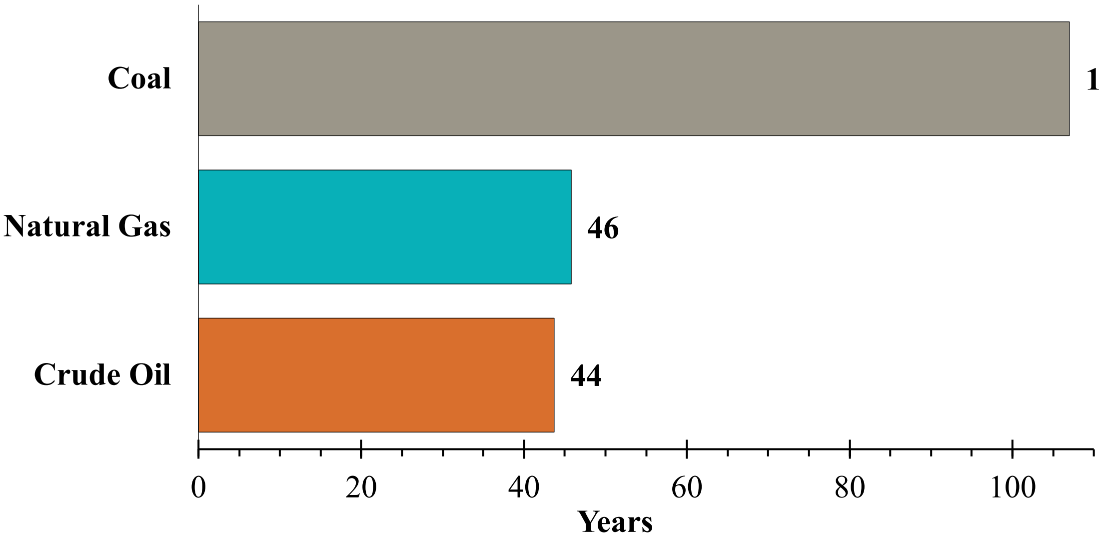

Figure 2 - Years estimation of fossil fuels left (data from Ritchie *et al.* 2020b).

Note that these values can change over time based on the discovery of new reserves, and changes in annual production (Ritchie *et al.* 2020b). Additionally, these finite reserves are still depleting and are becoming more expensive (Nanda *et al.* 2018). This possible depletion has created a demand for an alternative fuel source (Mahapatra *et al.* 2021). It is highly expected that due to the escalating energy demand, FF prices will remain high. Unfortunately, market prices are not constants. When the price of one FF rises as an example, whereas the prices of other outputs do not, the emissions and cumulative fossil energy demand allocated to this transport FF increase, in particular (Reijnders & Huijbregts 2009).

1.2 Protection

Biofuel production believably reduces carbon dioxide (CO_2) production compared to FF. It is important to get alternative energy sources, that will be increasingly able to replace the FF by reducing the effect of CO_2 emissions at the same time (Biernat *et al.* 2013). To react to the consumption of FF (Figure 1), a high potential to reduce FF CO_2 emissions in transportation is evident (Gruber *et al.* 2021). Modern times are facing a massive crisis with rising global energy demand (Figure 1) and CO_2 emissions due to the consumption of fossil fuels. Moreover, they are effective against greenhouse gases (GHGs) emissions and the impact of changing climate from transport and vehicles (Mahapatra *et al.* 2021).

There are quite a lot of thoughts encouraging biofuels such as Reijnders & Huijbregts (2009), Vassilev *et al.* (2012) or Nanda *et al.* (2015). Their studies consider those respective biofuels as sub-systems that do not contribute to the GHGs due to the CO_2-neutral conversion. An important reason for expanding the use of biofuels is possibly slowing down climate change. Released CO_2 after burning biomass is supposed to be rapidly sequestered again by the re-growth of new biomass - by the plants during photosynthesis leading to no net increase in atmospheric CO_2 levels. That means biofuels are considered to be CO_2-neutral sources of energy (Nanda *et al.* 2018). Current used FF for powering biofuel production may be associated with the emission of GHGs other than CO_2, such as nitrous oxide (N_2O) and methane (CH_4).

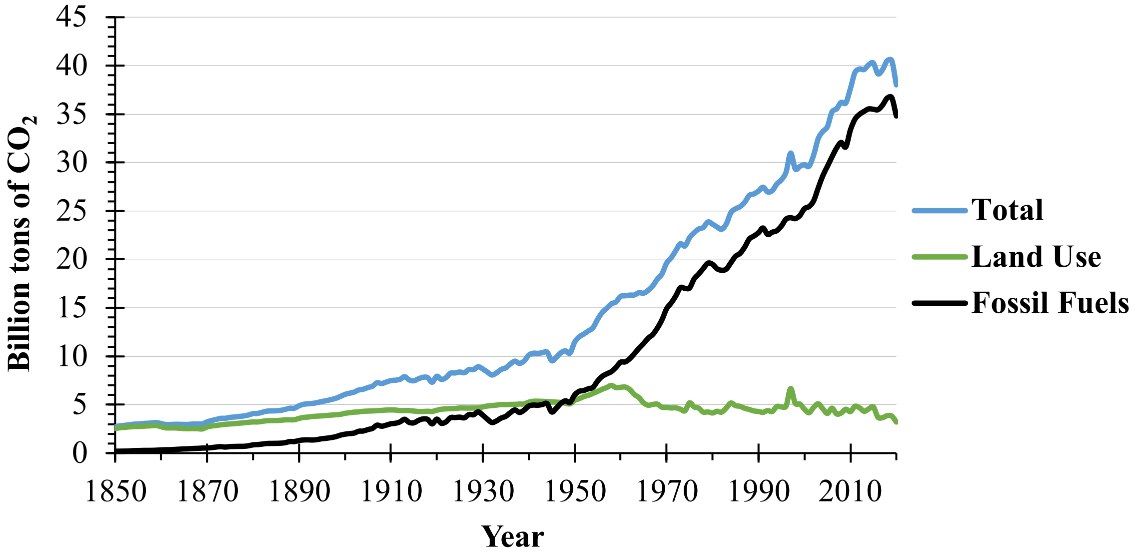

Figure 3 - The global emissions from fossil fuels and land use change (data from Ritchie *et al.* 2020b).

The burning of FF has greatly augmented atmospheric CO_2 concentrations (Dai *et al.* 2015), from 280 ppm before the Industrial Revolution to more than 400 ppm, with further increases expected in the next decade. Changes in CO_2 over time from the mid-19th century through to today are shown in Figure 3. As already mentioned above, Industrial Revolution was the driving force. The amount of GHGs was very low and its growth was relatively slow until the mid-20th century. The total amount of CO_2 quadrupled since then, humankind emits now over 34 billion tonnes each year (Ritchie *et al.* 2020a). The total global emissions of CO_2 mentioned in Figure 3 are separated into two sources - FF and land use (agricultural, residential, industrial, mining, and recreational). Overpopulation is not only related to the depletion of FF resources (Figure 1), but also directly related to global emissions. This correlation is referred to in Figure 4 in million metric tons of carbon (MMTC).

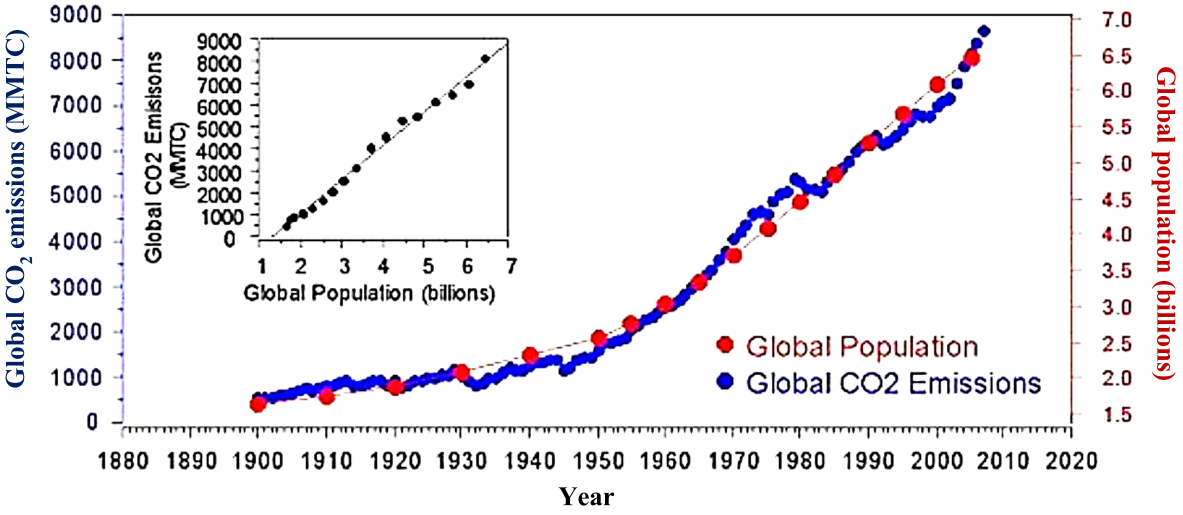

Figure 4 - The correlation of CO_2 emissions with the global population (Biernat *et al.* 2013).

The aviation industry should not be forgotten. Its contribution to CO_2 emissions is much lower than other segments of the transport industry (allegedly contributes to 2% of total GHGs), this contribution is likely to increase by 2 to 3% per year, as the industry is growing to meet the transportation demand (Pires *et al.* 2018). Therefore, there is a planned goal of reducing the net CO_2 production of the aviation industry by 50% by 2050. More people simply mean more vehicles. Due to the increasing demand for road vehicles and their reliance on FF, new solutions are needed to limit the number of emissions as the world economies continue to modernise (Mencigar 2020). Interest in biomass to produce heat, power, liquid fuels, hydrogen (H_2), and value-added chemicals with reduced GHGs emissions is increasing worldwide (Dai *et al.* 2015).

To reduce environmental pollution and zero carbon (C) emissions, the conversion of biomass into biofuels has been paid better attention to and is an innovative approach. Excessive use of FF has resulted in price hikes and GHGs that were not anticipated (Saravanan *et al.* 2022). Interestingly, synthetic liquid fuels (made from biomass) generally have also a very low content of sulphur and aromatic compounds compared to petrol or diesel from crude oil (Khodakov *et al.* 2007). It has been previously shown by Reijnders & Huijbregts (2009) that lignocellulose biomass (LIBS) as a substituting FF from sustainably managed forests in electricity production strongly reduced the life cycle of GHGs emissions per kWh, as indicated in Figure 5.

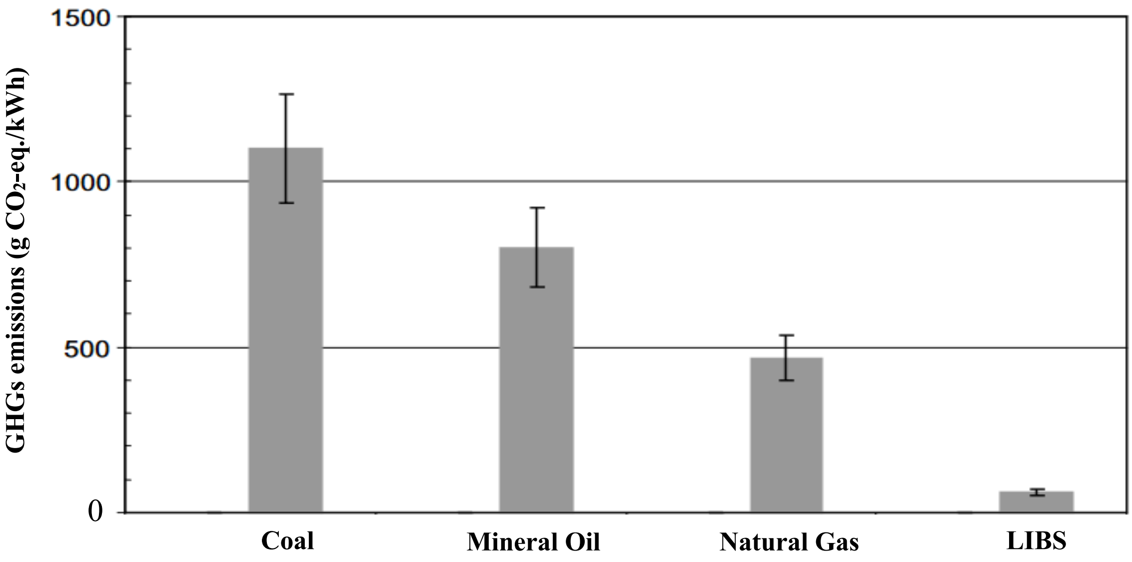

Figure 5 - Life cycle emission of greenhouse gasses for different types of electricity production (Reijnders & Huijbregts 2009).

The continued use of FF to meet the increasing energy demands (see above) poses a threat to the atmosphere due to increased greenhouse gas emissions and concerns related to global warming (Nanda *et al.* 2018). The use of biofuels produced from renewable and biogenic materials tends to mitigate GHGs emissions, supplement the growing energy needs, improve the overall energy efficiency of existing fuel systems, and invigorate employment in bio-based sectors (Nanda *et al.* 2015).

1.3 Recyclability

Biofuels can be manufactured from waste materials. Sanderson (2011) published that every year, more than 40 million tons of LIBS are produced, much of which is thrown away as waste material. Today, almost every industrial field is being explored for better energy usability and productivity. These waste materials are rich in organic matter that could be recovered for conversion to biofuels through a variety of thermochemical and biochemical technologies (Nanda *et al.* 2018). Biofuels derived from LIBS, particularly from crops, are being massively supported worldwide for meeting multiple strategy objectives such as climate change mitigation, energy security and development of the rural economy (Nanda *et al.* 2015). In addition, all products and waste materials that may be generated during the manufacturing process for liquid energy carriers, should use the strategy 3R - Recycling, Reduce, Reuse (Biernat *et al.* 2013) to reduce energy costs and protect the environment.

Biodiesel fuel production from recycled waste materials is emerging as an alternative energy source in many parts of the world (Goding *et al.* 2013). Throughout the past 20 years increasing attention has been given to the production of biofuels in gaseous, liquid, and solid forms from biomass waste sources (Mencigar 2020). Increased attention has been given to the production of LIBS because the production of biofuels from food crops is not optimal due to competition with the food market. Turning these discarded plant materials into biofuels is expedient as they do not compete with food crops and thereby they can reduce the demand for feedstock (Nanda *et al.* 2015). In contrast, LIBS in the form of waste residues from agriculture, forestry and energy crop systems is geographically abundant worldwide and has the potential to support the sustainable production of liquid transportation fuels.

1.4 Sustainability

Biomass is by its nature sustainable in the long term. At present, biomass is considered the world's most significant renewable energy source (RES) allowing to avoid further over-exploitation of unsustainable FF (Dai *et al.* 2015). That may be RES, such as wind, water (H_2O), geothermal or solar energy (Biernat *et al.* 2013). The loss of conventional FF cannot be sustained for years (Mahapatra *et al.* 2021). They are the prime sources of non-RES. All of these flaws in fossil fuels, together with their rapid depletion (Figure 2), have promoted the concept of alternate, inexpensive and RES-like biofuels (Saravanan *et al.* 2022).

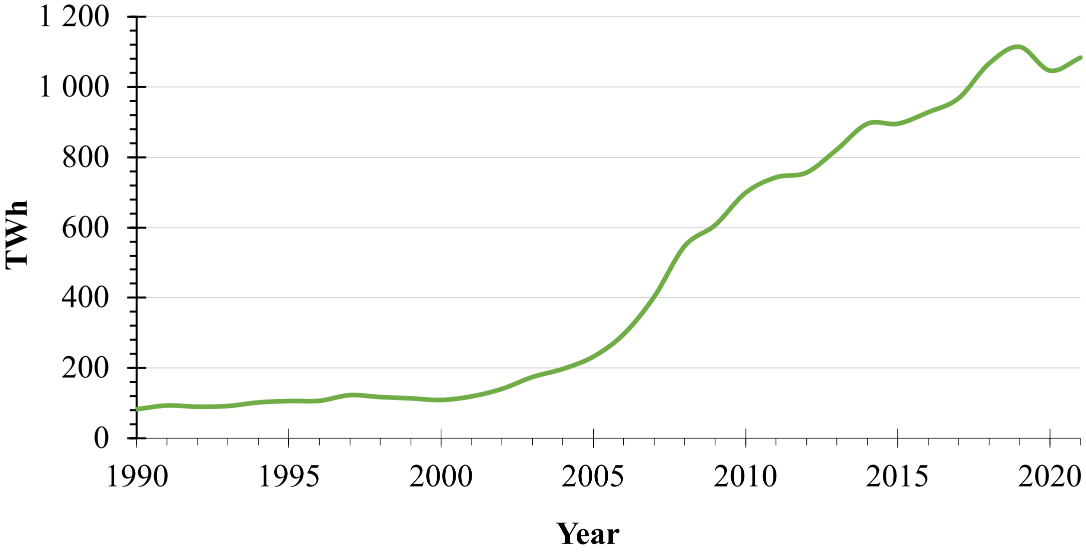

Figure 6 – The global biofuel energy production (data from Ritchie *et al.* 2020b).

A more sustainable, almost CO_2-neutral (see above) non-food source is woody biomass (Dai *et al.* 2015). It is essential to focus on the new approaches to the research, development, and production of biofuels and their processing technologies to reshape a sustainable bioeconomy (Nanda *et al.* 2018). The large focus on biofuel production could replace the use of petrol and other FF shortly. Sustainable biodiesel fuels and other RES are emerging as alternative RES in many parts of the world (Goding *et al.* 2013). These biofuels are now key transport fuels in many countries. Figure 6 shows modern biofuels (biodiesel and bioethanol only) production across the world.

Sustainable supply regards modern biofuels produced from what are currently considered waste, such as organic urban wastes, biomass from forest remediation and residues from forestry and agriculture which are not used as animal feed (Reijnders & Huijbregts 2009). Most of the solutions focus on the production of energy and fuels from RES (Mencigar 2020). Traditional biomass (the burning of charcoal, organic wastes, and crop residues) was an important energy source for a long period of human history. It remains an important source in lower-income settings today (Ritchie *et al.* 2020b). As a counterargument, Guo *et al.* (2015) mentioned 7 years ago that commercial production of bio-oil and biofuel from LIBS was still not economically viable due to inefficiencies in conversion and upgrading. All that remains is hope and faith in progress. With the contribution of new technologies, the process will be efficient and profitable, at last.

2 Hypothesis and Objectives

Production of biofuels from LIBS consists of several sections and unit operations. Many technologies for the conversion of biomass into intermediate products and many pathways of the possible upgrading routes of intermediate products into final fuels are available. The focus of this thesis was to confirm that the products of Fischer-Tropsch synthesis (FTS) from waste lignocellulosic materials are suitable intermediates for the production of motor fuels from renewable sources.

Further, several ways of biomass-to-liquid (BtL) processes were studied. This included the thermochemical conversion, upgrading, separation sections, FTS at low temperature (LT-FTS) and high temperature (HT-FTS) and different catalyst effects. Due to different FTS product profiles, thus different FTS fractions were obtained. These fractions were then evaluated and compared by gas chromatography with a flame ionization detector (GC/FID). All rigorous measurements were performed and included in the results section.

3 Literature Review

Bioenergy has drawn considerable interest as a sustainable RES to replace the exhausting FF and help in dealing with rising fuel prices of all kinds. In addition to the basic needs of survival, i.e. food, H_2O and oxygen (O_2), human life needs supplementary energy sources (e.g., electricity) for sustenance (Nanda *et al.* 2015). The key factors such as (1) increasing energy demand (Figure1), (2) exhausting FF resources (Figure 2), (3) rising fuel prices, (4) domestic energy security, (5) increasing GHGs emissions (Figures 3 and 4), and (6) global warming have propagated humankind's attention towards RES of energy. This tendency is clearly shown in Figure 7 as RES consumption, measured in TWh per year. Traditional biofuels refer to the consumption of fuelwood, forestry products and animal or agricultural wastes which are still prevalent for other RES.

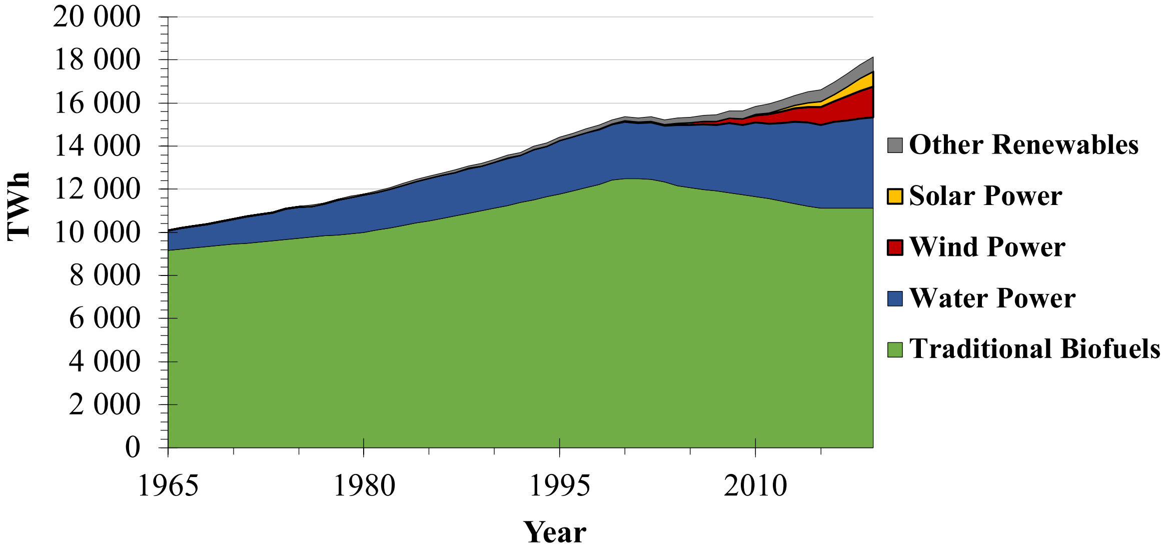

Figure 7 - The global renewable energy consumption (data from Ritchie *et al.* 2020b).

Although most of the alternative RES such as wind, solar, geothermal and nuclear are capable of generating heat and power, they cannot produce gaseous or liquid transportation fuels (Nanda *et al.* 2015). The transportation fuels are still dependent on FF, nevertheless, they slowly welcome incoming biofuels. In the following chapters, the content covering the characterization and distinctions of FF as well as biomass variety, biomass processing and the different processing units used in the production of biofuels is entailed.

3.1 Fuel Types

Determining the fuel to drive an internal combustion engine is one of the first steps involved in engine design. It is always necessary to evaluate the price of individual types of fuels, availability on the market (especially for fuels produced from biomass), harmful emissions of individual types of fuels or storability (Hromádko 2011). Fuels for reciprocating internal combustion engines can be divided, according to the source of origin, into the following categories:

3.1.1 Fossil Hydrocarbon-Containing Fuels

Although FF have accelerated global industrialization over the years so far, their experiential adverse effects cannot be repudiated. The direct effects of FF use are included but are not restricted to an increase in GHGs (especially CO_2), air pollution, smog in urban areas and H_2O pollution by oil spills. The indirect effects include acid rain, global warming, climate change and other extreme weather conditions (Nanda *et al.* 2015). Liquid fossil hydrocarbon-containing fuels (FHCF) are obtained by fractional distillation of crude oil. Fractional distillation is based on the fact that the boiling point of individual hydrocarbons increases with the increasing size of the molecules (see Table 1). By evaporation followed by condensation, individual types of liquid FHCF are obtained, as shown in Figure 8.

Table 8 - Fractions obtained by distillation of crude oil (redrawn from Blažek *et al.* 2006).

Fraction	Boiling point [°C]	*n*-alkanes contained
Gaseous hydrocarbons	< 5	C_1 - C_4
Petrol	30 - 85	C_5 - C_6
Naphtha	85 - 180	C_7 - C_{10}
Kerosene	180 - 270	C_{11} - C_{15}
Gas oil	270 - 370	C_{16} - C_{22}
Vacuum distillates	370 - 550	C_{23} - C_{45}
Vacuum residues	over 550	> C_{46}

Crude oil is a mixture of substances with different boiling points that can be distilled, and substances that cannot be distilled even under a deep vacuum. Some of the compounds contained in the crude oil can be distilled without decomposition under normal pressure, others can be distilled without decomposition only under reduced pressure. The lower the distillation pressure, the greater amount of substances that can be distilled (Blažek *et al.* 2006).

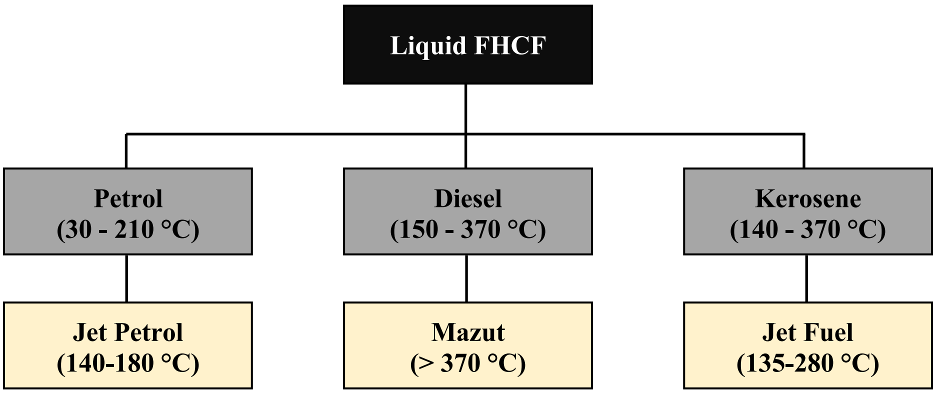

Figure 8 – The example of liquid fossil hydrocarbon-containing fuels separation based on evaporation temperature (inspired from Hromádko 2011).

The first stage of crude oil processing after purification (desalting) is the distillation to narrower fractions, which are further processed separately. At lower temperatures, during the distillation of crude oil, propane-butane is obtained and at higher temperatures, heavy fuel oils (HFO), mazut (low-quality HFO) and asphalts are obtained. More complex production processes, such as cracking or reforming processes, are used to increase the share proportion of petrol and diesel. Liquid FHCF can also be obtained by processing oily shales, natural gas can be gained by direct extraction and synthetic petrol is produced by liquefaction of the bituminous coal.

3.1.1.1 Liquefied Fuels

Petrol is designed for internal combustion engines with spark ignition (petrol engines), diesel for compression-ignition engines (diesel engines) and kerosene was previously used for petrol engines (mainly in 1920), today for jet engines in the overwhelming majority.

3.1.1.1.1 Petrol

On petrol, quite high demands are placed (Hromádko 2011). Evaluation can be performed from the point of view of the motor, fuel, as well as chemical:

- good anti-knock properties
- good evaporation at low temperatures in the range of 140-180 °C (see Figure 8) to ensure startability
- must not contain heavier fractions (above 210 °C) to prevent the oil film on the cylinder wall from being washed away and engine case oil dilution
- low sulphur content, which corrupts the fuel system, causes a decrease in petrol octane ratings and increases the pollutant content of the engine exhaust
- must not contain resins that cause clogging of the nozzles and settle in the suction line and on the suction valve
- long-term stability must ensure low storage losses

The dominant criterion of paramount importance is the octane number. It characterizes the anti-knock properties of petrol, i.e. resistance to detonation combustion. The second dominant parameter is the carburettor capacity and vaporability of petrol evaluated mainly by the distillation test, Reid vapour pressure (RVP) and evaporative heat test (Coker 2010).

3.1.1.1.2 Diesel

Diesel is a mixture of hydrocarbons with a boiling point in the range of 150 to 370 °C as seen in Figure 8. It is made by mixing kerosene with gas oil which is considered a heavier distillation product. The content of light components in the diesel is given by the requirement for ignition, and the content of heavy components is limited by the formation of deposits in the combustion chamber (Hromádko 2011). The paraffin excretion temperature is crucial for the use of diesel at low temperatures because those crystals clog fuel filters and thus interrupt the fuel supply to the engine. There is the European standard regulated by NBN EN 590 offering minimum fuel requirements and four diesel classes divided by criteria. A summary of these criteria is presented in Table 2. Individual classes are divided based on the cold filter plugging point (CFPP). This method is used to determine the low-temperature operability of diesel fuel, biodiesel, blends and gas oils (Leckel 2009).

Table 9 - The selected indicators for the Czech Republic according to NBN EN 590.

Indicator	Unit	Class B	Class D	Class F	Class 2
CFPP	°C	0	-10	-20	-32
Climate	-	Mild	Mild	Mild	Arctic
Expedition		15.04. - 30.09.	01.10. - 15.11. 01.03. - 14.04.	16.11. - 28.02.	-
FAME (max)	% (v/v)	7.0	7.0	7.0	-

Further, NBN EN 590 applies to automotive diesel fuel for use in diesel engine vehicles designed to run on automotive diesel fuel containing up to 7.0 % (v/v) fatty acid methyl ester (FAME). This substitution of fossil diesel with FAME reduces sulphur dioxide (SO_2) emissions but tends to increase the emissions of NOx from diesel, whereas the acute effects on respiratory organs do not change significantly (Reijnders & Huijbregts 2009).

3.1.1.1.3 Kerosene

A material from the distillation of crude oil that boils in the approximate range of 140-370 °C (see Figure 8), traditionally used as fuel for commercial jet aircraft (Coker 2010). Kerosene is a complex blend of up to >1000 different chemical compounds. As reported by Nanda *et al.* (2018), the chemical composition of jet fuels can be specified as roughly 60 % paraffins (alkanes), 20 % aromatic compounds (monocyclic and polycyclic hydrocarbons), and 20 % naphthenes (cycloparaffins or cycloalkanes).

In summary, the main components are linear and branched alkanes and cycloalkanes with a typical C chain-length distribution of C_6 - C_{16}. The composition of jet fuels has always been a compromise between the cost (availability of suitable raw material and the requirement for processing) and performance (propulsion properties, safety, and engine-friendliness) with very little emphasis on the environmental impact (Kallio *et al.* 2014). Sulphur contained in the jet fuel is present in its molecular form with H_2 and C along with traces of O_2 and nitrogen (N_2) named heterocyclics. This sulphur present in jet fuel has some impacts on the air quality standards and fuel lubricity (Nanda *et al.* 2018).

3.1.1.2 Gaseous Fuels

Gaseous fuels are more advantageous than liquid fuels in terms of mixture preparation. They enable better mixing and easier adherence to the mixing ratio of fuel and air and thus lower the content of pollutants in the exhaust gases. They do not wash away the fuel film from the cylinder walls and do not dilute the oil in the engine case (main demands mentioned for petrol, see chapter 3.1.1.1 - Petrol). Furthermore, they do not cause C deposits in the combustion chamber and also gaseous fuels have better anti-knock properties than liquid fuels, in general (Hromádko 2011). The main disadvantage of gaseous fuels, which prevents greater expansion, is difficult storage, distribution and low energy density - requiring a large built-in volume to accommodate the fuel tank on a vehicle. However, the requirements for exhaust gas purity are constantly tightening, which leads to efforts to increase the use of gaseous fuels in motor vehicles.

3.1.1.2.1 Propane-butane

The mixture of liquefied hydrocarbon gases in automotive is called liquified petroleum gas (LPG), which contains propane-butane. LPG is produced in refineries during crude oil processing, and it is also obtained as a by-product of natural gas or crude oil extraction. Propane and butane are heavier in the gaseous state than air. Both are high calorific gases, which are easily liquefied at relatively low pressure and normal temperature (at 20 °C, propane liquefies at a pressure of 0.85 MPa and butane at 0.23 MPa). The liquefaction of propane and butane reduces the volume by a ratio of 250 : 1 (1 litre of liquid is formed from 250 litres of gas phase). Compared to petrol, LPG has better anti-knock properties, but its calorific value is slightly lower. This causes a reduction in engine power of approximately 10 % (Hromádko 2011).

3.1.1.2.2 Natural Gas

Natural gas provides a significant reduction in pollutants in the exhaust gases of spark-ignition engines. It is assumed to help fight the greenhouse effect and urban air pollution. The use of compressed natural gas (CNG) has been expanding for many years, mostly in urban transportation (buses, taxis). However, diesel engines must be converted to petrol engines to use CNG. More than 90 % of natural gas is methane (CH_4), with ethane (C_2H_6) of 1 to 6 % and non-flammable components such as N_2 and CO_2. These non-flammable components reduce the quality of CNG.

The disadvantage of using CNG in comparison with LPG is the larger installation volume and the larger weight of the fuel tanks. CNG volume decreases in a ratio of 200 : 1 (with a filling pressure of 20 MPa). The amount of energy per unit volume is 4 to 5 times smaller than liquid FHCF (Hromádko 2011). Another possibility is the liquefaction of natural gas (LNG) by subcooling and storage in cryogenic tanks at an overpressure of 0.15 MPa (the gas volume decreases approximately 600 times). When the pressure in the cryogenic tanks increases, the gas must be vented which leads to significant losses by evaporation and it is a considerable disadvantage of LNG. To ensure the required reduction in exhalations, lower-quality mixtures are burned, resulting in a 10 to 15% reduction in the performance of petrol engines.

3.1.2 Biomass-Derived Fuels

Unlike FHCF, biomass-derived fuels are contemporaneous (non-fossil), renewable composite biogenic organic materials formed by natural or anthropogenic (technogenic) processes, belonging to RES. These materials comprise basically (1) natural constituents originated from growing land- and H_2O-based vegetation via photosynthesis or generated via animal and human food digestion and (2) technogenic products derived via processing of the above natural constituents (Vassilev *et al.* 2012). From a biorefinery perspective, biomass refers to a generic term for all organic material that could be potentially converted to fuels and chemicals. Feedstock for the production of biomass-derived fuels can be utilized as a diverse raw material, depending on the availability of biomass, cost-effectiveness, and geographic location (Saravanan *et al.* 2022). In principle, this is a result of photosynthesis in plants, algae, and some bacteria via the conversion of solar energy to carbohydrates and lipids.

In chlorophyll-containing living organisms, CO_2 reacts with H_2O in the presence of sunlight to produce carbohydrates as the building blocks of biomass (Nanda *et al.* 2018)

$$6CO_2 + 6H_2O \xrightarrow{\text{⚡}} C_6H_{12}O_6 + 6O_2 \qquad \textbf{(Equation 1)}$$

Fundamentally, as can be seen from Equation 1, solar irradiation is used for the conversion of CO_2 into glucose ($C_6H_{12}O_6$) and subsequently into biomass (Reijnders & Huijbregts 2009), which is processed further. Biernat *et al.* (2013) published properties in the expected terms of production and use of biofuels:

- sufficiently large quantities are available
- technical and energetic properties of determining their suitability to supply the engines or heating devices are demonstrated
- attractive prices for customers have been established (cheap production)
- lower risk for the environment than the FF, by less emission of toxic compounds and GHGs in the combustion process should be ensured
- acceptable economic indicators of engines or boilers and the safety of their use, and enable the lower operating costs of the equipment to be provided
- energy independence should be increased

Hereafter, the physical and chemical properties of biofuels may be used to provide insight into health and environmental behaviour. As with conventional fuels, highly volatile biofuels or biofuel constituents are expected to partition into the air from H_2O, soil surfaces, or open containers (Roberts & Patterson 2014). For acute human health effects, the potential exposure from inhalation is greater for shorter-chain, highly volatile biofuel constituents than for longer-chain, oily constituents for which skin contact is more likely.

When biofuels are burned, there is no increase in CO_2 in the planet's atmosphere (greenhouse effect), because the newly growing plants reintroduce it into their tissues (see Introduction chapter). The problem, nonetheless, is in their production. Biofuels can be categorized into first (1st GB), second (2nd GB), third (3rd GB) and even fourth-generation (4th GB) class depending on the feedstock used for their production. The difference between 1st GB and 2nd GB lies mainly in biomass as raw materials for their production. The product range for 1st GB is severely limited to ethanol produced from corn and distillers grains while 2nd GB such as bioethanol (cellulosic ethanol) and biobutanol do not pose any threat to the food supply or competition to arable lands (Nanda *et al.* 2018). This is because 2nd GB are derived from nonedible plant biomass. Consequently, 2nd GB production technologies are being developed with a focus on the use of LIBS as feedstock (see Figure 9 for details).

The 3rd GB biofuels are produced from sewage sludge, municipal solid wastes or derived from microalgae via transesterification or hydrotreatment of the algal oil (Lee *et al.* 2019). The last mentioned 4th GB are using genetically modified (GM) algae (Mahapatra *et al.* 2021) as a feedstock, especially. Details of the biofuel's development with an emphasis on 2nd GB fuels are shown in Figure 9 below.

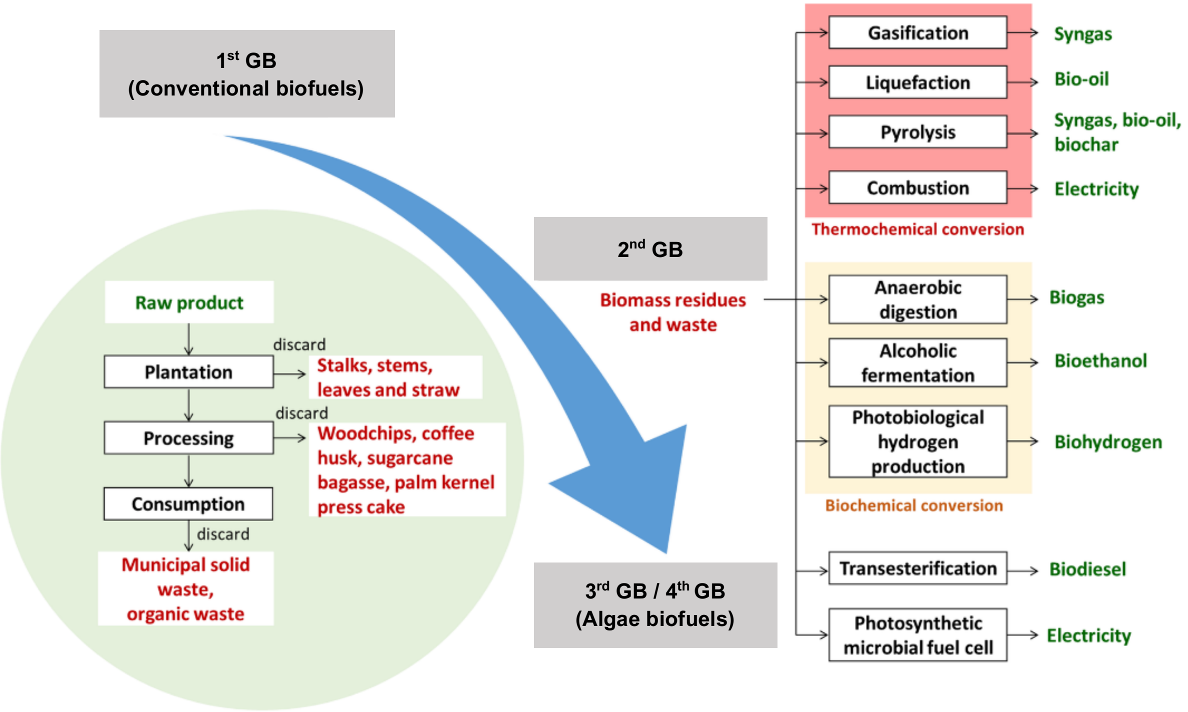

Figure 9 - Development of biofuels with highlights on the second-generation biofuels produced by biomass residues (redrawn from Lee *et al.* 2019).

Anyhow, there are described some disadvantages in the use of LIBS listed in Table 3. For instance low-yielding production, noticeable pressure on forests and natural areas or conversely, the need for arable land, which could otherwise be used for growing food crops and/or urban area development (Menon & Rao 2012). While 2nd GB are made from non-food raw materials (see above) containing LIBS (wood, wood chips, straw, grass, etc.), 1st GB need food biomass for production (sugar cane, beetroot, maize and almost all cereals) and it brings quite a huge problem that has lasted for several years and is still relevant today - rising food prices. The 1st GB used food grains and vegetable oils as feedstock which provided its own set of problems. Apart from raising the prices of the food market, even contributes to global warming as well as net energy losses depicted (Martin 2010).

Table 10 - Comparison of advantages and disadvantages of the various generations of biofuels (redrawn from Mahapatra *et al.* 2021).

Topic	1st GB	2nd GB	3rd GB	4th GB
Feedstock	Crops, edible oil and starch	Non-food crops	Non-food crops	Non-food crops
Land	Arable land	Arable land/forest	Non-arable land	Non-arable land
Benefits	Simple conversion process	No food chain supply, fewer production costs	Cheap raw material (waste food oil, waste/sea water)	Increased lipid content, absorbing CO_2, high energy with a better growth rate

Costs	Economically feasible	Economically less effective (complicated conversion technology)	Oil extraction processes are expensive	Initial investment and pilot setup are expensive
Water	Required portable water	Required portable water	Waste, saline and non-portable water	Waste, saline and non-portable water
Nutrient	Dependent on fertilizers and pesticides	Not dependent on any fertilizer treatment	Depends on C and N sources (nutrients can be recycled, and solar energy can be used).	Depends on C and N sources (nutrients can be recycled, and solar energy can be used).
Fertilizers, Pesticides	Principally used	Not consumed	Not consumed	Not consumed
Environmental risk	The usage of pesticides and fertilizers is a threat to the environment	A major risk is a deforestation	A major risk is a marine eutrophication	GMO release in the environment can be a threat.
Harvesting	By machine or hand picking	By machine or hand picking	Complicated and financially expensive	Complicated and financially expensive

More detailed properties and advantages of selected biofuels published by Nanda *et al.* (2018) are listed in Appendix No. 1. Among the different raw materials, LIBS has fascinated many researchers around the world (Saravanan *et al.* 2022). The additional advantages of using LIBS lay in using CO_2-neutral feedstock with higher availability due to less competition in comparison to food crops as well as higher security of supply due to ease of cultivation and more consistent geographical distribution of sources when compared with FF (Menon & Rao 2012). This comparison of biofuel generations (bioethanol and biodiesel) in CO_2 production is shown in the following Figure 10.

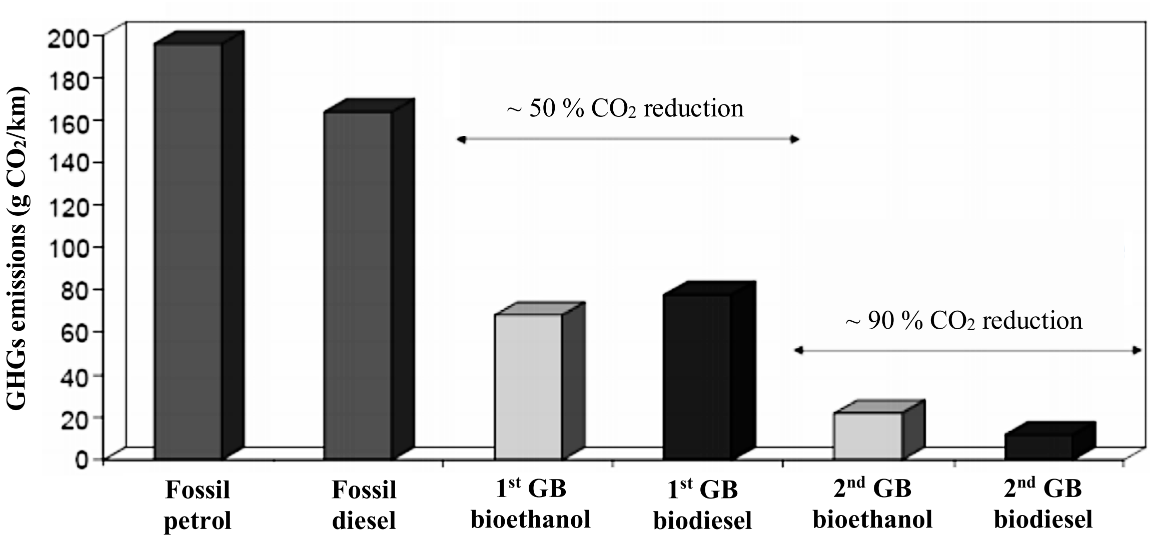

Figure 10 – Emission savings of CO_2 (Hromádko 2011).

As can be seen, the 1st GB bring only modest savings in CO_2 production due to energy intensity (Hromádko 2011). Another reason that is better to focus on production technologies of 2nd GB which bring more than 90 % savings in CO_2 production. The most commonly used biomass-derived fuels according to Hromádko (2011) are:

1st GB:

- Rapeseed methyl ester (RME)
- Bioethanol from sugar
- Bio-ethyl tert-butyl ether (bio-ETBE)
- Vegetable oil (rapeseed in CZ)

2nd GB:

- Lignocellulosic bioethanol
- Methanol
- FTS synthetic diesel
- Di-methyl-ether

As mentioned in Chapter 1.2, the aviation industry's approach to achieving lower net CO_2 production is the use of alternative jet fuels derived precisely from renewable resources (Pires *et al.* 2018). Regarding a simple approach - most waste plant matter is wood or straw-like material, which contains sugars that are hard to access. Many strategies to free these sugars are being investigated (Sanderson 2011), so that these energy-dense molecules can be converted into the fuels of the future. The basic strategies are shown in Figure 11.

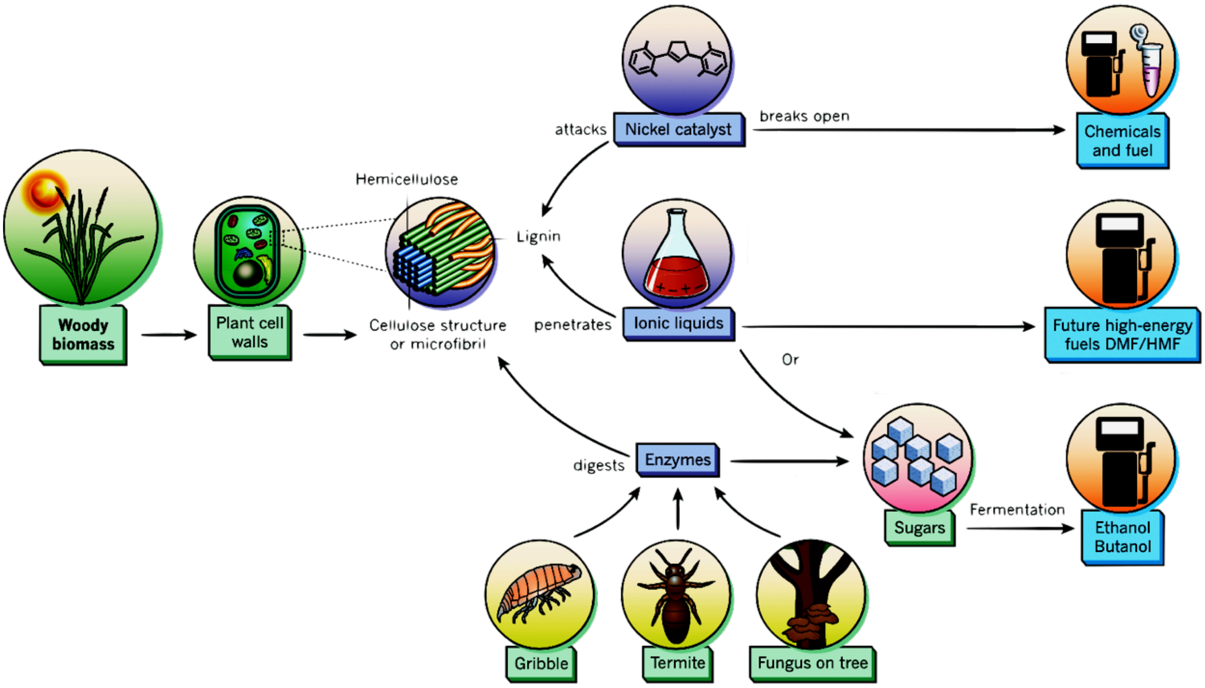

Figure 11 – Woody biomass: from the field to the pump (Sanderson 2011).

Microalgae as 3rd GB can offer a high potential to produce large amounts of lipids suited for biodiesel production. Marine biomasses such as seaweed, hyacinth, caltrop diatoms, duckweed, kelp, and Salvinia have candidacy for the production of biofuels, especially biodiesel (Vassilev *et al.* 2012). Besides, this fast-growing biomass can be applied directly to generate a wide range of biofuels (Lee *et al.* 2019). The genetic modification of 4th GB biomass holds a potential application in oil extraction methodology by inducing autolysis of cells and product secretary systems (Mahapatra *et al.* 2021). The general classification of biomass varieties as solid fuel resources according to origin is mentioned in Appendix No. 2 by Vassilev *et al.* (2012). These solar raw materials are widely available, economically cheaper and inexhaustible (related to the Introduction chapter).

3.1.2.1 Bioethanol

Historically, the production of ethanol (C_2H_5OH) from agricultural products and its use as a motor fuel is nothing new. Also in the early twentieth century, a significant part of train locomotives in Germany was powered by ethanol (Reijnders & Huijbregts 2009). Agrarian reasons as the motivation for bioethanol production were in the period before World War II. Ethanol production has become unprofitable after crude oil and natural gas took dominance of the energy market. Energy interest did not appear until the 1980s when crude oil prices have risen (Hromádko 2011). Bioethanol produced through the fermentation of starchy materials belongs to the category of 1st GB and category 2nd GB when it is made from lignocellulosic substrates using the widely known yeast *Saccharomyces cerevisiae* (Nanda *et al.* 2018).

The reaction describing biodegradation by yeast is explained with Equation 2 (Reijnders & Huijbregts 2009) and starts with a C_6 sugar and ends with ethanol:

$$C_6H_{12}O_6 \xrightarrow{\quad\quad} 2CO_2 + 2C_2H_5OH \qquad \text{(Equation 2)}$$

Ethanol can also be used to produce ethyl ester of t-butanol (ETBE) or ethyl esters of fatty acids, which can be applied in Otto and diesel motors respectively (Reijnders & Huijbregts 2009). Bioethanol barely covers the fuel industry as it is majorly dedicated to the alcohol and beverage industry. When is produced for non-consumable applications, it is made unfit for human intake by adding small amounts of toxic and unpleasant substances such as traces of methanol (CH_3OH) or petrol (Nanda *et al.* 2018). However, in the European Union (EU) only 3 % (v/v) are allowed for petrol blends, mainly because of their toxicity (Dahmen *et al.* 2017). Used as a fuel, bioethanol may reduce the emission of GHGs by 75 % concerning FF (see Figure 10), because it is an oxygenated fuel containing 35 % O_2, which exhibits clean burning characteristics such as reduction in GHGs and particulate matter along with the benefits of low vapour pressure (Nanda *et al.* 2018).

Bioethanol can be directly used, in its pure form, within modified spark-ignition engines or it can be blended with gasoline or diesel fuels. Even though one litre of ethanol contains 66 % of the energy provided by a litre of petrol (Sánchez *et al.* 2020), is used in the blend as a very efficient octane-boosting agent (enhancer), thereby could replace chemical additives such as methyl tertbutyl ether (MTBE) or tetraethyl lead in unleaded petrol. Bioethanol, as a petrol additive, can be used after its denaturation in several possible concentrations. European Standard (NBN EN 228+A1) specifies a maximum ethanol content of 10.0 % (v/v) for conventional petrol engines. On the other hand, it can be used with specially modified engines and potentially replace 32% of petrol consumption (Nanda *et al.* 2015) as a high percentage mixture (85 % bioethanol, 15 % petrol) with the designation E85 blend (Hromádko 2011). Another possible use of bioethanol is also in diesel engines with the designated mixture E95 containing 95 % bioethanol and 5 % additives. The reasons for such a high percentage of the mixture are their compatible physical properties, summarized in Table 4.

Table 4 - Comparison of petrol with bioethanol (Mahapatra *et al.* 2021).

	Petrol	**Bioethanol**
Density [kg/dm^3]	0.76	0.79
Viscosity [mm^2/s]	0.6	1.5
Flashpoint [°C]	Less than 21	Less than 21
Caloric value [MJ/kg at 20° C]	42.7	26.8
Caloric value [MJ/dm^3]	32.35	21.17
Fuel-equivalence	1	0.65

Remarkable is the existence of flexible-fuel vehicles (FFV) that have an internal combustion engine designed for more than one fuel. FFV have an internal combustion engine designed to run on petrol blended with either ethanol or methanol fuel, and both fuels are stored in the same common tank. The most common commercially available FFV in the world market is exactly ethanol FFV (Ryan & Turton 2008). In order to use bioethanol in the automotive industry, it must meet certain purity-like characteristics. The quality control of bioethanol is delineated in existing legislation mentioned in Table 5.

Table 5 - Maximum concentration levels (%, w/w) allowed in the existing standards for bioethanol quality control (Sánchez *et al.* 2020).

	ASTM D5798	**ASTM E3050**	**ASTM E3237**	**EN 15376**	**EN 15293**
Water [%]	< 1	< 10	-	< 0.3	< 0.4
Methanol [%]	< 0.5	-	-	< 1	< 1
Higher alcohols (C_3-C_5) [%]	-	< 2	-	< 2	< 6
Specific requirements	-	Ethanol > 90%; Hydrocarbon contamination < 1 %	-	Ethanol and saturated higher alcohols > 98.7 %	Acidity also tested with corrosion of the Cu strip
Acidity [%]	< 0.005	< 0.004	< 0.007	< 0.007	< 0.005

These five particular legislations are focusing on the specifications of biofuel blends of bioethanol, petrol and denatured or undenatured ethanol.

3.1.2.2 Biobutanol

Another alcohol often used as a fuel is a biobutanol, enlisting itself in the list of potential 2nd GB. Biobutanol was traditionally used as a solvent in various products such as cosmetics, detergents, hydraulic fluids, antibiotics, and drugs, as well as an intermediate in the manufacturing of methacrylate and butyl acrylate (Nanda *et al.* 2018). It is also used as an extractant in the synthesis of many pharmaceutical products. However, the exploitation of butanol as a biofuel is a relatively new application in the fuel market. Butanol, when compared to ethanol, is less volatile and explosive. Its production can be through either petrochemical pathways or fermentative pathways. Several studies prove that blending butanol with diesel and other fuels can also be a promising attribute.

Yilmaz *et al.* (2014) studied the effect of different blends of butanol-biodiesel on the performance and emission of the indirect injection engine. His team found that in comparison with biodiesel, the blended fuel showed lower rates of emission of NO_x with higher GHGs and hydrocarbon emissions. Simultaneously, Jin *et al.* (2011) reported that butanol is a potential fuel as compared with petrol or diesel fuel based on its combustive properties, engine performance, and emissions from the exhaust, respectively. Currently, *n*-butanol and isobutanol are the two isomers likely for use as biofuel. Conversely, *t*-butanol is unlikely to be used as a fuel due to much slower environmental degradation (Roberts & Patterson 2014). In conclusion, the properties of butanol seem to make it a better biofuel than ethanol and biodiesel along with the developmental strategies in butanol production.

3.1.2.3 Biodiesel, oils and their esters

Oils are generally obtained by compression moulding, but for the automotive industry, the production is through the two major techniques used for biomass conversion to bio-oil. They can be broadly categorized as fast pyrolysis and hydrothermal liquefaction. Pyrolysis is the rapid decomposition of organic compounds at high temperatures in an inert atmosphere to produce bio-oil, pyro-gas, and char. Hydrothermal liquefaction, on the other hand, involves the treatment of biomass at high temperatures and pressure in the presence of H_2O and a suitable catalyst (Nanda *et al.* 2018). The solution for conventional diesel engines is found in the treatment of pressed and purified oil by transesterification of fatty acids in vegetable oil or animal fat (Goding *et al.* 2013) to produce the corresponding fatty acid methyl esters (FAME), the process by which large molecules of oil are broken down into smaller ones using alcohol (Jeong *et al.* 2004). The first patent for making FAME was awarded in 1937 and applied in 1938 to power buses in Belgium (Reijnders & Huijbregts 2009).

Transesterification leads to the creation of various FAME depending on the oil used, i.e.:

- Rapeseed methyl ester (RME)
- Sunflower-methyl ester (SME)
- Palm oil-methyl ester (POME)
- Soya-methyl ester (SOME)
- Waste used oil-methyl ester (WUOME)

Transesterification can proceed with the help of an inorganic base catalyst (Reijnders & Huijbregts 2009), such as sodium hydroxide (NaOH), potassium hydroxide (KOH) or sodium methoxide ($NaOCH_3$). This process reduces the viscosity and creates a fuel-air mixture - biodiesel - that corresponds to the diesel fuel. The distribution of carbon ranges will mirror the carbon lengths in the fatty acid feedstock. FAME are described by their carbon length and number of unsaturated bonds (Roberts & Patterson 2014). The typical FAME in biodiesel ranges from C_{14} to C_{22} of ethanol or methanol. This chemical nature makes biodiesel a suitable substitute for conventional diesel fuel (Nanda *et al.* 2018). The comparison of fossil diesel and biodiesel made from FAME is seen in Table 6.

Table 11 - Comparison of fossil diesel with biodiesel (Mahapatra *et al.* 2021).

	Diesel	**Biodiesel (FAME)**
Density [kg/m^3]	840	880
Viscosity [mm^2/s]	5	4
Flashpoint [°C]	80	120
Caloric value [MJ/kg at 20° C]	42.7	37.1
Caloric value [MJ/dm^3]	32.87	32.65
Fuel-equivalence	1	0.97
Cetane number	50	56

The calorific value of oils is somewhat lower, but still comparable to diesel. Unfortunately, other parameters (mainly viscosity and flash point) show that direct use in a conventional diesel engine is not possible (Hromádko 2011). The viscosity can be reduced by heating the oil and adjusting the flow rates of the injectors with a suitable setup. However, a major problem arises from the formation of relatively large droplets of oil and its low evaporation rate. This leads to the formation of carbon and engine seizure, eventually. Both the fuel quality and efficiency are dependent on the FAME content, which is in turn largely dependent on the starting material, or feedstock (Goding *et al.* 2013). Europe is the producer of RME from rapeseed oil (especially the Czech Republic), and in tropical and subtropical zones, POME is the main product. To assess the performance of this biodiesel and blend, fuel performance studies were conducted.

The comparative data regarding specific fuel consumption and exhaust emissions, including levels of carbon monoxide (CO), CO_2, smoke density and NO_X were acquired. The fuel consumption amount of oil operations at high loads was similar to or greater than that observed during regular diesel operations. The use of biodiesel is associated with lower smoke density than would be seen with regular diesel (Jeong *et al.* 2006). However, biodiesel and its mixtures increased the emission of CO, CO_2, and NO_X, to a greater degree than was seen with regular diesel. Moreover, preliminary taken experiments show possible genotoxic potential sometimes even higher for RME emissions than diesel fuel (Topinka *et al.* 2012). Mixed biodiesel, consisting of a mixture of biodiesel and RME, is commonly supplied on the market. The content of RME in the mixture must be at least 30% and all producers guarantee a 90% biodegradability in case of soil contamination within 21 days (Hromádko 2011).

3.1.2.4 Algae

The benefit of using algae as a source of 3rd GB is higher productivity as compared to terrestrial plants (Nanda *et al.* 2018). Some algal species are capable of accumulating large amounts of triacyl glycerides, which form the major precursor for biodiesel production (see Chapter 3.1.2.3). Moreover, there is no requirement for highly fertile agricultural land to cultivate microalgae as a 3rd GB feedstock (see Table 3), thanks to its aquatic nature. Algae produce more oil than most other agricultural biomass used (Nanda *et al.* 2018). Several biofuels that can be derived from algae include methanol (produced from anaerobic digestion of algae), biodiesel (produced by processing of algal oil - see Figure 9), and biohydrogen (photobiologically produced by algae) - more about H_2 in Chapter 3.1.3.

In particular, the optimization of algal biomass production and the triacyl glyceride content needs more research attention (Nanda *et al.* 2018). The GM of microalgal biomass as a 4th GB holds a potential application in oil extraction methodology by inducing autolysis of cells and product secretary systems (Mahapatra *et al.* 2021). Genome editing tools such as zinc-finger nuclease (ZFN), transcription-like effector nucleases (TALEN), and clustered regularly interspaced palindromic sequences (CRISPR/Cas9) are widely used for genetic modification of 4th GB, chiefly stated algae.

3.1.2.5 Biogas

Biogas is obtained by methanogenic fermentation of organic substances. The most common substances are manure, slurry, or waste from municipal wastewater treatment plants (sludge gas). To produce biomethane at a commercial scale, it is essential to develop and utilize the gasification techniques (Nanda *et al.* 2018) of woody biomass (see Chapter 3.2.). Biogas is basically a synthetically derived natural gas (SNG) - biomethane (Biernat *et al.* 2013). As mentioned by Chen *et al.* (2015), biogas contains mainly two molecules: CH_4 and CO_2. Nevertheless, traces of different common gases (H_2S, NH_3, H_2, N_2, O_2, CO) and saturated or halogenated carbohydrates can be present. Also, the gas mixture is saturated with water with the possible presence of solid particles and siloxanes. Biogas composition also varies with the biomass digested as shown in Table 7.

Table 7 - Typical compositions [%] of synthetic natural gas from three different biomasses (redrawn from Chen *et al.* 2015).

Component	Agricultural waste	Landfills	Industrial waste
Methane CH_4	50 - 80	50 - 80	50 - 70
Carbon dioxide CO_2	30 - 50	20 - 50	30 - 50
Hydrogen sulphide H_2S	0.70	0.10	0.80
Hydrogen H_2	0 - 2	0 - 5	0 - 2
Nitrogen N_2	0 - 1	0 - 3	0 - 1
Oxygen O_2	0 - 1	0 - 1	0 - 1
Carbon monoxide CO	0 - 1	0 - 1	0 - 1
Ammonia NH_3	Traces	Traces	Traces
Siloxanes	Traces	Traces	Traces
Water H_2O	Saturation	Saturation	Saturation

Biogas is used in most cases to drive stable motors used to produce electricity with full utilization of waste heat (cogeneration units). The disadvantage is unstable gas production because the anaerobic fermentation processes take place best at a temperature of 40 °C

(Hromádko 2011). There is a shortage of biogas in winter when more electricity and heat are needed, and vice versa. And it is also a must in winter to use the part of the produced gas to heat the fermenter. Alternatively, methane may be converted into liquid fuels using the Fischer–Tropsch reaction (see Chapter 3.2.1) or via a process with ethylene as an intermediary (Reijnders & Huijbregts 2009).

The biogas parameters can be changed by a cleaning system to be identical to natural gas and can thus be used as CNG or LPG (see Chapter 3.1.1.2.2). When biogas is used as fuel for transport vehicles, it is injected into the same engines configured for natural gas. This means that CO_2, H_2S, NH_3, particles, H_2O, and other trace components must be removed to obtain a fuel with a CH_4 content of 95 % (v/v) for high calorific value and engine safety (Chen *et al.* 2015).

3.1.3 Hydrogen

Probably is the fuel of the future if the problems with its production and distribution are eliminated. From a long-term perspective, H_2 appears to be the only possible substitute for FHCF (Singla *et al.* 2021). Production of H_2 from RES feedstocks such as agricultural waste and other waste streams contributed to minimizing the GHGs. This increases flexibility and improves the economics of the production and distribution of H_2 (Nanda *et al.* 2018). The use of a variety of photosynthetic organisms (see Chapter 3.1.2.4) has been proposed that directly or indirectly biocatalyse the splitting of H_2O into H_2 and O_2 (Reijnders & Huijbregts 2009). The H_2 can be produced also via the gasification of biomass (see Chapter 3.2.) by a downstream water gas shift (WGS) reaction of the syngas converting CO with H_2O into additional H_2 (Dahmen *et al.* 2017).

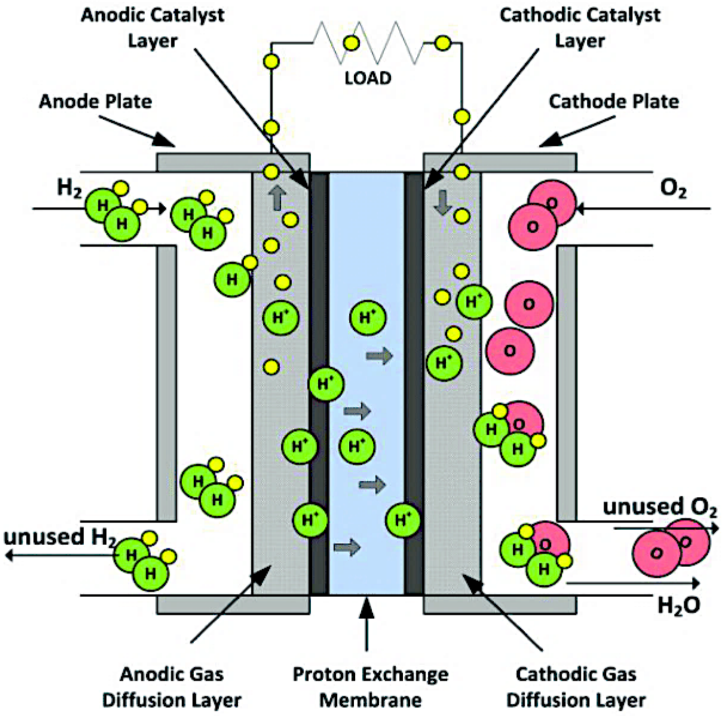

Figure 12 - Proton exchange membrane fuel cell principle (Fărcaş & Dobra 2014).

The H_2 is essentially an accumulator of energy that can be stored or transported over long distances. Yet, the low-efficiency transformation of other types of energy into H_2 (production cost) remains still a problem. The cheapest way to obtain H_2 is to break down hydrocarbons (natural gas, crude oil) in an open thermochemical cycle. More expensive is H_2O decomposition, electrolysis, or possibly direct thermal decomposition. The precondition for the expansion of the use of H_2 as a fuel is a price reduction. A great advantage during the H_2 combustion in reciprocating engines is a significant reduction in fuel consumption at partial engine loads (Hromádko 2011).

Another great advantage is that only NO_X are present in the exhaust gases of the H_2 engine, which can be suppressed by flue gas recirculation. In addition to combustion, hydrogen is widely used as a fuel in fuel cells. The fuel cells are significantly more promising because their efficiency is twice as high as internal combustion engines. In fuel cells, the chemical energy contained in the fuel is directly converted into electrical energy with an efficiency of 60 % depending on the cell type. The process taking place in fuel cells is essentially an inverse process of water electrolysis. A key device in the hydrogen-based energy system is the proton exchange membrane (PEM) fuel cell (Fărcaş & Dobra 2014). PEM fuel cell is practically an electrochemical energy converter, where one oxygen atom and two H^+ protons with a couple of electrons coming through the load, form an H_2O molecule, as shown in Figure 12. During this reaction, an electromotive force is exhibited concerning the load and heat is released into the environment. For vehicle applications, PEM fuel cell has disadvantages - the price of PEM fuel cells and the need for an electricity accumulator. Electricity accumulators increase the cost of the power unit and reduce its efficiency.

3.2 Biofuel Production

Biofuels seem to be a promising substitute for FF and an objective towards the mitigation of climate change as has already been repeated and quoted above. It has been also clarified that biofuels are produced from RES feedstocks and are not subjected to shortages in supply (see Chapter 1). When choosing the type of LIBS to use as feedstock several other factors need to be considered. Some of these are the availability of raw materials, geographical conditions, feedstock cost, effects on soil, water, biodiversity, and others (Mencigar 2020). It can be anticipated that the production costs for biofuels will steadily decrease in the future with technological developments in biomass conversion technologies and feedstock production (Nanda *et al.* 2015). But before any conversion technology finds its place, the first step is to realize what is exactly the chemical composition of LIBS is, and the second step is to get to know what kind of preliminary treatment (PTR) is necessary to utilize.

3.2.1 Composition of Lignocellulosic Biomass

Food crops and LIBS are both forms of plant biomass. Plant biomass is grown through photosynthesis with the conversion of solar energy, CO_2, and H_2O into carbohydrates (see Equation 1). Most carbohydrates are stored in a polymeric form (Qian 2014). Lignocellulose is a complex matrix made up of the plant cell walls (Dahmen *et al.* 2017) which consists CEL, a thick LIG, pectin and HEM structure that wraps around the CEL molecules

(Saravanan *et al.* 2022) and glycosylated proteins on a moisture-free basis (Nanda *et al.* 2014). It is a major component of plants that provides the structure and is usually present in roots, stalks, and leaves. The molecular formulas and percentage representations on a dry matter basis are shown in Table 8.

Table 8 - More detailed structural and mineral composition [%] of lignocellulosic biomass, inspired by Nanda *et al.* (2014) and Dahmen *et al.* (2017).

Substance	Molecular Formula	Composition	
Cellulose	$(C_6H_{10}O_5)_n$	30 - 60	-
Hemicellulose	$(C_5H_8O_4)_n$	15 - 25	-
Lignin	$[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_n$	20 - 40	-
Pectin	$C_6H_{10}O_7$	35	-
Carbon	C	-	50
Hydrogen	H	-	6
Oxygen	O	-	44
Nitrogen	N	-	> 1
Phosphorus	P	-	> 1
Sulphur	S	-	> 1
Chlorine	Cl	-	> 1

LIG is known that acts as an adhesive between cellulosic and lignocellulosic polysaccharides by crosslinking the structures and giving the plant rigidity as well as resistance to rotting. It is comprised of organic polymers and could act as a source of chemicals, particularly aromatic compounds which are currently obtained mostly from FF (Zakzeski *et al.* 2010).

The elemental composition of moisture and ash-free LIBS is in a narrow range, as shown in Table 8. It is practically the same for wood, straw, and other herbaceous types of biomass (Dahmen *et al.* 2017). Minor constituents such as hetero atoms containing molecules with nitrogen from proteins, phosphorus, and sulphur or chlorine are usually below 1 % (w/w). The amount of each constituent varies based on the type of LIBS, whether it is agriculture or forestry residue or obtained from energy crops (Pandey *et al.* 2019).

3.2.2 Preliminary Treatments of Biomass

Most of the PTR energy needs are determined by the ultimate particle size and crystallinity reduction of the LIBS. As Saravanan *et al.* (2022) show clearly in Figure 13, there are several ways for performing biomass PTR - (1) physical, (2) chemical, (3) physicochemical and (4) biological. It is important to mention that PTR methods do not have to be strictly separated, but in most cases, a combination of multiple PTR methods is used. A complex comparative analysis of the pros and cons of different PTR methods for LIBS is described in Appendix No. 3 by Saravanan *et al.* (2022).

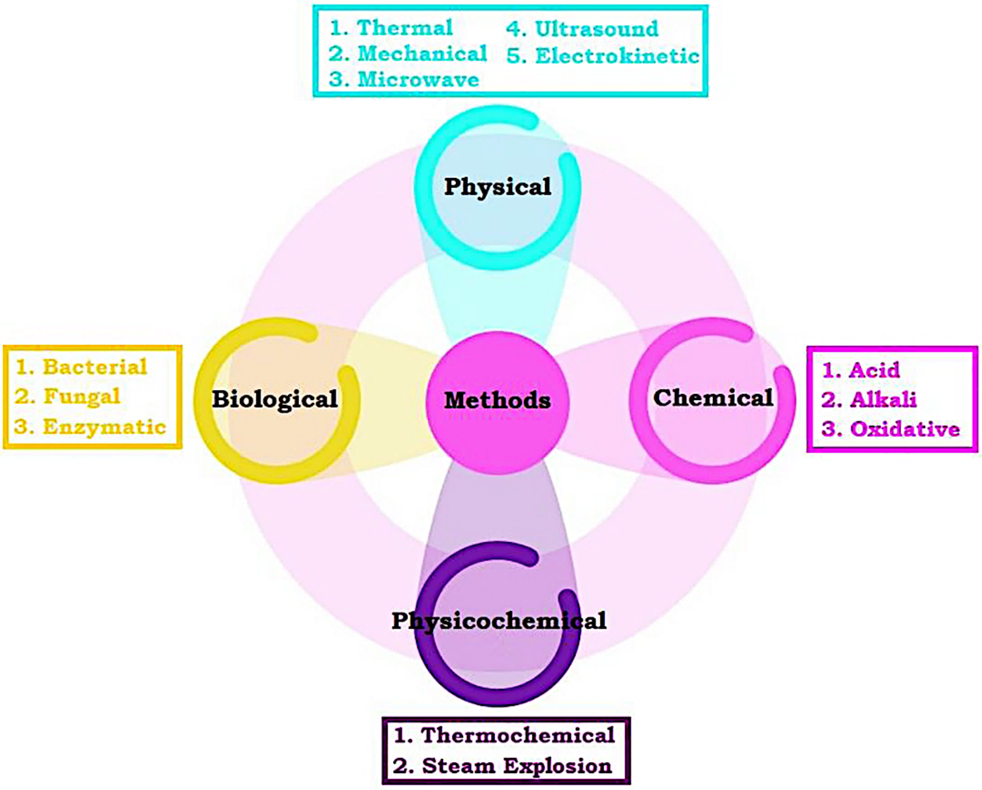

Figure 13 – Different pre-treatment methods forgoing the conversion of lignocellulosic biomass to biofuel (Saravanan *et al.* 2022).

Physical - category of mechanical extrusions including all common physical preparation methods (see Figure 13). For instance, grinding, compression and crushing methods come under this technique. The microstructure of LIBS must be decreased using the mechanical splintered technique to increase the contact surface for further chemical (acid) or biological (enzyme) PTR (Saravanan *et al.* 2022). However, thermal PTR is one of the most effective physical techniques, where the complex compounds are broken down into sugars, which in turn enhanced the following biological PTR (fermentation process). It could develop the methanogenic and acidogenic digestibility process of LIBS.

Chemical - This PTR has mostly been used to increase cellulose (CEL) biodegradability by removing lignin (LIG) and hemicellulose (HEM), as well as to reduce the degree of polymerization and CEL crystallinity to a limited extent. As the name suggests and s shown in Figure 13, acids and bases play a strong role in this PTR method.

Physicochemical - Various techniques including steam explosion, torrefaction, and ammonium fibre explosion. In this PTR method in the presence or absence of a chemical, LIG and HEM are eliminated and CEL is degraded, by altering the working pressure and temperature conditions (Saravanan *et al.* 2022).

Biological - approach uses microorganisms such as bacteria and fungi (see Figure 13) to modify the LIBS, making it more susceptible to enzymatic digestion. Generally speaking, enzymes help to release the fermentable sugars from HEM and CEL and reduce the recalcitrance of LIBS to enhance biogas generation. During enzymatic PTR, pure enzymes are used to accelerate the degradation of LIBS.

3.2.3 Biomass-Energy Conversions

The production of biofuel depends on the feedstock provided, leading to biomass-energy conversion technologies. In Europe, LIBS feedstock is particularly well suited since wood has historically been the most popular choice for energy production and is still finding uses elsewhere today (Mencigar 2020). These technological processes are highly variable and depend on various factors. According to Mahapatra *et al.* (2021), there are two main categories of biomass conversion: (1) thermochemical processes (pyrolysis, gasification, carbonisation, combustion, liquefaction, or supercritical fluid extraction) and (2) biochemical processes (fermentation, anaerobic digestion).

Thermochemical processes involve heating or burning biomass under supervised temperature and oxygen conditions. The lowest energy-dense product is raw LIBS, which is combusted for heat or electricity production. Higher energy densities are achieved by upgrading the low-energy-dense gaseous or liquid fuels. The production of high-energy dense fuels with a composition similar to liquid FF is the most effective way to displace the use of FF in the transportation sector. The thermochemical conversion of biomass to synthetic fuel is referred to as a biomass-to-liquid (BtL) method. This method is considered one of the most promising to produce biofuels, from which high-quality FTS fuels are synthesized (Swain *et al.* 2011).

Biofuel made by BtL is superior in comparison to liquid FF in the sense that it has severely lower CO_2 emissions, low NOx emissions, no particulate matter and an adjustable quality (Ibarra-Gonzalez & Rong 2019). BtL technologies allow using of almost every type of dry biomass, organic residue, or waste. Principally, the technologies are similar to the already established coal-to-liquid (CtL) or gas-to-liquid (GtL) processes (Dahmen *et al.* 2017) also proceeding via syngas by gasification of coal and reforming of natural gas, respectively. From the mentioned techniques, pyrolysis and gasification have already been extensively researched and are commercially viable. Pyrolysis during BtL converts biomass into bio-oil, biochar, and non-condensable gases. The limited uses and difficulty in downstream processing of bio-oil have limited the application of the pyrolysis technology itself. Pyrolysis may also sometimes be considered as a PTR only (see Chapter 3.2.1 above and Figure 13), because generated bio-oil can be used as feedstock for further gasification.

The following Equation 3 (Dai *et al.* 2015) illustrates a typical net pyrolysis reaction and major pyrolysis products:

$$\underset{\textbf{(SAWDUST)}}{CH_{1.46}O_{0.67}} \xrightarrow{🔥} \underset{\textbf{(BIO-OIL)}}{0.71\ CH_{1.98}O_{0.76}} + \underset{\textbf{(CHAR)}}{0{,}21\ CH_{0.1}O_{0.15}} + \underset{\textbf{(GAS)}}{0{,}08\ CH_{0.44}O_{1.23}} \qquad \textbf{(Equation 3)}$$

Equation 3 demonstrates that pyrolysis is used as a BtL conversion method only and not as a PTR method. For the preparation, only mechanical PTR of the physical category for the input biomass was ensured, as seen in Figure 13. As for gasification, it started to become a promising technology for biomass utilization with a positive environmental impact in the 1970s. Because of the energy crisis at that time, considerable research and development work on gasification took a huge place (Dai *et al.* 2015). Gasification is becoming a more modern and sophisticated technology and it has still renewed interest, because of climate change and other environmental concerns, as well as increased fuel prices, limited supply, and security issues. Gasification is intended to break down hydrocarbons into low-molecular-weight gases (primarily CO, H_2, CO_2, H_2O, and CH_4) by first thermally depolymerizing the biomass, followed by reforming and partial combustion reactions (Dai *et al.* 2015). In comparison with the biochemical process below, the thermochemical conversion uses much higher temperatures, faster processing time and higher conversion rates at lower operation costs (Mencigar 2020). As feedstock, the thermochemical is well suited for both wet and dry LIBS and requires no chemical PTR, but solely the reduction in size (physical PTR) and drying if necessary.

Biochemical processes involve converting biomass with the use of enzymes and microorganisms. Essentially, the carbohydrates from HEM and CEL are at first exposed to the chemical PTR (see Figure 13) in separate stages in order to extract the LIG and sugars. Afterwards, the sugars are fermented with the use of yeast, fungi or bacteria and the products are further chemically treated to synthesise BtL products, which are mostly composed of different alcohols. Additionally, gasification of carbonaceous feedstocks including LIBS leads to the formation of synthesis gas or syngas composed of biohydrogen (see Chapter 3.1.2.4) which could be in the next step processed as an intermediate for FTS (Dahmen *et al.* 2017). And at the end, FTS converts this hydrogen syngas to new renewable hydrocarbons (Gruber *et al.* 2021).

3.2.4 Fischer-Tropsch Synthesis

The first experiments on the catalytic hydrogenation of CO were carried out at the beginning of the 20th century. The abundant reserves of natural gas (see Figure 2) in many parts of the world have made it attractive to commission new plants based on FTS technology (Khodakov *et al.* 2007). In 1902, Sabatier and Senderens described the production of synthetic oil from CO and H_2 (Gruber *et al.* 2021). They synthesized CH_4 from a mixture of CO or CO_2 with H_2. The reaction was performed on cobalt (Co) or nickel (Ni) catalysts at temperatures of 180 - 200 °C and under atmospheric pressure. Using different catalysts, in 1920 they produced a mixture containing predominantly hydrocarbons called *Kogasin* (kohle-gas-benzin). In 1922, after the end of World War I, chemists Hans Fischer and Franz Tropsch managed to obtain a liquid product from CO and H_2 called *Synthol* (Blažek *et al.* 2006). It was a mixture of alcohols, ketones, aldehydes, and acids made under high pressure (>10 MPa) over alkalized iron (Fe) chips at 400 °C. This product was further transformed, after heating under pressure, into *Synthine* - a mixture of hydrocarbons.

Important progress in the development of FTS was made in 1923. It was found that heavier hydrocarbons could be produced when the *Synthol* process was conducted at lower pressure (0.7 MPa). Heavy hydrocarbons were the main products of CO hydrogenation on Fe/ZnO or Co/Cr_2O_3 contacts. In 1926, Hans Fischer and Franz Tropsch published their first reports about hydrocarbon synthesis (Khodakov *et al.* 2007). The first unit for the production of liquid fuels by indirect CtL was built in 1933 in Germany. In 1939 Germany had already nine factories using this technology. Indirect CtL is performed by the creation of synthesis gas first, containing mainly CO and H_2 and subsequently a mixture of liquid fuels is produced from it (Blažek *et al.* 2006).

The production of alkanes, alkenes and alcohols by the FTS in Equation 4 is simply described by Blažek *et al.* (2006) and Gruber *et al.* (2021):

$$\begin{aligned}
(2n+1)H_2 + nCO &\longrightarrow C_nH_{2n+2} + nH_2O \\
2nH_2 + nCO &\longrightarrow C_nH_{2n} + nH_2O \\
2nH_2 + nCO &\longrightarrow C_nH_{2n+1}OH + (n-1)H_2O
\end{aligned} \qquad \textbf{(Equation 4)}$$

It is quite well predicted that the share of RES in the power generation sector grows worldwide (see Figure 7). Thus, the need to store the excess electricity produced by fluctuating RES is going to grow alike. And here FTS comes in a modern sense. Today modern concepts can use FTS for example in wind-diesel technology (Gruber *et al.* 2021), in a combination of recyclability and sustainability (see Chapters 1.3 and 1.4). This wind-diesel technology is explained in Figure 14.

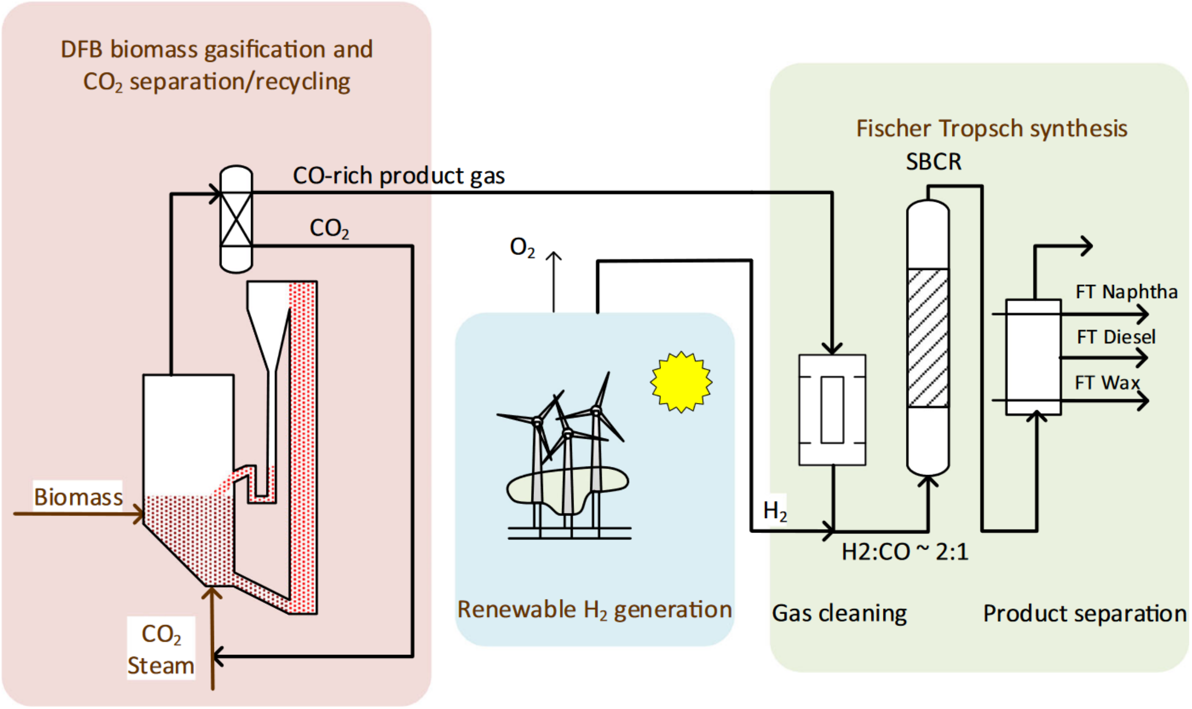

Figure 14 – Basic concept of wind-diesel technology (Gruber *et al.* 2021).

The wind-diesel technology enables the integrative use of excess electricity combined with biomass-based fuel production. Surplus electricity can be converted to H_2 via electrolysis in the first step. The fluctuating H_2 source is combined with biomass-derived CO-rich syngas from the gasification of LIBS feedstock. In Figure 14, gasification is performed in dual fluidized bed (DFB) and created CO-rich product gas is then piped to the 20-litre slurry bubble column reactor (SBCR). Typical FTS takes place in the SBCR, where H_2 and CO are converted to hydrocarbons with chain lengths ranging from C_1 to $> C_{60}$.

Usually, FTS produces hydrocarbons ranging from CH_4 to hydrocarbons with more than 60 carbon atoms. In such a carbon range, the formed hydrocarbons made by FTS are in all states of matter - gaseous, liquid and even solid. Based on the chain length, the FTS products can be divided into a few groups, as seen in Table 9 (Oakey 2016).

Table 9 - Carbon chain groups products of Fischer-Tropsch synthesis (Oakey 2016).

Group	*n*-alkanes contained
SNG	C_1 - C_2
LPG	C_3 - C_4
Light petroleum	C_5 - C_7
Heavy petroleum	C_8 - C_{10}
Middle distillate	C_{11} - C_{20}
Kerosene	C_{11} - C_{12}
Diesel	C_{13} - C_{20}
Wax	$> C_{22}$

According to Bell *et al.* (2011), the information above and values from Table 9, FTS produces a synthetic crude-like oil, and the unique properties of this oil require special considerations during refining to produce petroleum products. The products of an integrated FTS biorefinery designed to produce renewable transportation fuel could be premium diesel and kerosene (Gruber *et al.* 2021). As mentioned above, the first catalysts were based on Co, the newer ones are based on Fe. Fe-based catalysts operate at higher temperatures than Co catalysts but provide more branched hydrocarbons and oxygen compounds. The choice of the right catalyst for the FTS to proceed is entirely essential.

3.2.4.1 Catalysts

The catalytic performance of FTS strongly depends on the methods of catalyst preparation. As already said, the discovery of hydrocarbon synthesis by Fischer and Tropsch published in 1926 was related to Fe and Co as catalysts (Schulz 1999). Both Co and Fe catalysts have been used in the industry for hydrocarbon synthesis. They have been applied in the first FTS plant of Ruhrchemie in 1935. Gorimbo *et al.* (2018) reported that when N_2 is co-fed to a fixed bed FTS reactor loaded with a Co catalyst, the selectivity to C_{5+} (particular C_5 - C_{19}) fraction is enhanced. Preparation of Co catalysts involves several important steps: (1) choice of appropriate catalyst support, (2) choice of method of deposition of the active phase, (3) catalyst promotion, and (4) oxidative and reductive treatments (Mencigar 2020).

Co catalysts are usually more expensive, but they are more resistant to deactivation. Fe catalysts usually produce more olefins. However, Co and Fe are not the only elements that can be used in FTS. Metals of group VIII have noticeable activity in the hydrogenation of CO to hydrocarbons. Ruthenium (Ru) followed by nickel (Ni) are the most second active metals for the hydrogenation of CO. The most active is Ru, working at the lowest reaction temperature of only 150 °C and very high molecular weight products (MW up to 106 g/mol) have been isolated. It produces the highest molecular weight hydrocarbons, where mechanistic conclusions should be the easiest – much easier than with Fe as the catalyst (Schulz 1999), in particular. The molecular average weight of hydrocarbons produced by FTS decreased in the following sequence: **Ru > Fe > Co > Rh > Ni > Ir > Pt > Pd**. Thus, only Ru, Fe, Co, and Ni have catalytic characteristics which allow considering them for commercial production. Ni catalysts under practical conditions produce too much CH_4 and Ru is too expensive (Mencigar 2020). On top of that, worldwide reserves of Ru are insufficient for large-scale industries.

3.2.4.2 Temperature Dependency

Currently, there are widely used two FTS operating modes in the industry (Dry 2002), divided by temperature dependency - (1) high-temperature FTS (HT-FTS) and (2) low-temperature FTS (LT-FTS), as shown in Figure 15. Most of the FTS technologies developed in the last two decades are based on the LT-FTS process (Khodakov *et al.* 2007).

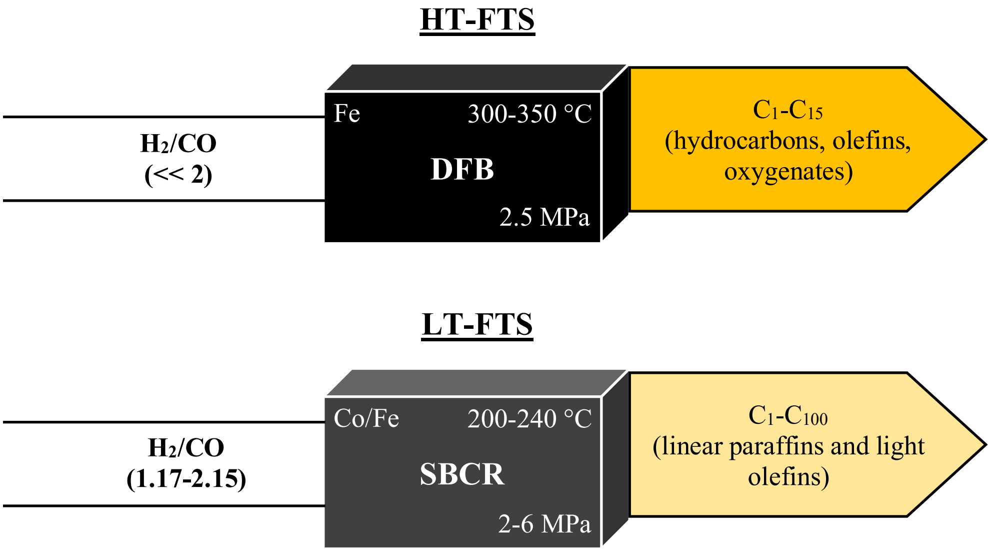

Figure 15 - Characterization of individual Fischer-Tropsch synthesis based on high/low temperature (inspired from Khodakov *et al.* 2007).

In the HT-FTS process syngas reacts in a dual fluidized bed (DFB) in the presence of a Fe-based catalyst to yield hydrocarbons in the C_1-C_{15} hydrocarbon range. This process is primarily used to produce liquid fuels, although many valuable chemicals (R-olefins) can be extracted from crude synthetic oil. Conditions of HT-FTS are mentioned in Figure 15 and Table 10. HT-FTS shift the reaction selectivity to lower carbon number products (especially CH_4), more hydrogenated products, more branched products and more by-products such as oxygenates (ketones, alcohols, aldehydes, carboxylic acid) and aromatic compounds (Oakey 2016). Oxygenates in the aqueous stream are separated and purified to produce alcohols, acetic acid, and ketones including acetone, methyl ethyl ketone, and methyl isobutyl ketone.

On the other hand, the LT-FTS process is running in SBCR mainly for the synthesis of linear long-chain hydrocarbon waxes and kinds of paraffin (see Figure 15). In LT-FTS both Fe and Co catalysts can be used. These LT-FTS processes have involved syngas with a high H_2/CO ratio, which is generated by vapour forming, auto thermal reforming, or partial oxidation using natural gas as a feedstock (Khodakov *et al.* 2007). Conditions of LT-FTS are also mentioned in Figure 15 and Table 10. Moreover, high-quality sulphur-free diesel fuels are produced in this process. Therefore, LT-FTS results in much higher carbon chain products. It seems that

LT-FTS is better in terms of fuel production since fewer upgrading units need to be used for conversion to liquid fuel.

Table 10 - Conditions for high/low temperature Fischer-Tropsch synthesis (Oakey 2016).

Parameter	HT-FTS	LT-FTS
Products	Petrol, light olefins	Waxes and diesel fuels
Temperature range [°C]	300 - 350	200 - 240
Pressure [MPa]	2.5	2 - 6

The obtained long carbon chains can be hydrocracked to produce high-quality petrol and diesel in desired fractions (Oakey 2016), depending on the market needs. That could be the reason, why most FTS technologies are based on it.

3.3 Biofuel Analysis

The chemical analysis serves to characterize and determine the current state of the produced fuels. At the end of the production process, biofuels may contain inorganic pollutants as well as organic compounds whose presence may negatively affect their quality in different ways. Both quantification and qualification are dealt with in the analysis of biofuels.

The main method that meets the prescribed standard and has been the most widely used method for the analysis due to its generally higher accuracy in quantifying minor components is gas chromatography (GC). Also, a combination of GC with another expanding method is possible. Sánchez *et al.* (2020) used in their study a GC instrument with a flame-ionization detector (GC/FID) for the determination of major compounds, whereas a gas chromatography with mass spectrometry (GC/MS) instrument was selected for identifying minor and trace organic components. Quantification using GC/FID determined major organic compounds according to the C range. The content of individual fractions depends logically on their boiling point (see Table 1). Additional identification using GC/MS showed containing one of these functional groups in the samples: alcohols, aldehydes, ketones, esters, ethers, hydrocarbons, aromatic hydrocarbons, aromatic hydrocarbons, nitrogen compounds, organic acids, and furane derivates.

The product analysis through three different detectors of online GC was performed by Gorimbo *et al.* (2018). His lab used FID and two thermal conductivity detectors (TCDs). TCD-A was used to analyse CH_4, CO_2, N_2 and CO with ultra-high purity (UHP) helium (He) as a carrier gas, while TCD-B was used to analyse H_2 with UHP argon (Ar) as a carrier gas. Styarini *et al.* (2013) quantified eight organic compounds in only one sample of lignocellulosic bioethanol utilizing GC/FID. In a different study, Habe *et al.* (2013) applied GC/FID and GC/MS for the analysis of 13 bioethanol samples belonging to 1st GB (mainly originating from sugarcane) and only detected 16 pollutants. Besides, these authors analysed also four bioethanol specimens belonging to 2nd GB with 29 detected compounds other than ethanol. The objective of their work was thus to develop a method based on GC for a wide identification and quantification of volatile organic compounds (VOCs) in bioethanol and biobutanol samples.

Further, several analytical methods have been used to characterize the chemical components of biodiesel. The United States (ASTM 7398–11, D 6751) and EU (EN 14214) have set standards based on GC/FID (Goding *et al.* 2013) for the separation of FAMEs in biodiesel based on boiling point (see Table 1). GC/FID and GC/MS have been used to demonstrate that the relative concentration of FAMEs in biodiesel varies between feedstocks, in addition. The FAME content of biodiesel fuels has traditionally been determined using GC with a polar stationary phase. Quantitative metrics describing the resolution of important FAME pairs indicate high resolution on all polar columns, yet the best resolution, particularly of geometric isomers, is achieved on the cyanopropyl column (Goding *et al.* 2013). The extent of retention on polar columns is dependent on both polarity and solubility in the phase. Short-chain, nonpolar solutes are less soluble in the phase and elute quickly, while in the longer-chain, polar solutes interact with the phase longer and are more retained.

The ultimate analysis of hydrocarbon fuel is expressed in Equation 5 by Dai *et al.* (2015) in terms of the principal elements (C, H, O, N, S) after setting aside the H_2O (moisture) and the inorganic constituents (ash):

$$\mathrm{C + H + O + N + S + ash + moisture = 100\ \%\ (w/w)} \qquad \textbf{(Equation 5)}$$

Speaking of FTS (see Chapter 3.2.4), the manufactured products originating from FTS could be expressed with the Anderson-Schulz-Flory (ASF) distribution (Jenčík *et al.* 2021), as shown in Figure 16, from which deviations can be described and summarized (Bell *et al.* 2011). Yield versus carbon number was estimated using ASF.

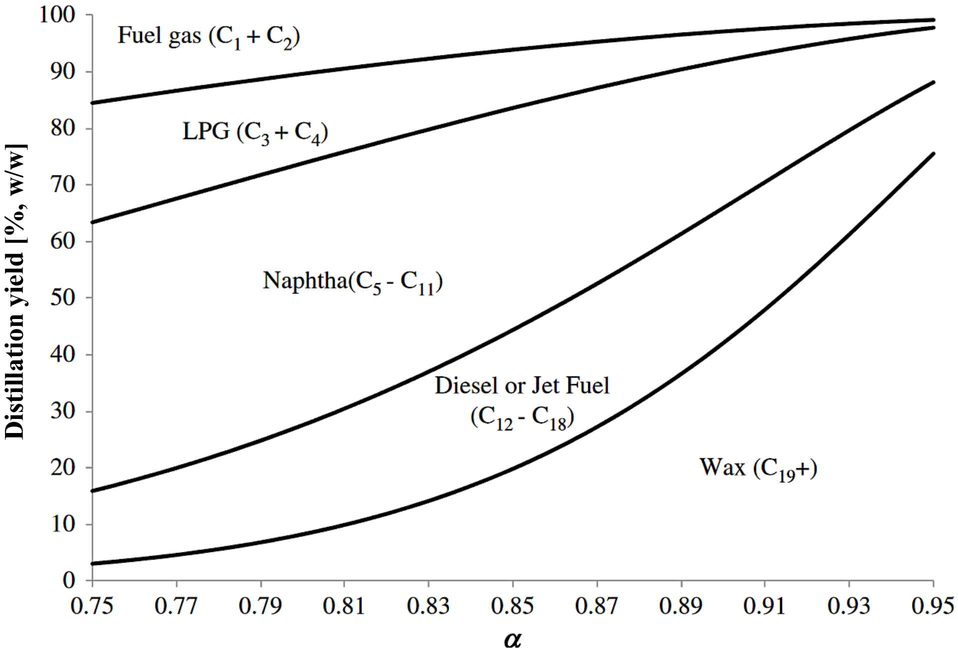

Figure 12 - Product distillation yield for a Fischer-Tropsch synthesis as a function of chain growth parameter (Bell *et al.* 2011).

Carbon numbers were used to estimate distillation boiling ranges. GC for the ASF can experimentally determine the mass fraction (W_n) of hydrocarbons with n carbon atoms (Gruber *et al.* 2021). Subsequently, the **chain growth parameter (α)** can be determined from the straight-line proportion of the ASF plot using the following Equation 6:

$$\log\left(\frac{W_n}{n}\right) = n \times \log(\alpha) + \log\frac{(1-\alpha)^2}{\alpha} \quad \textbf{(Equation 6)}$$

Variations on the ASF distribution equations are used to improve the fit to experimental measurements of molecular weight distributions (Bell *et al.* 2011). There have been used also other analysis methods to analyze biofuels or blended fuels, such as infrared spectroscopy, liquid chromatography with spectroscopic and evaporative light-scattering detection (Sie 1993), as well as supercritical fluid chromatography (Leckel 2005), and two-dimensional gas chromatography (GC×GC) with FID and time of flight mass spectrometry. However, according to published research, GC is the best choice for the analysis of biofuels, regardless of the fuel type.

4 Materials and Methods

As a part of the diploma thesis, products made from waste lignocellulosic materials based on Fischer-Tropsch synthesis (FTS) were analysed in cooperation with the research organization ORLEN UniCRE a.s., Litvínov workplace. Individual samples of hydrocarbon fractions were analysed using gas chromatography with a flame ionization detector (GC/FID). Based on the comparison of retention times with hydrocarbon standards, *n*-alkanes were identified as the majority components in the samples. A database of fractions obtained under various experimental conditions during their subsequent modification was created and the possibilities of their use were discussed in Chapter 6.3.

4.1 Technological Process

The process of producing biofuels from solid biomass was broken down into eight distinct steps adapted from the work of Technology (2021), shown in Figure 17.

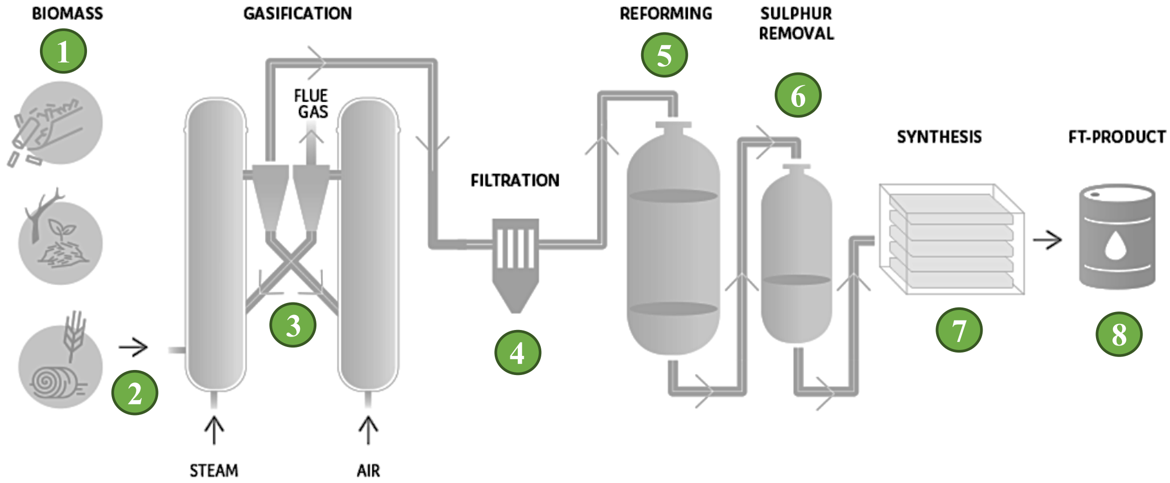

Figure 17 - The diagram representing the exact Fisher-Tropsch synthesis used to produce biofuels in the case of this thesis (Technology 2021).

These steps included: (1) selecting the feedstock, (2) pre-treatment, (3) gasification, (4) purifying the resulting gas into a useful synthesis gas, (5) carrying out steam reformation, (6) removing any sulphur present, (7) creating raw biofuel through FTS and (8) upgrading the resulting product to make it suitable for use as a transportation fuel.

4.1.1 Lignocellulosic Source

Table 11 - Estimated lignocellulose source (Frilund *et al.* 2020).

Source	H_2S [ppmv]	COS [ppmv]	other organic S-species [ppmv]
Woody biomass	20 - 250	0.1 - 5	< 1
Herbaceous biomass	100 - 500	1 - 20	< 10

The LIBS originated solely from waste materials as the utilization of agricultural residues and demolition wood according to Frilund *et al.* (2020), indicating in Table 11. This source exhibited higher concentrations of impurities, such as H_2S and carbonyl sulphide (COS). Due to this reason, the filtration (Figure 17, step No. 4). and sulphur removal (Figure 17, step No. 6) processes were impended.

4.1.2 Biomass Pre-treatment

This step has been reproduced from Technology (2021) and involved reducing the size of the material to particles smaller than 3 millimetres through shredding, followed by the removal of up to 15 % of the initial weight in water content through drying.

4.1.3 Biomass Gasification

The pre-treated LIBS was converted to gas by a novel DFB gasifier (Frilund *et al.* 2020). The reactor was partitioned into two distinct zones: (A) the steam gasification zone (where LIBS was fed directly) and (B) the air combustion zone. The material circulates continuously between these zones, simultaneously supplying heat for the gasification process, using designed temperature operation conditions of 700 - 820 °C under the pressure of 0.1 - 0.3 MPa.

4.1.4 Gas Filtration

The gas flow from the DFB was further cleaned from carried ash, tar and chlorine at small quantities of around 0.01 % (w/w) of dry mass in the HCl form (Frilund *et al.* 2020). High-temperature gas filtration of these impurities was developed by COMSYN project (Technology 2021) at 800 °C, using metallic filters (Sinter Metal Filters, GKN). Removing HCl was achieved with a metallic filter composed of a zinc-based adsorbent, according to Frilund *et al.* (2020):

$$\mathrm{ZnO} + 2\mathrm{HCl} \longrightarrow \mathrm{ZnCl_2} + \mathrm{H_2O} \qquad \textbf{(Equation 7)}$$

4.1.5 Steam Reformation

The gas flow still contained leftovers of a wide range of light and polyaromatic hydrocarbons (tar residues). These hydrocarbons were converted to H_2 and CO by using a catalytic steam reforming reactor (SRR) according to Technology (2021). To mitigate the potential formation of coke by inlet air, which could obstruct the reactor, an oxygen-permeable membrane was installed in the reformer to isolate oxygen from the air. Operational conditions were held around 900 °C.

4.1.6 Sulphur Removal

In COMSYN project (Technology 2021), the elimination of sulphur in the form of H_2S to a level of 1 ppm was accomplished by two parallel catalyst reactors with a fixed or moving bed, operating at 350 - 400 °C, in which ZnO served as sorbent:

$$\mathrm{ZnO} + \mathrm{H_2S} \longrightarrow \mathrm{ZnS} + \mathrm{H_2O} \qquad \textbf{(Equation 8)}$$

4.1.7 Fuel Synthesis

The fuel synthesis was achieved with highly efficient two-stage FTS fixed micro-channel reactors in INERATEC's in-house plant like a skid-based-unit operation (Pfeifer *et al.* 2022). Reactors were based on LT-FTS cobalt molybdenum oxide catalyst on an alumina carrier (Topsoe TK-250, Haldore) and held around 200 °C under 2 MPa pressure, using part of the off-gases from gasification (Chapter 4.1.3). During LT-FTS, gas molecules originating from syngas were converted to longer-chain as described in Equation 4. The LT-FTS products and the by-product H_2O were collected after each reactor.

4.1.8 Product Upgrade

LT-FTS products were in the last step transported to ORLEN UniCRE a.s. oil refinery for further upgrading as a part of biofuel processing, using hydrocracking, hydro isomerisation and steam cracking (Technology 2021). The final LT-FTS fuels were produced by separation (Hájek *et al.* 2021) within a temperature range of 35 - 360 °C in the atmospheric/vacuum distillation column.

4.2 Description of Analyzed Samples

Once the products underwent their final distillation, they were categorized and supplemented with three commercial samples (Natural 95, Diesel and Diesel B7) as references, shown in Table 12. Diesel samples were 50x diluted in hexane before use.

Table 12 – An overview of the analysed Fischer-Tropsch synthesis fractions including references.

Sample Name	Distillation Range	Fraction Category
Light Naphtha	35 - 85 °C	petrol
Benzene Fraction	85 - 110 °C	petrol
Heavy Naphtha	80 - 180 °C	petrol
Paraffinic Diesel	180 - 360 °C	diesel
Middle Distillate	up to 360 °C	diesel
Natural 95	-	reference (petrol)
100% Diesel (no FAME)	-	reference (diesel)
Diesel B7	-	reference (diesel)

4.3 Laboratory Chemicals and Analytical Standards

Table 13 - The list of used chemicals and standards.

Chemical	Distributor	Catalogue No.
Benzene p.a.	Merck	32212-1L
C_7 - C_{30} Saturated alkanes	Merck	49451-U
Ethanol p.a.	Lach-Ner s.r.o.	20025-A96-M1000-1

Isooctane p.a	Merck	32291-1L-M
n-Hexane (hypergrade)	Merck	1.04369
n-Hexane p.a.	Lach-Ner s.r.o.	20031-AT0-M1000-1
Pentane neat (standard for GC)	Czech Metrological Institute	CRM 10-2-01

4.4 Analysis of Samples

4.4.1 Gas Chromatography

The composition of samples was analysed by a gas chromatograph (Nexis GC-2030, Shimadzu) using a flame ionization detector (FID). The GC was equipped with a low polarity phase fused-silica capillary column with dimensions of 30 m x 0.25 mm i.d., film thickness 0.20 µm (SH-Rxi-5ms, Shimadzu), 5 % crossbond diphenyl/95 % dimethyl polysiloxane. The oven temperature and operating conditions were optimized for petrol/diesel fraction separately, see following Table 14. High-purity nitrogen 4.8 was used as a carrier gas at a nominal flow rate. Each sample was injected using an autosampler (AOC-20i Plus, Shimadzu) equipped with a 10 µl syringe (Hamilton Company) as follows: 0.2 µL of petrol sample and 1 µL of diesel sample with a split ratio of 1: 50.

Table 14 - Gas chromatography conditions and column characteristics for each fraction.

Parameter	Petrol Fractions	Diesel Fractions
Temperature T_1 [time]	40 °C [2 min]	60 °C [2 min]
Temperature T_2 [time]	230 °C [5 min]	280 °C [10 min]
Ramp rate	8 °C/min	
Injector temperature	250 °C	300 °C
Split	1 : 50	
Detector temperature	280 °C	300 °C
GC gas (N_2) flow rate	1.53 mL/min	1.47 mL/min
GC gas (N_2) pressure	103.0 kPa	108.2 kPa
GC Model	SHIMADZU Nexis GC-2030	
FID gas (H_2) flow rate [air]	32 mL/min [200 mL/min]	
Column type	SH-Rxi-5ms	
Stationary phase	Crossbond 5% diphenyl/ 95 % dimethyl polysiloxane	

The inlet and transfer line temperatures were held at 250 °C and 280 °C for petrol samples, and 300 °C for diesel samples, respectively. Hydrocarbon's length distribution was determined using the retention time compared to the standards. Retention times and peak areas were calculated in Shimadzu Lab Solutions, and the percentage representation was calculated in Microsoft Excel 365. The peak area of each sample was summed and the percentage that each hydrocarbon contributed to the total area was calculated as a peak area percentage.

4.4.2 Physical Measurements of Paraffinic Diesel

The Department of Chemistry at the Czech University of Life Sciences conducted additional physical measurements and calculations, such as density, kinematic viscosity, flash point, aniline point and cetane number of the Paraffinic Diesel based on the methods precisely explained by Hönig (2013).

In the beginning, diesel density was converted using Equation 9 to American Petroleum Institute (API) gravity:

$$\mathrm{API}_{\mathrm{gravity}} = \frac{141.36}{\mathrm{density} + 0.0030} - 131.5 \qquad \textbf{(Equation 9)}$$

In the next step, the value of the aniline point was expressed in degrees Fahrenheit:

$$\mathrm{A}\,[°\mathrm{F}] = 1.8 \times \mathrm{A}\,[°\mathrm{C}] + 32 \qquad \textbf{(Equation 10)}$$

Using the output of $\mathrm{API}_{\mathrm{gravity}}$ and A [°F] from above, the diesel index was calculated:

$$\mathrm{D}_{\mathrm{index}} = \frac{\mathrm{API}_{\mathrm{gravity}} \times \mathrm{A}\,[°\mathrm{F}]}{100} \qquad \textbf{(Equation 11)}$$

The final calculation of the cetane number was carried out by Equation 12:

$$\mathrm{C}_{\mathrm{number}} = 12.9 + \frac{2 \times \mathrm{D}_{\mathrm{index}}}{3} \qquad \textbf{(Equation 12)}$$

5 Results

5.1 Sample Collection

All obtained petrol and diesel samples were taken from different steps of the same distillation process and sorted from the lightest fraction to the heaviest one (see Table 12 for details). Described set of fractions was analysed by gas chromatography utilizing the optimum temperature programs.

5.2 Analysis

A commercial mixture of *n*-alkanes (C_7 - C_{30} in hexane with additional C_5 neat) was used to optimize the temperature programs for GC analyses (individually for petrol and diesel fractions, see Table 14). The extent of retention on a low polar column is dependent on both polarity and solubility in the phase. Short-chain, nonpolar solutes are less soluble in the phase and elute quickly, while longer-chain, polar solutes interact with the phase longer and are more retained.

5.2.1 Petrol Fractions

The petrol fractions (Light Naphtha, Benzene Fraction, Heavy Naphtha, and commercial sample Natural 95) were analysed by GC/FID at a temperature program from 40 to 230 °C. The individual components of samples were identified according to the retention times of standards (*n*-alkanes, benzene, isooctane), and the quantification was performed according to peak areas (the peak area of each component was related to the sum of all peak areas). The percentage amounts of *n*-alkanes in analysed samples are presented in following Table 15.

Table 15 - The amount [%] of *n*-alkanes in the petrol fractions after gas chromatography with a flame ionization detector analysis.

RT [min]	*n*-alkane	Light Naphtha	Benzene Fraction	Heavy Naphtha	Natural 95
1.907	C_5	32.768	0.081	-	2.676
2.404	C_6	16.934	7.702	0.280	1.036
3.492	C_7	-	62.454	12.393	1.485
5.266	C_8	-	2.413	16.377	1.074
7.403	C_9	-	0.043	18.914	0.403
9.500	C_{10}	-	-	18.810	0.024
11.633	C_{11}	-	-	6.281	0.019
13.577	C_{12}	-	-	0.078	0.050
15.397	C_{13}	-	-	0.018	0.098
17.094	C_{14}	-	-	0.147	0.021
18.634	C_{15}	-	-	0.074	0.025
Total		**49.7**	**72.7**	**73.4**	**6.9**

5.2.1.1 Light Naphtha Fraction

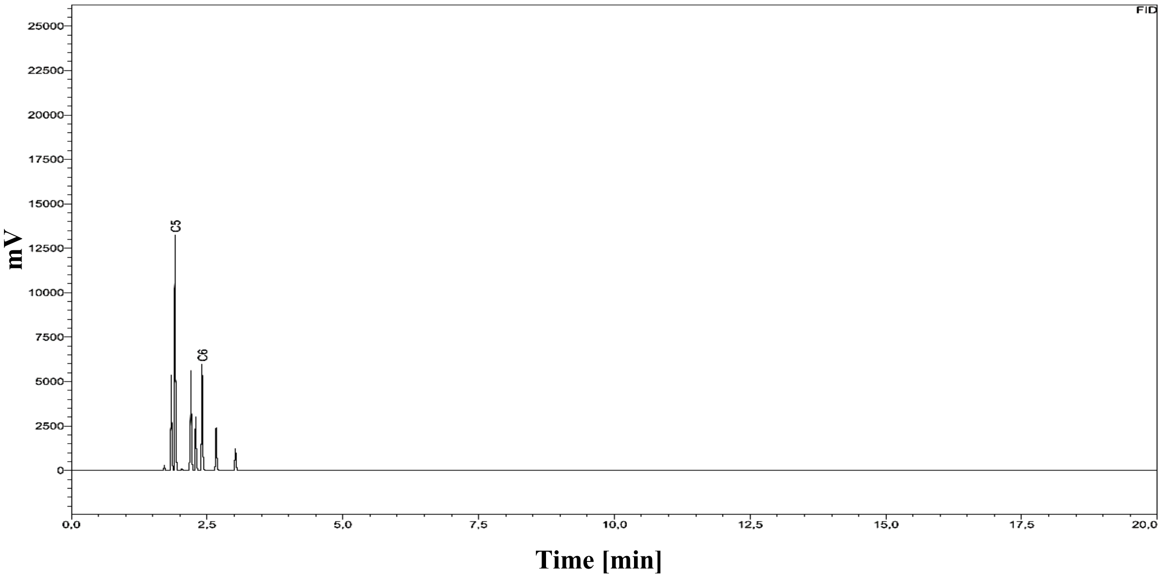

Figure 18 - The chromatogram of the Light Naphtha fraction.

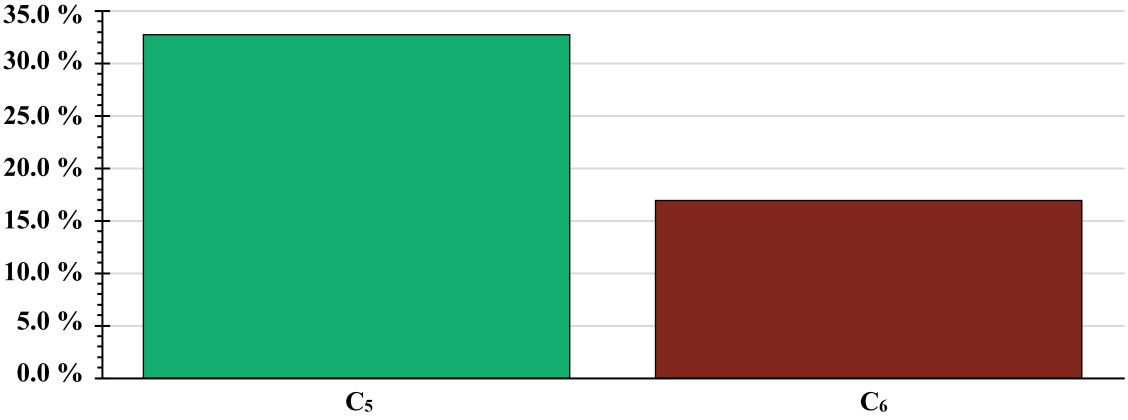

Figure 19 - *n*-Alkane content [%] in the Light Naphtha fraction.

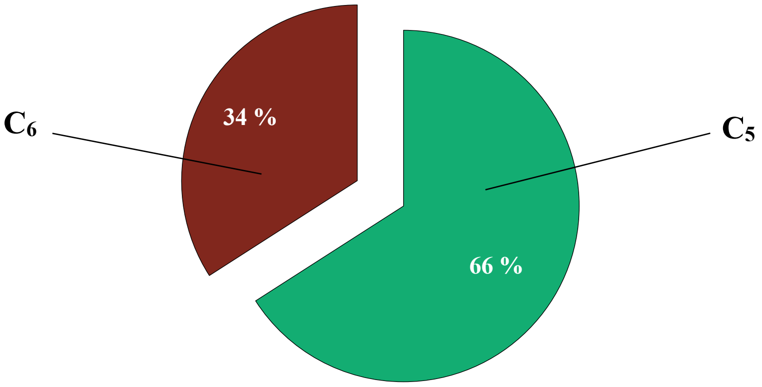

Figure 20 - Relative abundance [%] of *n*-alkanes in the Light Naphtha fraction.

5.2.1.2 Benzene Fraction

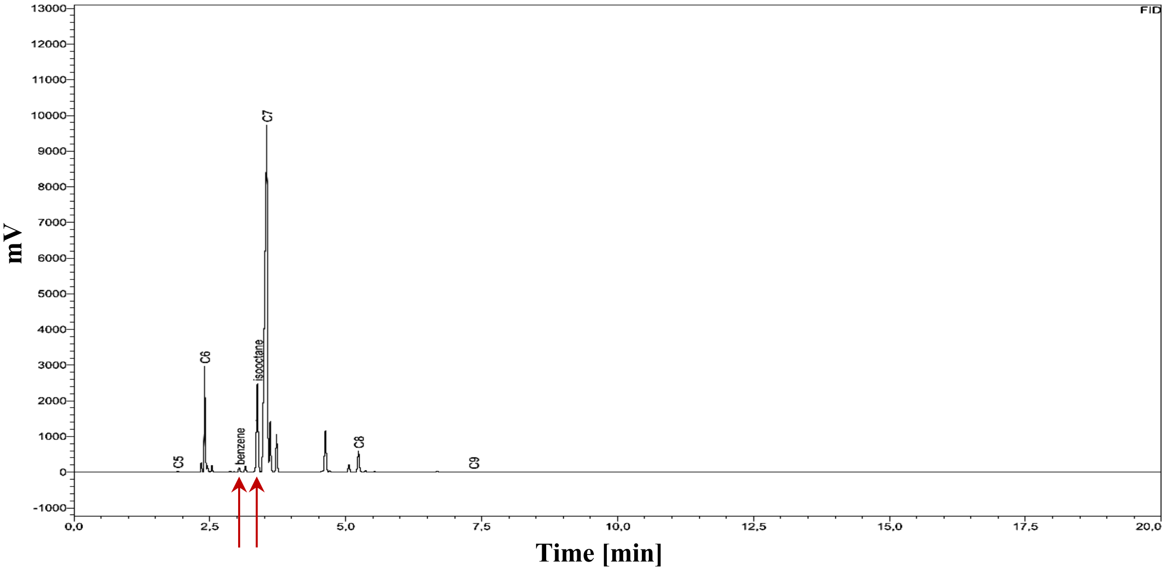

Figure 21 - The chromatogram of the Benzene Fraction with the benzene and isooctane indication.

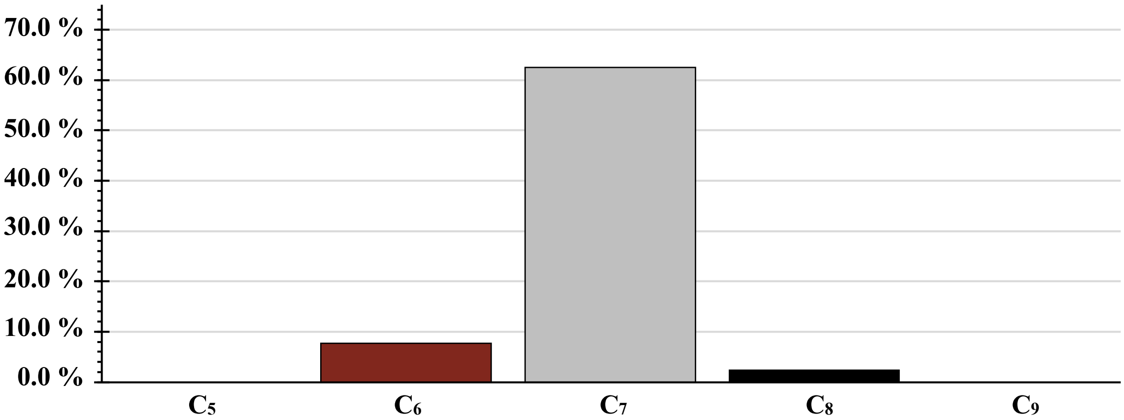

Figure 22 - *n*-Alkane content [%] in the Benzene Fraction.

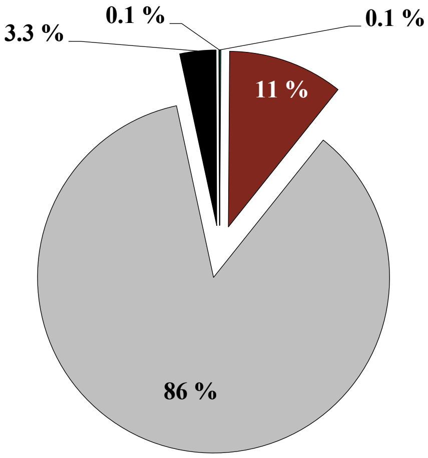

Figure 23 - Relative abundance [%] of *n*-alkanes in the Benzene Fraction.

5.2.1.3 Heavy Naphtha Fraction

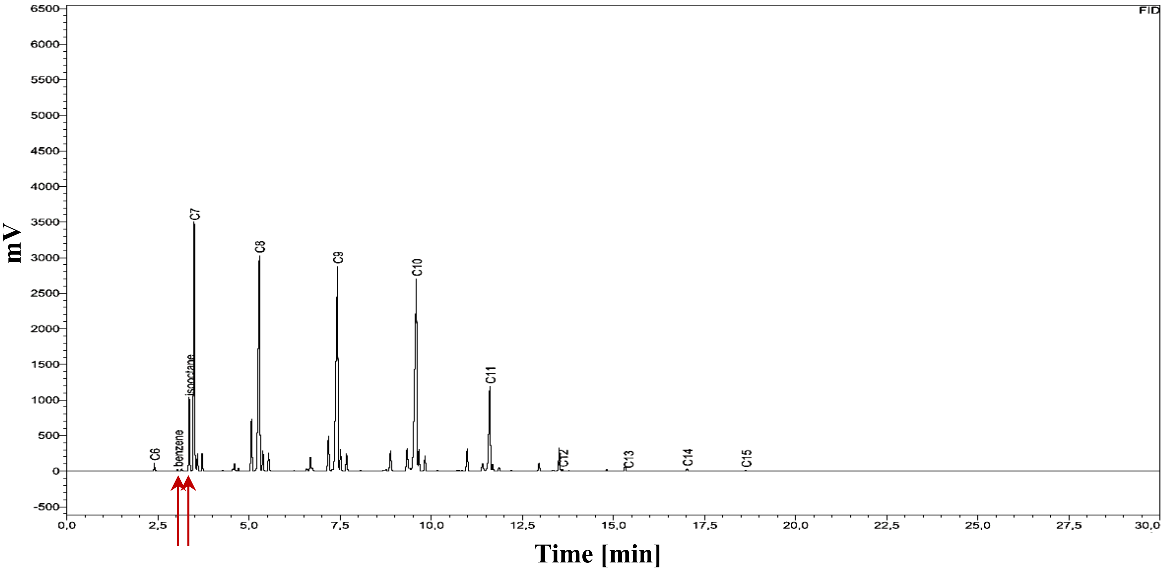

Figure 24 - The chromatogram of the Heavy Naphtha fraction.

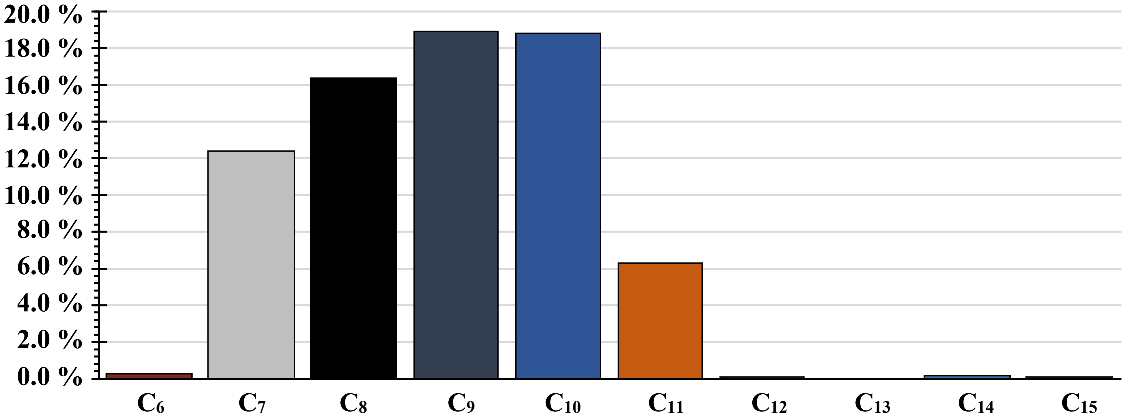

Figure 25 - *n*-Alkane content [%] in the Heavy Naphtha fraction.

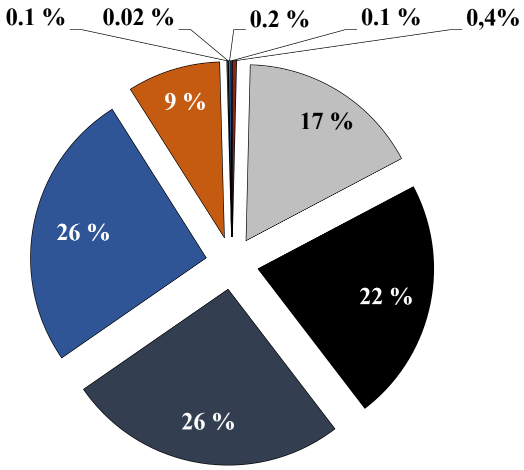

Figure 26 - Relative abundance [%] of *n*-alkanes in the Heavy Naphtha fraction.

5.2.1.4 Natural 95

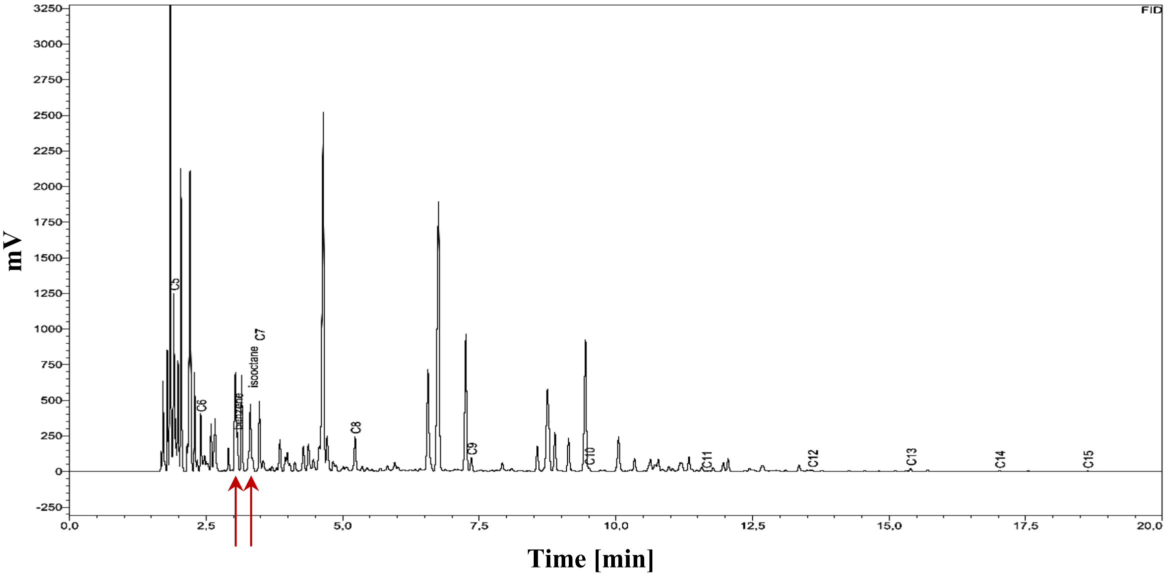

Figure 27 - The chromatogram of the Natural 95 (petrol reference).

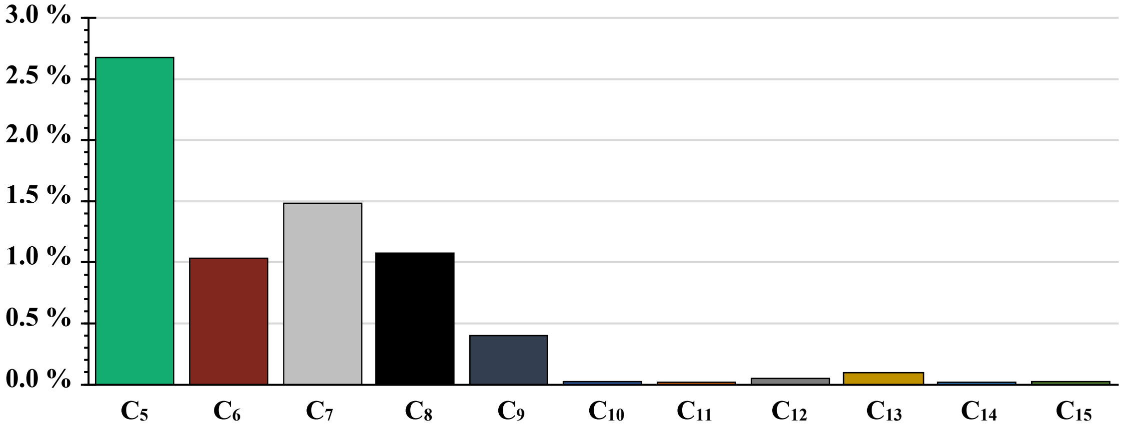

Figure 28 - *n*-Alkane content [%] in the Natural 95 (petrol reference).

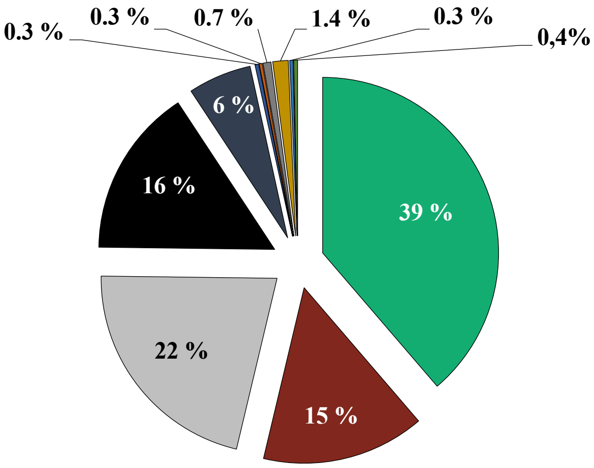

Figure 29 - Relative abundance [%] of *n*-alkanes in the Natural 95 (petrol reference).

As can be seen, a chromatogram was recorded for each petrol fraction, followed by a bar graph indicating the *n*-alkane content [%] corresponding to the chromatogram and finally a pie chart representing the relative abundance [%] of the *n*-alkanes for each other. Isooctane as an important component of petrol (used as an antiknock agent) was further identified in almost all petrol fractions. Representing peaks of isooctane correspond to 3.353 min. Meanwhile, the retention times of 3.053 min correspond to benzene. Both chemical compounds are highlighted on chromatograms (Figures 21, 24 and 27) using red arrows. It is very important to mention that the concentration of benzene is up 1 % so it is within the standard NBN EN 228+A1. All charts are further compared to the standard (Natural 95) and further elaborated in the Discussion (see Chapter 6.3.1).

5.2.2 Diesel Fractions

The diesel fractions (Paraffinic Diesel, Middle Distillate, and the commercial samples 100% Diesel/no FAME and Diesel B7) were analysed by GC/FID at a temperature program from 60 to 280 °C. The individual components of samples were identified according to the retention times of standards (*n*-alkanes), and the quantification was performed according to peak areas (the peak area of each component was related to the sum of all peak areas). The percentage amounts of *n*-alkanes in analysed diesel fraction samples are presented in Table 16.

Table 16 - The amount [%] of *n*-alkanes in the diesel fractions after gas chromatography with a flame ionization detector analysis.

RT [min]	*n*-alkane	Paraffinic Diesel	Middle Distillate	100% Diesel (no FAME)	Diesel B7
2.570	C_7	-	-	-	0.132
3.615	C_8	-	0.075	0.086	0.137
5.212	C_9	-	0.270	0.307	0.454
7.125	C_{10}	0.151	0.760	1.114	1.159
9.099	C_{11}	0.792	1.733	2.386	1.733
11.010	C_{12}	1.514	3.123	2.174	1.736
12.821	C_{13}	1.844	4.804	2.239	2.467
14.527	C_{14}	1.978	6.572	2.072	2.107
16.138	C_{15}	2.167	8.642	2.429	2.587
17.662	C_{16}	2.123	9.961	1.909	2.092
19.107	C_{17}	2.145	10.818	1.636	1.904
20.479	C_{18}	2.412	11.276	1.562	1.772
21.788	C_{19}	2.272	11.301	1.198	1.495
23.039	C_{20}	1.558	8.731	1.130	1.485
24.236	C_{21}	1.531	1.738	1.021	2.038
25.382	C_{22}	1.694	-	0.603	0.918
26.481	C_{23}	1.405	-	0.318	0.521
27.539	C_{24}	0.921	-	0.148	0.272
28.554	C_{25}	0.407	-	0.095	0.120
29.533	C_{26}	0.074	-	-	-
Total		**25.0**	**79.8**	**22.4**	**25.1**

Representative chromatograms were recorded for each diesel fraction, displayed in Figures 30, 33, 36 and 39. The following bar graphs indicate the *n*-alkane content [%] corresponding to the chromatograms and finally pie charts represent the relative abundance [%] of the *n*-alkanes for each other. The reference sample (Diesel B7) has a noticeable presence of methyl oleate with a corresponding retention time of 24.295 min, as highlighted on the chromatogram (Figure 39) using a red arrow. Additional physical measurements (from Chapter 4.4.2) of Paraffinic Diesel (Figures 30, 31 and 32) are provided in Table 17 supplied with NBN EN 15940+A1+AC requirements. Further elaboration is in the Discussion (see Chapter 6.3.2).

5.2.2.1 Paraffinic Diesel

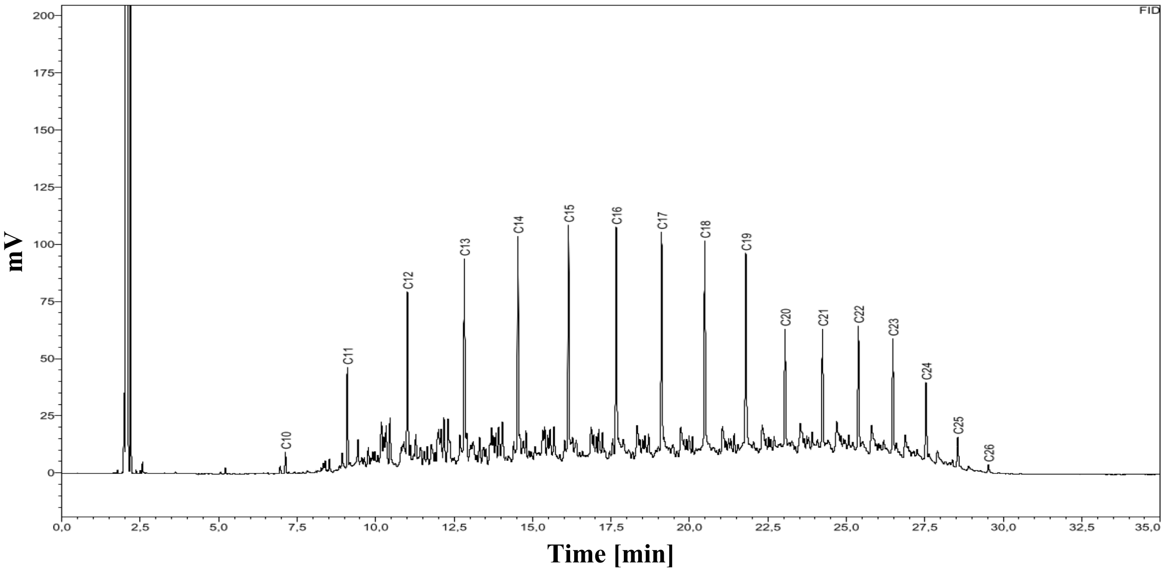

Figure 30 - The chromatogram of the Paraffinic Diesel fraction.

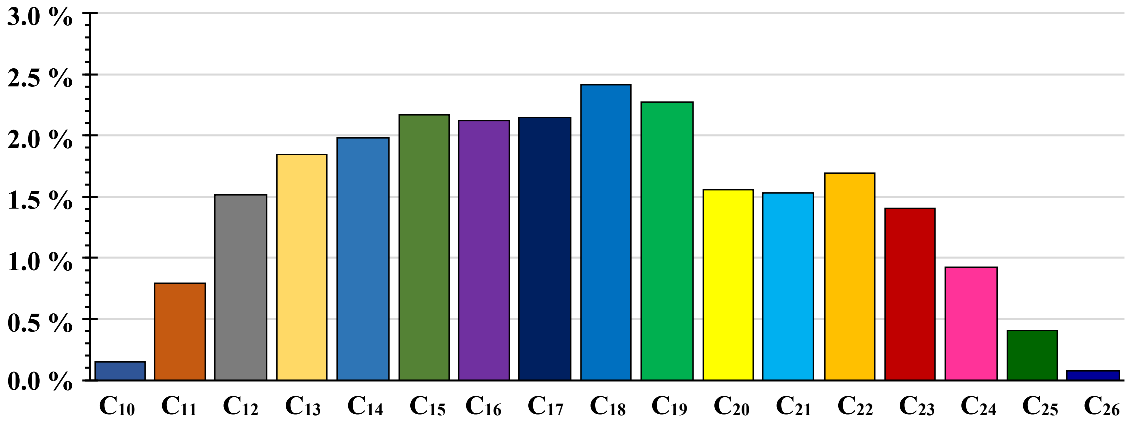

Figure 31 - *n*-Alkane content [%] in Paraffinic Diesel fraction.

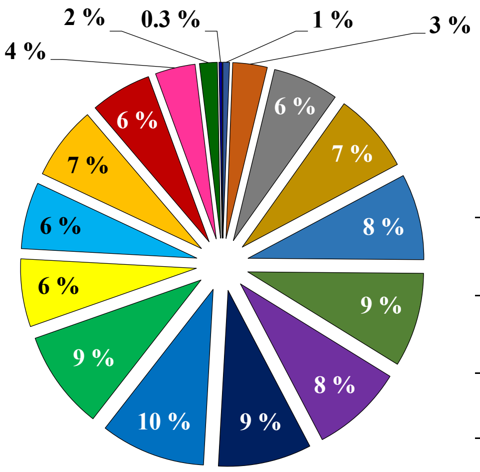

Figure 32 - Relative abundance [%] of *n*-alkanes in Paraffinic Diesel fraction.

Table 17 - Physical measurements of Paraffinic Diesel related to legal context.

Parameter	**Result**	**NBN EN 15940 (+A1+AC)**	
		Min	**Max**
Density at 22 °C [kg/m^3]	805	780	810
Kinematic viscosity at 40 °C [mm^2/s]	3.55	2	4.5
Flash point [°C]	77	> 55	-
Aniline point [°C]	93	-	-
Cetane number	71	-	-

5.2.2.1 Middle Distillate Fraction

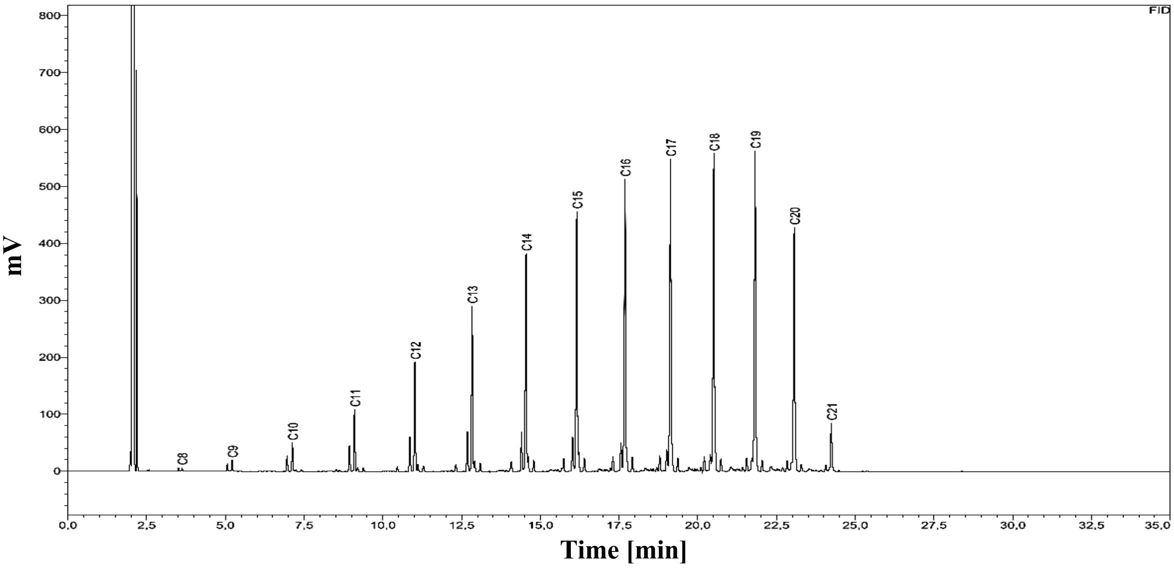

Figure 33 - The chromatogram of the Middle Distillate fraction.

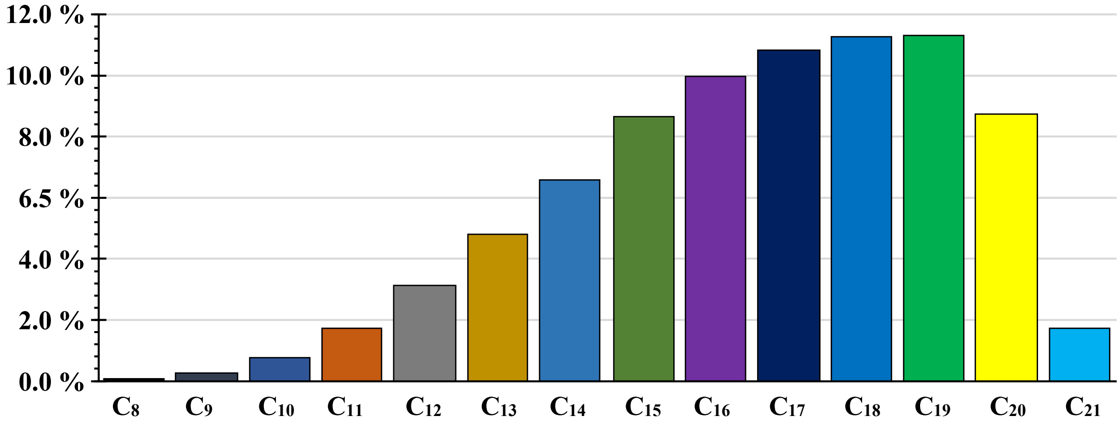

Figure 34 - *n*-Alkane content [%] in the Middle Distillate fraction.

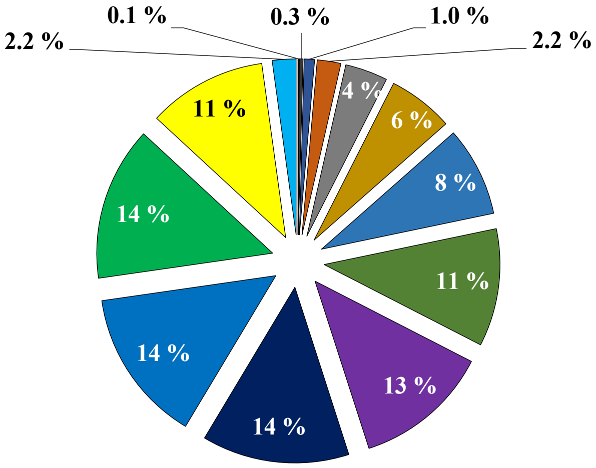

Figure 35 - Relative abundance [%] of *n*-alkanes in the Middle Distillate fraction.

5.2.2.2 100% Diesel (no FAME)

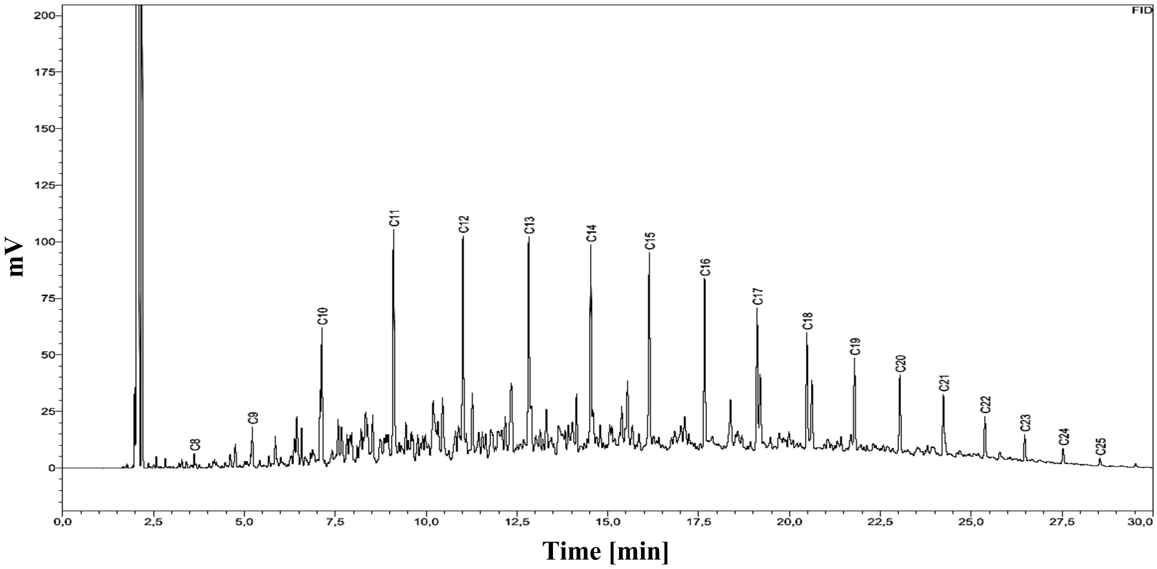

Figure 36 - The chromatogram of the 100% Diesel/no FAME (diesel reference).

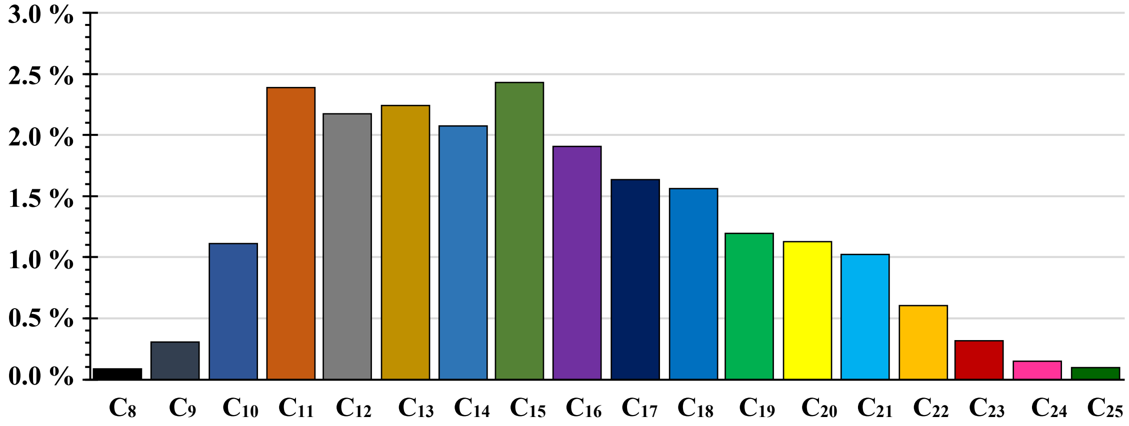

Figure 37 - *n*-Alkane content [%] in the 100% Diesel/no FAME (diesel reference).

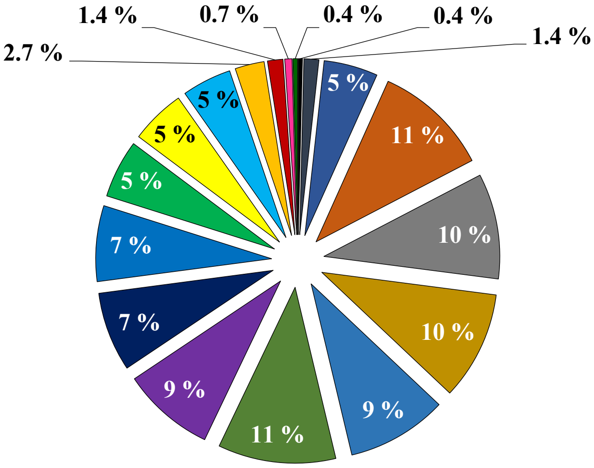

Figure 38 - Relative abundance [%] of *n*-alkanes in the 100% Diesel/no FAME (diesel reference).

5.2.2.3 Diesel B7

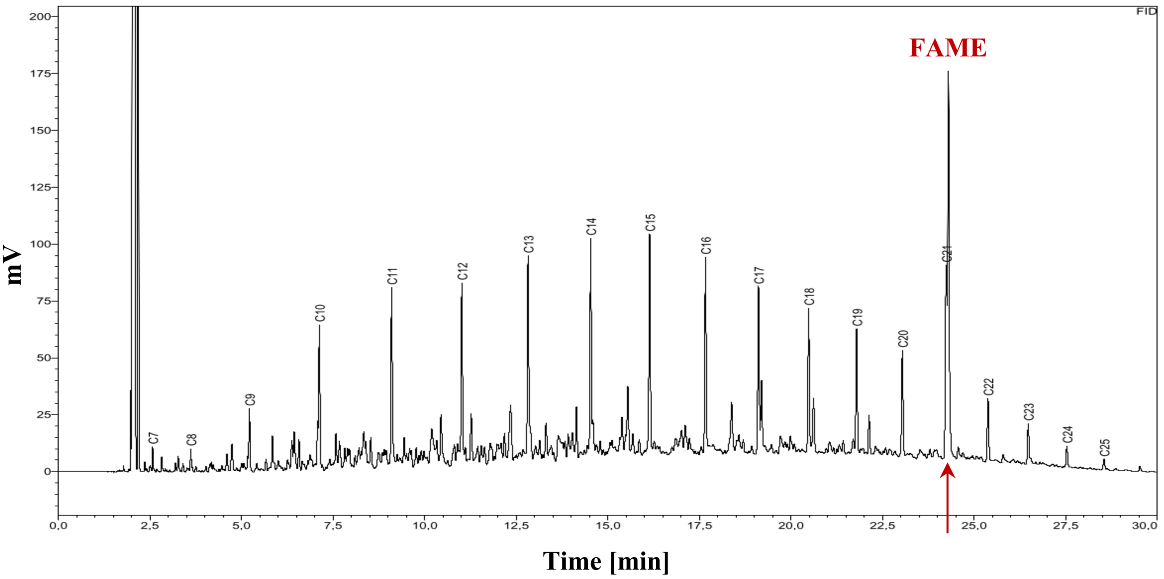

Figure 39 - The chromatogram of the Diesel B7 with methyl oleate indication (diesel reference).

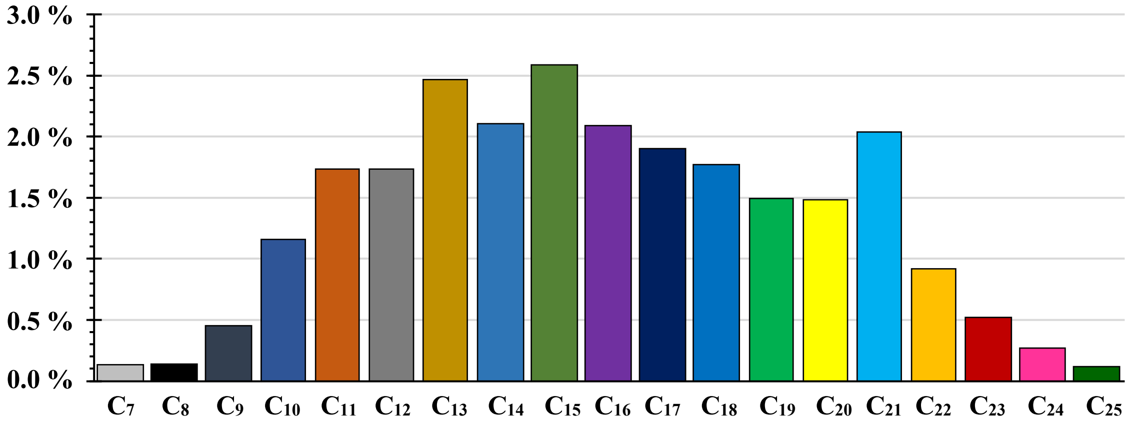

Figure 40 - *n*-Alkane content [%] in the Diesel B7 (diesel reference).

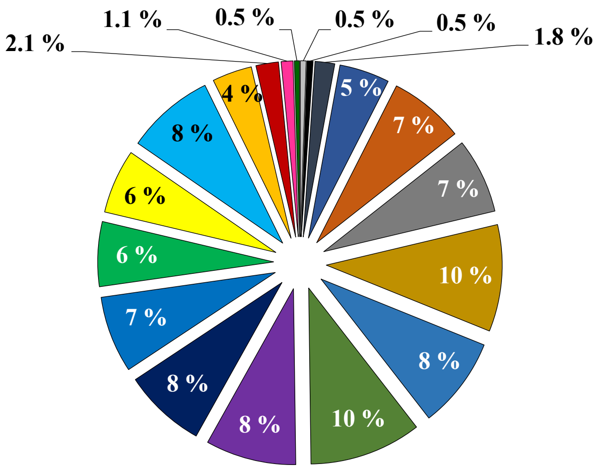

Figure 41 - Relative abundance [%] of *n*-alkanes in the Diesel B7 (diesel reference).

6 Discussion

6.1 Biofuels and Relation to Impurities

The production of biofuels by FTS from LIBS involves several steps (see Chapter 4.1). The major challenges are not only the efficiency and low cost, but beyond catalysts mentioned in Chapter 3.2.4.1, the purity of the synthesis gas is justifiably the next debated issue. During FTS, the stringent gas purity requirements of downstream synthesis catalysts are required (Frilund *et al.* 2020). Dense particles, such as ash, tar and chlorine are removed during the gas filtration step (see Chapter 4.1.4). However, the most problematic impurities are considered sulphur compounds. Sulphur present in the syngas is a catalyst poison and is especially harmful during the whole process of FTS. Therefore, it has to be removed to the level of 1 ppm in the synthesis gas (Technology 2021). The technological process used in Chapter 4.1.6 used catalyst reactors, but useful could be an alternative wet-scrubbing traditional method to remove sulphur compounds along with other acid gases (including chlorine). Speaking of the environment, it would be appropriate to focus additionally on an exploration of various sorbent materials, especially those with potential for reuse. Similarly what the EU-funded international project called „Compact Gasification and Synthesis process for Transport Fuels" (COMSYN) was attempting to do (Technology 2021).

According to Hájek *et al.* (2021), petrol fractions as biocomponents do not contain sulphur or polyaromatic hydrocarbons nor benzene, precisely because the FTS process is optimized to remove them. This research is supported by the team of Jenčík *et al.* (2021) who declares that the products of FTS generally do not contain also salts, heavy metals and nitrogen, which as N_2O is part of the GHGs and participates in climate change (see Chapter 1.2). Integration of these advanced fuels into conventional fuel production is our generation one step closer to a reduction in dependence on crude oil and a better environment.

6.2 Chromatography Used for Chemical Composition

The analysis of biofuels is more detailed in Chapter 3.3. Nevertheless, for basic GC/FID a sample must be volatilized and carried by an inert gas through a capillary column. The compound then passes the column and reacts with the stationary phase. The longer it takes the higher the retention time. The consequent identification of the molecules is possible thanks to the retention time when compared to a reference. The development of a standard set of separation conditions would allow the generation of unique fingerprints for direct comparison of biofuels from different feedstocks. As seen in Chapter 5, GC/FID method was a suitable choice for the determination of *n*-alkanes emerging from FTS products, in the context of this work.

As an additional use of GC/FID, it is convenient to highlight the work of Sánchez *et al.* (2020) about profiling organic compounds in bioethanol samples. Bioethanol is the subject of the Chapter 3.1.2.1, where blends with petrol are described with related European Standard (NBN EN 228+A1). Sánchez *et al.* (2020) demonstrated using GC/FID that, for a given production process, different distillation fractions contain unequal VOC profiles. Some VOCs were more concentrated in the lightest fraction and their concentration decreased in heavier ones. He further claims a direct relationship between the boiling point and the fractions where analytes were present. A similar observation applies to FTS products. The produced hydrocarbons by FTS are usually separated by fractional distillation and refined the same way as conventional crude oil. Fractional distillation is responsible for upgrading/separation of the FTS products (see Table 12) and creates final fuel fractions: (1) light distillates (petrol fractions) are highly volatile, have small molecules and low boiling points, (2) heavy distillates (diesel fractions) have the lowest volatility and high boiling points (Blažek *et al.* 2006).

There is also a specific need for a set of conditions that can be used to elucidate adequate separation of a range of FAMEs in a variety of biodiesels. As stated in Chapter 3.1.2.3, transesterification also plays a major role in the generation of biodiesel and corresponding FAMEs. Goding *et al.* (2013) selected GC/FID with different columns for separation and GC/MS for identification of individual FAMEs (see Chapter 3.3). He indicates in his paper that the order of elution of FAMEs is dependent on chain length (C_{18} follows after C_{16}), as well as the degree of unsaturation (C_{18} follows after $C_{18:1}$), but only on a weakly polar phase (5 % phenyl-modified polydimethylsiloxane). In the ongoing experiments using more moderately polar columns (50 % phenyl-modified polydimethylsiloxane), the dependency was evident in reverse order (C_{18} still followed after C_{16}, yet $C_{18:1}$ followed after C_{18}). His publication emphasizes that the correct choice of column is very important for the final interpretation of the analysed data.

Alkanes are non-polar compounds, hence a low-polarity column specifically tested for hydrocarbons was used (see Table 14) during the analyses. In the case of this work, the retention time of 3.3 minutes of isooctane (2,2,4-trimethylpentane) was known among the analytes, as seen in Figures 21, 24 and 27. Since C_8 (and even C_7) follows after isooctane, it can be assumed that in the case of the analysed petrol fractions and chosen weak polar column, *n*-alkanes elute later than their branched isomers, based on obtained results. Structural isomers of *n*-alkanes are formed by starting with C_4. However, the branching of alkanes can be at more than one place in the molecule, thus the number of possible isomers increases rapidly with the number of C atoms. Furthermore, in a study related to chromatograms of alternative and commercial jet fuels by Pires *et al.* (2018), the *n*-alkanes distribution varies among different fuels. The differences between the compositions are deduced by different feedstocks and processes used to produce them.

6.3 Assessment of the Biofuels Potential

Recent developments in LIBS bioconversion mechanisms have demonstrated the potential for efficient biofuel production (Saravanan *et al.* 2022). Of the overall FTS production process, only the liquid product containing hydrocarbons starting with C_5 and more are relevant for analysis in this thesis. These are suitable as such for potential gasoline, diesel or even kerosene use. Hydrocarbons in the gas form (C_1 - C_4) are often reused in the gasification process (Technology 2021). The analyses of each sample fraction consist of the chromatogram, the corresponding processed data (see Table 15 and 16) expressed subsequently in a bar chart indicating the absolute representation of *n*-alkanes in the sample and the relative representation of *n*-alkanes among each other within the sample (shown in the related pie chart).

Achieve fuels for low production costs is the key to commercialization, during the last decade. Pires *et al.* (2018) mentioned a reduction in the production cost of alternative kerosene by blending it with commercial jet fuel (lower amount of H_2 used in the deoxygenation process). Using optimized FTS, the COMSYN project aimed the reduction of biofuel production costs down to 0.80 €/l (Technology 2021).

6.3.1 Synthetic Envopetrol

Conventional commercial E5 petrol (Natural 95) of fossil origin consists of alkanes mainly between C_5 and C_{10} with a very small content of higher hydrocarbons up to C_{15} (see Figures 27 and 28). Overall, the assumption is that the same petrol sample is predominantly a mixture of paraffins, naphthenes (cycloalkanes), aromatics, olefins (alkenes) and ethanol up to 5 % (v/v). Isomerization has a positive effect on the quality of petrol - the more branched alkanes it contains, the higher the quality (opposite effect to diesel). The ratios vary based on a variety of factors. Comparing the contents of *n*-alkanes in three FTS petrol fractions (Light Naphta, Benzene Fraction, Heavy Naphta) with this reference sample, a fairly negative conclusion can be drawn. Unfortunately, FTS petrol fractions are not much comparable either due to too high *n*-alkane content (see Figures 24 and 25) or because of a completely different representation of individual *n*-alkanes (Figures 18, 19, 20, 21, 22 and 23). Both *n*-alkane percentages (absolute/relative) are outside of the applicable range of commercial petrol.

These arguments are consistent with current research. The scientific work of Hájek *et al.* (2021) recommends the creation of a low-percentage mixture of 3 % (v/v) of FTS petrol fractions with commercial fossil petrol precisely for reasons of direct inapplicability and also to minimize the negative effects of fossil petrol (similar to E5 petrol instructed by NBN EN 228+A1). FTS petrol can be declared as a biocomponent for fossil petrol without any further necessary catalytic upgrading. The blending of biofuel with fossil fuel may be part of the aviation practice as well. Pires *et al.* (2018) state that all deviations from current jet fuel specifications are likely to be compensated by blending the alternative kerosene with the commercially available jet fuels. The possibility of further chemical treatment of FTS petrol fractions (isomerisation, reforming, etc.) should be mentioned. Such treatment will reduce the *n*-alkane content and increase the octane number.

The mislabelling of petrol with additives as a biopetrol should also be addressed. There is not yet any form of synthetic „biopetrol" that can be used as a substitute for fossil petrol. In all cases, it is always the addition of a cleaner compound (e.g., bioethanol - see Chapter 3.1.2.1 - to increase octane number) to conventional fossil petrol. With this FTS synthetic petrol blended into fossil petrol, it should properly be labelled as an Envopetrol (environmentally friendlier petrol). In contrast, this is not the case for biodiesel (see below).

6.3.2 Synthetic Biodiesel

Commercial fossil diesel (100% Diesel/no FAME and Diesel B7) consists of all the classes of hydrocarbons (75 %) - paraffin between C_7 and C_{25} (see Figures 37 and 38) with certainly the most important middle range between C_{10} and C_{21} (other *n*-alkanes are below 1 % in absolute sample content), naphthenes, aromatics, olefins in small concentrations (Lois *et al.* 2003) and in case of Diesel B7 also FAME (methyl oleate and other methyl esters) up to 7.0 %

(v/v), seen in Figure 39. Isomerization has a negative effect on diesel - the less branched alkanes it contains, the higher the quality (opposite effect to petrol). Comparing the contents of *n*-alkanes in two FTS diesel fractions (Paraffinic Diesel, Middle Distillate) with reference samples, it is possible to declare their mutual similarity. In Figures 30 and 31, the *n*-alkane content [%] of individual *n*-alkanes from FTS can be seen almost in the same range as for commercial diesel. The same statement applies to the comparison of the relative abundance [%] of *n*-alkanes (see Figure 32). The fraction called Paraffinic Diesel was produced from higher molecular weight products (waxes) which were processed by hydrocracking to more suitable lower-weight products afterwards (see Chapter 4.1.8). The purpose of the hydro-cracking unit is to shift the product yield towards the shorter chained products.

That said, the Paraffinic Diesel appeared to be the most suitable of all fractions to be used as a motor fuel, supplementary physical measurements were undertaken (Chapter 4.4.2). As it is intended as a diesel fuel, it must meet the standard NBN EN 15940+A1+AC describing requirements for marketed and delivered Paraffinic Diesel fuel obtained by hydrotreatment. When comparing Paraffinic Diesel to fossil diesel, in the case of density the fossil diesel has a density of 840 kg/m^3 (see Table 6), whereas Paraffinic Diesel has a lower density of 805 kg/m^3 (see Table 17), which is consistent within the specified maximum of 810 kg/m^3 by NBN EN 15940+A1+AC (shown in Table 17). The determination of the density is important, especially for diesel fuel, where it is also used to calculate the cetane number. Notably, the viscosity of fossil diesel is 5 mm^2/s (see Table 6), while Paraffin Diesel has a value of 3.5 mm^2/s (see Table 17). Viscosity also meets the standard NBN EN 15940+A1+AC establishing a maximum of 4.5 mm^2/s (shown in Table 17). Even though the flash point of fossil diesel is 50 °C (see Table 6), Paraffin Diesel has a higher flash point of 77 °C (see Table 17), which surpasses NBN EN 15940+A1+AC with the required minimum of 55 °C (shown in Table 17). A big positive is the cetane number, which has a fossil diesel of value 50 (see Table 6), markedly lower than the Paraffinic Diesel of value 71 (see Table 17), making it a considerable advantage of Paraffinic Diesel. The last fraction of the Middle Distillate is slightly different, due to the shift to heavier *n*-alkanes and their quite higher content (Figures 33, 34 and 35). It would indicate that the Middle Distillate fraction could be used also as an additive, but this time for fossil diesel.

These conclusions are also matched by recent publications. Jenčík *et al.* (2021) claimed that FTS biodiesel has almost identical properties as a commercial diesel and in properties such as cetane number it even outperforms it. He further claimed that this also applies to blends with fossil diesel. Regarding the Middle Distillate fraction, his team specially mentioned this fraction has an excellent cetane number, although higher dissolved *n*-alkanes begin to return to a solid state at lower temperatures. Another interesting study focusing on biodiesel produced from FAMEs by Goding *et al.* (2013) discovered not only the good characteristics of biodiesel compared to commercial diesel but also that the same feedstock produced in different locations and harvest seasons provides always biodiesel with chemical similarities.

FTS biodiesel could be potentially used as a transportation fuel without any further necessary upgrading. The question is whether these fuels will be still referred to by the prefix „bio-“. According to current social developments, FTS belongs to the category of synthetic fuels. The prefix „bio-“ could also indicate just the origin - Diesel B7 (with FAME content) is currently referred to as biodiesel. In most cases FTS diesel could be used completely as a substitute, hence biodiesel has rightfully earned its name.

6.4 Future Steps

The results of the analysis and assessment of the individual FTS fractions investigated in this diploma thesis are consistent with data published in the literature. However, a more comprehensive study in this area should be performed. Further interesting results could be obtained by analysing different batches produced from different input LIBS and comparing them with each other. Additional work with chemometric methods of analysis would further investigate the importance of column choice and feedstock type.

Obviously, the analysis should not stop at the determination of *n*-alkanes. Screening should be extended with the identification of individual chemical components. Gas chromatography combined with mass spectrometry (GC/MS) should be an integral part of similar studies (see Chapter 3.3). Fragmentation of compounds leaving the GC column leads to their subsequent detection in the MS and such spectra are unique for each molecule, allowing their eventual identification. Fragmentation patterns are reproducible and can be used to produce quantitative measurements. In addition to the linear *n*-alkanes, fragments of branched-chain alkanes, cyclic alkanes, alkenes, and aromatics can be identified. Generally, the contents of aromatic compounds in fuels must be controlled (Pires *et al.* 2018). Using these individual fingerprints, the chemical composition of potential motor fuels can be determined, and it allows the creation of relevant chemical databases.

Finally, it would be interesting and quite important to find out the octane (petrol fractions) and cetane (diesel fractions) numbers in the remaining samples. It would provide information on the quality characteristics during combustion (see Chapter 3.1.1.1.1 and Table 6). The eventual drop in octane number can be solved by adding an octane booster (Hájek *et al.* 2021). Furthermore, the cold flow parameters (e.g., CFPP) and distillation curve of Paraffinic Diesel could be measured to expand the information about analysed samples. Nevertheless, as Nanda *et al.* (2018) said, thorough research and development will lead to a better understanding of the production and utilization of these biofuels for a greener and cleaner future.

7 Conclusion

- The master's thesis aimed to examine and compare the chemical composition of selected hydrocarbon fractions obtained by FTS from waste LIBS materials and to assess the possibilities of their use as motor fuels.
- Samples were synthesized in collaboration with ORLEN UniCRE a.s.
- Experimental analyses were handled in the Department of Chemistry of the Faculty of Agrobiology, Food and Natural Resources at the Czech University of Life Sciences.
- At the beginning of this master's thesis, the current information about various types of transportation fuels was demonstrated, and main advantages such as substitutability, protection, recyclability, and sustainability were described.
- Using GC/FID and standards, a limited fingerprint for each FTS fraction was generated. With the help of these fingerprints, the *n*-alkane composition of a variety of petrol and diesel fractions was determined.
- It was found that the *n*-alkanes representation of the FTS petrol fractions is not much comparable to conventional petrol and their further chemical processing is recommended.
- On the other hand, the *n*-alkanes representation of FTS diesel fractions is almost comparable to conventional diesel. FTS biodiesel is a candidate for biofuel production from renewable energy sources and waste materials.
- The analysed Paraffinic Diesel sample, made from FTS waxes meets the EU standards of a drop-in fuel.
- The results are compatible with previously published experiments, indicating that the analysis can be repeated under different conditions.
- It is concluded that the utilization of LIBS as an energy source is becoming essential to understand technological advancements for their conversion along with life-cycle assessment concerning low carbon footprint (along with flexibility in the production of biofuels, biochemicals or biomaterials).
- The obtained data are part of a complex scientific study that will be published.

8 References

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9 List of Abbreviations

1st GB - First-generation biofuels
2nd GB - Second-generation biofuels
3rd GB - Third-generation biofuels
4th GB - Fourth-generation biofuels
API - American Petroleum Institute
ASF - Anderson-Schulz-Flory
Bio-ETBE - Bio-ethyl tert-butyl ether
BtL - Biomass-to-liquid
CEL - Cellulose
CFPP - Cold filter plugging point
CNG - Compressed natural gas
COMSYN - Compact gasification and synthesis process for transport fuels
CtL - Coal-to-liquid
DFB - Dual fluidized bed
DMF - Dimethylfurfural
EU – European Union
FAME - Fatty-acid-methyl ester
FF - Fossil fuels
FHCF - Fossil hydrocarbon-containing fuels
FTS - Fischer-Tropsch synthesis
GC/FID - Gas chromatography with a flame ionization detector
GC/MS - Gas chromatography with mass spectrometry
GCxGC - Two-dimensional gas chromatography
GHG - Greenhouse gas
GM - Genetically modified
GtL - Gas-to-liquid
HEM - Hemicellulose
HFO - Heavy fuel oil
HMF - Hydroxymethylfurfural
HT-FTS - High-temperature Fischer-Tropsch synthesis
LIBS - Lignocellulosic biomass
LIG - Lignin
LNG - Liquefied natural gas
LPG - Liquefied petroleum gas
LT-FTS - Low-temperature Fischer-Tropsch synthesis
MMTC - Million metric tons of carbon
MTBE - Methyl tertbutyl ether
PEM - Proton exchange membrane
POME - Palm oil-methyl ester

PTR - Pre-treatment
RES - Renewable energy source
RME - Rapeseed-methyl ester
RVP - Reid vapour pressure
SBCR - Slurry bubble column reactor
SME - Sunflower-methyl ester
SNG - Synthetic natural gas
SOME - Soya-methyl ester
SRR - Steam reforming reactor
TALEN - Transcription-like effector nucleases
TWh - Terawatt-hours
UHP - Ultra-high purity
WUOME - Waste used oil-methyl ester
ZFN - Zinc-finger nuclease

10 Appendices

No. 1 - Properties and advantages of selected biofuels (inspired from Nanda *et al.* 2018)

Biofuel	Feedstock	Fuel properties and advantages
Ethanol	Corn, distiller's grains, molasses, straw, bagasse, woody biomass, and other LIBS	Oxygenated fuel
		Blended with gasoline at flexible ratios
		High fuel concentrations require vehicle engine modification
Butanol	Corn cobs, straw, woody biomass, grasses, and other LIBS	Superior fuel properties than ethanol and comparable with gasoline
		No blends with gasoline required
		Compatible with the current vehicle engines at high concentrations
Bio-oil	LIBS, waste organic materials, and waste rubber	Energy-dense fuel source
		Can be used directly to generate power in-house refinery
		Precursor of fine chemicals and industrially relevant bio-products
Algal oil	Microalgae and macroalgae	Cultivation of algae can lead to CO_2 capture in parallel with oil production
		Algal oil is rich with triglycerides and fatty acids
		De-oiled algae can be used in a nutrient-rich diet for livestock
Biodiesel	Vegetable oil, algal oil, and animal fats	Improves lubricity compared to that of conventional diesel
		Produced through transesterification of nonedible oil and waste edible oil
		High energy density compared to alcohol-based fuels
Hydrogen	LIBS, algae, water, sewage sludge, and industrial effluents	The superior heating value of 140 MJ/kg
		Energy carrier and vector
		Feedstock for fuel cells
		It's a clean fuel as its burning produces only water and no emission of pollutants and particulates
Biomethane	Waste organic materials and lignocellulosic materials	Production of biomethane requires less maintenance and capital investment
		Invigorates rural livelihood and employment
		Independent on seasonal and geographical variations
		Biomethane can be used as a domestic cooking fuel and in household heating and electricity generation
Jet Fuel	Halophytes, LIBS, sewage sludge, algae, *Camelina*, *Jatropha*, and oilseed crops	Its utilization decreases the dependence on fossil resources
		Reduces environmental impacts from aviation-related emissions
		Uses cheaply available feedstocks
		Blends of biokerosene and conventional aviation fuels can reduce the fuel cost

No. 2 - General classification of biomass varieties as solid fuel resources according to the origin (redrawn from Vassilev *et al.* 2012)

Biomass Group	**Biomass sub-groups, species and varieties**
Wood and woody biomass	Coniferous or deciduous, angiospermous or gymnospermous and soft or hard such as stems, barks, branches (twigs), leaves (foliage), bushes (shrubs), chips, lumps, pellets, briquettes, sawdust, sawmill and others from various wood species
Herbaceous and agricultural biomass	Annual or perennial, arable or non-arable and field-based or processed-based biomass from various species such as: • Grasses and flowers (alfalfa, arundo, bamboo, banana, cane, miscanthus, reed canary, ryegrass, switchgrass, timothy, others) • Straws (barley, bean, corn, flax, mint, oat, paddy, rape, rice, rye, sesame, sunflower, triticale, wheat, others) • Stalks (alfalfa, arhar, arundo, bean, corn, cotton, kenaf, mustard, oregano, sesame, sunflower, thistle, tobacco, others) • Fibres (coconut coir, flax, jute bast, kenaf bast, palm, others) • Shells and husks (almond, cashew nut, coconut, coffee, cotton, hazelnut, millet, olive, peanut, rice, sunflower, walnut, and others) • Pits (apricot, cherry, olive, peach, plum, others) • Other residues (fruits, pips, grains, seeds, coir, cobs, bagasse, food, fodder, marc, pulps, cakes, and others) from various species
Aquatic biomass	Marine or freshwater, macroalgae or microalgae and multicellular or unicellular species (blue, blue-green, brown, golden, green and red algae; diatoms, duckweed, giant brown kelp, kelp, salvinia, seaweed, sweet-water weeds, water hyacinth, others)
Animal and human biomass wastes	Bones, chicken litter, meat-bone meal, sponges, various manures, others
Contaminated biomass and industrial biomass wastes (semi-biomass)	Municipal solid waste, demolition wood, refuse-derived fuel, sewage sludge, hospital waste, paper-pulp sludge, waste papers, paperboard waste, chipboard, fibreboard, plywood, wood pallets and boxes, railway sleepers, tannery waste, others
Biomass mixtures	Blends from the above varieties

No. 3 - Comparative analysis of pros and cons of different pre-treatment methods for lignocellulosic biomass (redrawn from Saravanan *et al.* 2022).

Type	**Pre-treatment**	**Pros**	**Cons**
Physical	Mechanical	Increasing crystallinity of biomass and easy operation control	High energy consumption
	Microwave	Increasing porosity, surface area and less energy consumption	Not environmentally compatible, generation of waste materials, high cost
	Ball mining	High efficiency when combined with other pre-treatment processes and no release of toxic compounds	Less product efficiency and generation of waste materials
	Ultrasound	Increasing porosity, surface area and higher efficiency	High cost, temperature and pressure
	Electrokinetic	Easy, simple operation and forming the electric potential across the cell wall of biomass	Not suitable for dry biomass
Chemical	Acid	Less reaction time, cost-effective and higher efficiency	Degradation of yield, bioreactor corrosion might occur, the release of toxic chemicals, causing environmental pollution and high water consumption
	Alkali	Less reaction time, cost-effective and higher efficiency	
	Ionic liquid	Recycling and reuse	High energy demand, cost and waste generation
	Organic solvent	Higher fractionation, conversion and high-purity product	The high cost (solvent), waste generation
Physicochemical	Steam explosion	With higher efficiency (lignin removal, hemicellulose solubilization), the porosity of biomass increases by rupturing	High cost, temperature and pressure
	Autohydrolysis	Higher efficiency and hydrolysis rate	High water consumption and energy demand
	Hydrothermal	Increasing cellulose digestibility, less energy consumption and environmentally compatible	High energy demand and not suitable for softwood biomass
Biological	Bacterial	Environmentally compatible, cost-effective and higher hydrolysis rate	Long duration process
	Fungal	Environmentally compatible, cost-effective, less energy consumption, higher hydrolysis rate and easy operation	The hydrolysis rate is very slow, long duration process and generation of waste materials
	Enzymatic	Environmentally compatible, less energy consumption, immobilized enzymes, recycling and delignification	The high cost (Enzyme purification & production) and high maintenance cost