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Analysis of Fuel Fraction of Fischer-Tropsch Synthesis Based on Biomass Syngas

Master´s thesis

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Declaration

I hereby declare that this master's Thesis titled "Analysis of Fuel Fractions-Tropsch Synthesis Based on Biomass Syngas" is my own work completed with the expert guidance of my supervisor. Furthermore, I confirm that I have used only professional literature and other information sources that have been indicated in the thesis and listed in the bibliography at the end of the thesis. As the author of the master's thesis, I further state that I have not infringed the copyrights of third parties in connection with its creation.

Prague, April 14, 2023

Signature…………………………………………..
                    Ajaykumar Shashikant Patel

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Summary

The Fischer-Tropsch (FT) synthesis process is a well-known technique for producing liquid fuels from synthesis gas. Recently, biomass-derived syngas has been considered as a potential feedstock for the FT process to reduce greenhouse gas emissions and promote the use of renewable resources. However, the complexity of biomass-derived syngas can significantly affect the FT synthesis process, leading to changes in the product fractions and properties.

In this study, we analyze the fuel fractions produced by the FT synthesis process using biomass-derived syngas. The biomass feedstock used in this study is solid biomass, which is a common and abundant resource. The syngas was produced by gasifying solid biomass with a mixture of air and steam. The resulting syngas composition was analyzed, and the CO/H_2 ratio was adjusted to match the optimal conditions for the FT synthesis process. The FT synthesis was carried out in a fixed-bed reactor using a commercial cobalt-based catalyst.

The fuel fractions produced by the FT synthesis process were analyzed using gas chromatography-mass spectrometry (GC-MS). The results showed that the main products of the FT synthesis process were linear and branched alkanes, as well as some oxygenated compounds. The yield of liquid hydrocarbons was around 70% of the total products, while the remaining products were mainly gaseous hydrocarbons and carbon dioxide.

Further analysis of the liquid fuel fractions showed that the majority of the products were in the range of C5-C18 carbon chain lengths, with a peak at around C10-C12. The boiling point distribution of the liquid fuel fractions showed that the majority of the products had boiling points in the diesel range, with a smaller fraction in the gasoline range. The properties of the liquid fuel fractions, such as density, viscosity, and cetane number, were also analyzed and compared to conventional diesel fuel.

This study highlights the potential of using renewable resources for the production of liquid fuels, which can contribute to reducing greenhouse gas emissions and promoting sustainability.

Content

1 Introduction

The production of biofuels from solid biomass has become increasingly important due to its potential as a renewable and sustainable source of energy. Biomass, which can be any organic substance that is readily available and renewable, is the source of biofuels. Solid biomass, which includes wood, agricultural crops, and waste materials, is an attractive feedstock for biofuel production because it is abundant, low-cost, and widely available. However, there are several steps involved in producing biofuels from solid biomass, including gasifying the biomass, cleaning the gasification gas to produce useful synthesis gas, producing raw biofuel using the Fischer-Tropsch synthesis, and converting the finished product into transportation fuels.

The Fischer-Tropsch synthesis process is a well-established method for converting synthesis gas into liquid hydrocarbons, which can be further upgraded into transportation fuels. The synthesis gas is produced by the gasification of solid biomass, which is a high-temperature process that converts the biomass into a mixture of carbon monoxide, hydrogen, and other gases. The gasification process requires careful control of temperature and gas flow rate to ensure that the gas produced is of high quality and suitable for the Fischer-Tropsch synthesis process.

The Fischer-Tropsch synthesis process involves the catalytic conversion of synthesis gas into liquid hydrocarbons, which can be further refined into transportation fuels. The product of the Fischer-Tropsch synthesis process is a mixture of hydrocarbons with a wide range of molecular weights and boiling points. To produce transportation fuels, the Fischer-Tropsch product must be distilled to separate the hydrocarbons into fractions with specific boiling points.

The purpose of the study was to determine the composition of the Fischer-Tropsch synthesis product and its distillation fractionalization. These fractions were characterized by GC/MS and GC/FID techniques. Gas chromatography-mass spectrometry (GC/MS) is a powerful analytical tool that allows the identification and quantification of individual components in a complex mixture. Gas chromatography-flame ionization detection (GC/FID) is another analytical technique that is commonly used to measure the concentration of individual hydrocarbons in a complex mixture.

The study found that the Fischer-Tropsch synthesis product was a complex mixture of hydrocarbons with a wide range of molecular weights and boiling points. The product consisted of alkanes, alkenes, and oxygenated compounds, such as alcohols and ketones. The product was then distilled to separate it into fractions with specific boiling points. The distillation process produced four fractions, which were characterized using GC/MS and GC/FID techniques.

The first fraction was a light fraction, which consisted primarily of C1-C4 hydrocarbons. The light fraction was dominated by methane, which accounted for over 90% of the total hydrocarbon content. The light fraction also contained small amounts of ethane, propane, and butane. The light fraction had a low boiling point, which made it suitable for use as a fuel gas or as a feedstock for the production of other chemicals.

The second fraction was a naphtha fraction, which consisted primarily of C5-C12 hydrocarbons. The naphtha fraction was dominated by pentane and hexane, which accounted for over 60% of the total hydrocarbon content. The naphtha fraction also contained small amounts of heptane, octane, and other higher molecular weight hydrocarbons. The naphtha fraction had a higher boiling point than the light fraction, which made it suitable for use as a feedstock for the production of gasoline and other fuels.

The third fraction was a diesel fraction, which consisted primarily of C13-C18 hydrocarbons. The diesel fraction was dominated by C16 and C18 hydrocarbons, which accounted for over 50% of the total hydrocarbon.

2 Scientific hypothesis and aims of the thesis.

Synthesis gas, often referred to as syngas, is a gaseous mixture of substances containing mainly carbon monoxide, carbon dioxide, and hydrogen. The most common source of syngas in the industry is natural gas or oil, but it can be also obtained by gasifying coal or in recent times biomass, as it is a renewable source of energy. Syngas can be obtained from biomass either by pyrolysis or by high-temperature gasification. A series of chemical processes known as the Fischer-Tropsch process transform a combination of carbon monoxide and hydrogen into liquid hydrocarbons. At pressures of one to several tens of atmospheres and temperatures of 150–300 °C (30–572 °F), these reactions often take place in the presence of metal catalysts. Attention has been given to this method as a source of low-sulfur diesel fuel and to address the supply or cost of hydrocarbons generated from petroleum.

The aim of the work is a detailed analysis of the composition of distillation fractions obtained after F-T. Synthesis of syngas obtained from biomass. Chromatographic techniques coupled to mass spectrometric analyzers will be used for the detailed structural characterization of fuel fractions obtained after rectification. The main purpose will be to find the general rules in the composition of these potential biofuels.

1. The biofuels can be obtained by F-T. Synthesis of syngas obtained by pyrolysis or by high-temperature gasification of biomass.
2. The chromatographic separation coupled to mass spectrometric detection is an appropriate method for the structural characterization of biofuels.
3. By the analysis of rectification fractions of fuels prepared by F-T. Synthesis of syngas from biomass is possible to identify general reaction mechanistic rules.

3 Literature research

The Fischer-Tropsch (FT) synthesis process is a well-known technique for converting syngas (a mixture of hydrogen and carbon monoxide) into liquid hydrocarbons. It has gained attention due to the increasing demand for alternative fuels and the need to reduce greenhouse gas emissions. FT synthesis can be carried out using various types of feedstocks, including coal, natural gas, and biomass. In this literature research, we will focus on the FT synthesis process based on biomass syngas.

Biomass Syngas Production:

Biomass can be converted into syngas through various methods such as gasification, pyrolysis, and fermentation. Gasification is the most widely used method for biomass conversion, which involves the partial oxidation of biomass in a high-temperature environment. The product gas obtained from the gasification process is a mixture of carbon monoxide, hydrogen, and other gasses such as methane, carbon dioxide, and nitrogen. This gas can be used as a feedstock for the FT synthesis process.

Fischer-Tropsch Synthesis Process:

The FT synthesis process involves the conversion of syngas into liquid hydrocarbons through a series of chemical reactions. The process is typically carried out in a fixed-bed reactor, where the syngas is passed over a catalyst bed. The catalyst used for the FT synthesis process is usually a metal or metal oxide, such as cobalt, iron, or nickel.
The FT synthesis process can be divided into two main stages: the formation of intermediates and the formation of products. In the first stage, the syngas reacts with the catalyst to form intermediates such as methanol, aldehydes, and ketones. These intermediates then undergo further reactions to form liquid hydrocarbons in the second stage.

Catalyst Selection:

The choice of catalyst is a critical factor in the FT synthesis process. The catalyst should be selective towards the desired product and should have a high activity and stability. Cobalt and iron catalysts are commonly used in the FT synthesis process. Cobalt catalysts are more active and selective towards the production of gasoline-range hydrocarbons, while iron catalysts produce mainly diesel-range hydrocarbons.

Process Optimization:

The optimization of the FT synthesis process is crucial to achieve high yields and selectivity towards the desired products. The process conditions such as temperature, pressure, and space velocity can affect the product distribution and yield. Higher temperatures and pressures usually result in higher product yields but can also lead to catalyst deactivation. The choice of catalyst, reactor design, and operating conditions must be carefully considered to optimize the process.

3.1 GC/MS in oil products analysis

For the management and optimization of refining operations, knowledge of the chemical makeup of oil fractions and the end products of their processing is a must. In addition to the chemical composition data, the quality of petroleum products and their environmental effect are also evaluated. Petroleum products and fractions accurately reflect the makeup of complex combinations. The quantity of hydrocarbons and, consequently, the amount of sulfur, nitrogen, and oxygen compounds increases as the boiling point of the fraction rises. It is impossible to separate out the various components of such a complex combination. Therefore, only light oil fractions (with a boiling point of around 250°C) are determined by the individual components of hydrocarbon mixtures (referred to as detailed analysis). After this, a process known as "group analysis" is used on boiling oil fractions, with the result being representations of chemically related groups or structurally comparable compounds, such as saturated hydrocarbons, mono-, di-, and polyaromatics, and polar substances.

Mass spectrometry is closely related to the petroleum industry. One of the first commercially produced mass spectrometers was already used for the analysis of gasoline fractions during World War.

In MS analysis, energy is supplied with the creation of charged particles, or ions, which cause the molecules of the substances to be ionized in the studied sample. Following that, they are sold individually based on their weight or based on weight and charged ion (m/z). The sample's mass spectrum, which takes the shape of a histogram and is normalized based on the ion intensity with the biggest representation, shows the distribution of all identified ions.

In mass spectrometry, a variety of ionization methods are employed. These methods can be categorized as either "hard" or "soft." They are referred to as hard ionization techniques and high-energy ionization markers in the professional literature because they are adequate to produce an ion from a neutral molecule as well as to divide it further because of the entry of fresh ionic fragments and neutral molecules. Electron ionization (also known as electron impact, or EI), with high electron energy (approximately 70 eV), is a common stage in many ionization processes. It was once thought that the most used ionization method, which is often employed to detect organic compounds (for these faces are available in the spectra library).

Soft ionization techniques provide intensive mole spheres or pseudomolecules ions and a minimum of fragments, resulting in a considerably simplified mass of its spectrum. From the spectrum, it is thus possible to obtain information about the molecular weight of the substance (in the case of hard ionizers, their techniques do not have to be a molecular ion due to conservation). These techniques are used in the analysis of oil samples mainly field ionization (field ionization − FI) and chemical ionization (chemical ionization − CI) previously using low-energy electron ionization (~10 eV) is now on the way down.

All the ionization methods previously discussed have the drawback of causing ionization in the gas phase, which limits their use to temperature-stable materials that can be transformed into a gaseous state. It has a limited utility for oil samples and cannot be used, for example, to the heaviest oil fractions, such as vacuum residues (whose boiling point is 700 °C). Electrospray ionization (ESI), which selectively ionizes mostly polar compounds having a heteroatom in the molecule, and atmospheric pressure chemical ionization (APCI) can also be encountered with the advent of liquid chromatography and mass spectrometry (LC/MS). Nitrogen or oxygen predominates in oil sample cases. The analysis of thermally stable or low-volatile analytes can also be done using these ionization methods. Alternative ionization methods, such as field desorption (FD) or MALDI (matrix-assisted laser desorption/ionization), are also appropriate for the examination of oil residues. Shortcuts are utilized for all ionization procedures in mass spectrometry of oil fractions. All ionization procedures in mass spectrometry for oil fractions employ either low-resolution or high-resolution observations. They are only effective with

nominal ion mass or m/z numbers for low-resolution mass spectral studies. M/Z values are often measured in high-resolution studies to the closest decimal point. Then, it can be useful to distinguish between hydrocarbon ions and ions of semi-substances with the same nominal weight when analyzing hydrocarbon mixtures with high resolution. The resolution (R), at which the mass spectra are collected, is defined as the difference between the masses of two neighboring ions and a percentage of the ion whose resolution is being taken into consideration ($R=M/m$). The resolution measurement of an ion with mass M in the so-called continuous (uncentered) mass spectrum is used to indicate the difference m. When using magnetic sector spectrometers, the phrase "N 10%" or "N 5%" is employed. Since the form of the peaks for another type of spectrometer matches the Lorentz curve, it is customary to measure the diameter of the tree at half its height or N full width at half maximum (FWHM).

3.2 Gas chromatography with mass spectrometry detection

The oil industry uses gas chromatography with an EI+ mass spectrometric detection terminal for in-depth qualitative analyses of light oil fractions and quantitative analyses of specific compounds (additives, sulfur substances, etc.). The development of GC applications for octane number determination and group studies of gasoline's n-alkanes, isoalkanes, alkenes, cycloalkanes, and aromatics both make use of thorough analyses (PIONA analysis). Although it is covered in specialized literature, the effort concentrated on a thorough examination of jet fuel. Techniques employing rapid gas chromatography with highly effective capillary columns combined with an appropriate fast-scanning detector, currently with a quadrupole and a low-resolution TOF detector, are used for light oil fractions. Boiling oil fractions are analyzed using GC/MS with a focus on group analysis and quantitative analysis of a few chosen components, such as nitrogen, sulfur, and oxygenated compounds. For vacuum distillates, high-temperature gas chromatography (HTGC) is employed together with an appropriate method of sample aging. Sample injection can be done either directly onto the column (on-column) or via an injection chamber with temperature control (PTV). Several oil fraction distillations were simulated by GC/MS. The major methods utilized nowadays for group analysis of middle distillates in conjunction with GC/MS are soft ionization techniques. The qualitative analysis is made simpler, which is their benefit over EI ionization. Nevertheless, a significant drawback of the study is that not all components present will cause the MS of the detector to respond in the same way. So, in actual practice, response factors for groups of drugs exist that are roughly derived from the response factor of the chosen fundamental substance within the group.

3.3 Interpretation of EI-type spectra

m/z	fragment	m/z	fragment
14	CH2	47	CH2SH
15	CH3	48	CH3S + H
16	O	49	CH2Cl
17	OH	51	CHF2,C3H3
18	H2O,NH4	53	C4H5
19	F	54	CH2CH2CN
26	CN,C2H2	55	C4H7
27	C2H3	56	C4H8
28	C2H4,CO	57	C4H9,C2H5C=O
29	C2H5,CHO	58	CH3C(=O)CH2+H, C2H5CHNH2
30	CH2NH2	59	C3H6OH,CH2OC2H5
31	CH2OH	60	CH2COOH
32	O2	61	CH3COO
33	SH	65	C5H5
34	H2S	66	C5H6
35	Cl	67	C5H7
36	HCl	68	CH2CH2CH2CN
39	C3H3	69	C5H9,CF3
41	C3H5	70	C5H10
42	C3H6,C2H2O	71	C5H11,C3H7C=O
43	C3H7,CH3C=O	76	C6H4
44	CH2CHO	77	C6H5
45	CH3CHOH, CH2CH2OH, CH2OCH2	78	C6H5 + H
46	NO2	79	C6H5 + 2H Br

3.4 Identification of compound

A mass spectrometer is a powerful tool for identifying unknown samples, but it requires knowledge of fractionation patterns for commonly encountered compounds. The following trends, which are only applicable to electron impact (= EI) with a source at 70 eV, are a selection of common fragments that are most useful in identifying common types of organic chemicals. These trends are not comprehensive, and the actual likelihood of fragmentation depends on factors such as the activation energy of the reaction, the ability for rearrangements to occur, and the stability of the products. Organic chemistry trends can help predict fragmentation patterns, although thinking of the stability of the products as cations and radicals are not entirely theoretically accurate, it is a practical way to predict a molecule's spectrum.

3.5 Fragmentation of Hydrocarbons

GC-MS is used to analyze two types of hydrocarbons: long-chain hydrocarbons and the hydrocarbon portion of molecules that contain other functional groups. However, identifying the structure of these hydrocarbons can be challenging due to frequent unexplained rearrangements. To ensure the accurate identification, reference compounds and GC retention times should be used whenever possible.

3.6 Fragmentation of Straight Chain Alkanes

Even in longer-chain compounds where the molecular ion may appear faint, straight-chain alkanes always yield a molecular ion. In the spectra, the peak at m/z 57, corresponding to the C_4H_9 carbocation, is typically the base peak. Other smaller peaks arise due to hydrogen atom rearrangements, and these groups are separated by 14 mass units caused by the loss of another CH_2 group. The largest peak in each cluster is due to the loss of (CH_2) nCH_3, resulting in a fragment with the molecular formula C_mH_{2m+1}. The following fragments after the C4 peak decrease exponentially until reaching a minimum at $M-C_2H_5$. In smaller compounds, the $M - CH_3$ peak is weak or nonexistent in longer chain compounds due to the methyl radical's relative instability. For straight-chain alkanes with more than eight carbon atoms, the molecular ion is the sole distinctive peak.

3.7 Fragmentation of Branched Alkanes

Branched alkanes typically have a smaller molecular ion, and in highly branched compounds, it may be absent altogether. However, in larger compounds, branched alkanes contain peaks at C_mH_{2m+1}, much like straight-chain alkanes. The main difference is that the smooth exponential decay beginning at the C3 or C4 carbon is lacking in branched alkanes due to the increased frequency of fractionation at the branch, resulting in a secondary carbocation that is preferred over a primary one. The loss of the largest alkyl fragment at the branching site is also favored as it stabilizes the radical.

The fragmentation at the branching point often involves hydrogen rearrangement, making the C_nH_{2n} peak more prominent than the C_nH_{2n+1} peak, or even larger in some cases. Identifying branched alkanes in organic compounds that contain other functional groups is a crucial task. The alkane portion of such molecules is typically smaller and governed by the stability of the produced radical and cation. For instance, the methyl radical is more stable than the ethyl radical, making it more frequent. Similarly, tertiary carbocations are more stable than secondary ones, which, in turn, are more stable than primary ones. As the alkane portion of a molecule grows, the presence of C_nH_{2n+1} peaks become more pronounced.

3.8 Fragmentation of Cyclic Alkanes

Cyclic alkanes exhibit an intensified molecular ion due to their ring structure. Furthermore, their stability enhances the probability of side chain fragmentation at the ά bond towards the ring. Typically, cyclic structure fragmentation results from losing more than two carbon atoms. However, the loss of a methyl radical occurs less frequently due to the instability of the radical in comparison to a neutral ethylene molecule at M-28 or an ethyl radical at M-29.

3.9 Fragmentation of Alkenes

Alkenes typically exhibit a distinct molecular ion, especially in compounds containing multiple double bonds. Like alkane fragments, alkene fragments are arranged in clustered units. The $CnH2n-1$ and $CnH2n$ peaks in alkenes are more prominent than the $CnH2n+1$ peak in alkanes. The presence of double bonds facilitates the formation of resonance-stabilized cations, with allylic cleavage leading to the production of an allylic cation. Determining the position of double bonds in each molecule can be challenging, and reference spectra are often required due to double bond migration. Additionally, cyclic alkenes can undergo retro-Diels-Alder fragmentation.

4.0 Fragmentation of Aromatics

When a compound contains an aromatic ring, it typically produces a noticeable molecular ion. If a hydrogen molecule is removed from the benzene ring, a common peak at M - 1 is observed. Benzene rings that have alkyl substituents generate a peak at m/z 91, which is usually caused by a tropylium ion resulting from rearrangement. Additionally, the peak at m/z 65 observed in most aromatic compounds is due to the elimination of an acetylene molecule from the tropylium ion. If the benzene ring has highly branched substituted groups, the resulting fragments will be larger than m/z 91 and will increase in intervals of 14 units, resulting in highly substituted cations and large radicals like simpler branched alkanes. The fragment at m/z 105 is relatively small since it produces a primary carbocation and an unstable methyl radical. Substituted benzene rings undergo ά cleavage followed by hydrogen rearrangement, which produces peaks at m/z 77 from $C6H5+$, m/z 78 from $C6H6+$, and m/z 79 from $C6H7+$. Side chains with more than two carbon atoms create a peak at m/z 92, with unbranched groups producing a more prominent peak than branched groups.

4 Methodology and Materials

4.1 Gas Chromatography-Mass Spectrometry (GC/MS)

Gas chromatography-mass spectrometry (GC-MS) is a powerful analytical technique used to identify and quantify the components of complex mixtures. It combines two separate techniques - gas chromatography and mass spectrometry - to provide a highly selective and sensitive method for the analysis of organic compounds.

Gas chromatography involves separating the components of a mixture based on their relative affinity for a stationary phase and a mobile phase. In GC-MS, the stationary phase is typically a solid or liquid coating on a column, and the mobile phase is an inert gas such as helium. The sample is injected into the column, and as it travels through the column, the different components of the mixture interact differently with the stationary phase, leading to their separation. The time it takes for a component to travel through the column is known as its retention time, and this can be used to identify the component.

Mass spectrometry involves ionizing the separated components and then measuring the mass-to-charge ratio (m/z) of the resulting ions. In GC-MS, ionization is typically done using electron ionization (EI), which involves bombarding the molecules with high-energy electrons, causing them to fragment into smaller ions. These ions are then separated based on their mass-to-charge ratio using a magnetic field or electric field. The resulting mass spectrum provides a unique fingerprint of the molecule, which can be used to identify it.

The combination of gas chromatography and mass spectrometry provides a highly sensitive and selective method for the analysis of complex mixtures. The separation provided by gas chromatography allows for the isolation of individual components, while mass spectrometry provides highly specific identification of those components.

GC-MS is widely used in a variety of fields, including environmental analysis, forensics, pharmaceuticals, and food analysis. In environmental analysis, GC-MS is used to identify and quantify pollutants in air, water, and soil samples. In forensics, GC-MS is used to identify drugs and other compounds in blood and urine samples. In pharmaceuticals, GC-MS is used to monitor the purity and potency of drugs. In food analysis, GC-MS is used to detect and quantify contaminants such as pesticides and mycotoxins.

There are several different modes of mass spectrometry that can be used in GC-MS, each with its own advantages and disadvantages. Electron ionization (EI) is the most used mode, as it provides highly reproducible spectra and is well-suited for the identification of small molecules. Chemical ionization (CI) is a softer ionization technique that can be used to ionize larger molecules, but it is less reproducible than EI. Electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) are soft ionization techniques that are typically used for the analysis of larger molecules such as peptides and proteins.

GC-MS is a highly versatile analytical technique that provides a wealth of information about the components of complex mixtures. It is widely used in a variety of fields and is an essential tool for the identification and quantification of organic compounds. As the technology continues to improve, GC-MS is likely to become even more powerful and widely used in the years to come.

4.2 Process Analysis
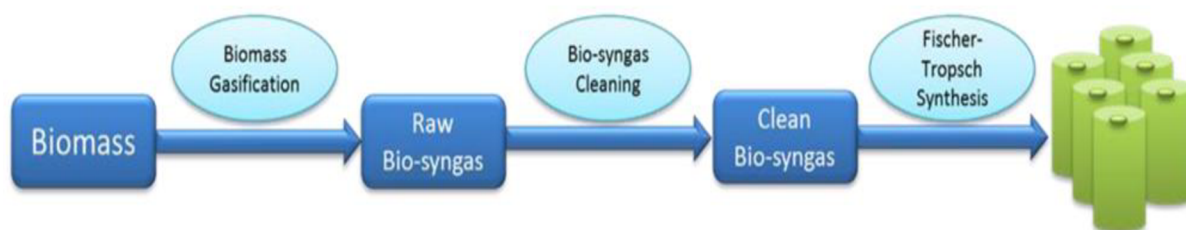
Flow sheet of the Biomass to Liquid via Fischer–Tropsch Synthesis (BTL-FT) process.

Mass Spectral peaks can be identified to have originated from the fragmentation of specific hydrocarbon sources including:

Alkanes: m/z = 57 / 43.
Alkenes: m/z = 55 / 41
Aromatics: m/z = 75-78, /130-138

Compound type	Common lines
Alkanes	29, 43, 57, 71, 85, 99
Alkenes/cycloalkanes	27, 41, 55, 69, 83, 97
Aliphatic alcohols	31, 45, 59, 73, 87, 101
Aromatics	38, 39, 50-2, 63-5, 75-8
Acids/esters	45, 59, 73, 87, 101
Alkyl amines	30, 44, 58, 72, 86, 100
Chloroalkyl	49, 63, 77, 91, 105
Alkyl silanes	31, 45, 59, 73, 87, 101

4.3 Searchable Databases

The abundance of databases and their extensive compound collections have reduced the significance of interpreting spectra. The National Institute of Standards and Technology (NIST) and the Wiley Registry of Mass Spectral Data are the most frequently used databases, encompassing more than 200,000 compounds. While these databases are valuable in routine analysis and sometimes the only means to identify a compound, they should not be the sole tool for chemical interpretation. Like any tool, it is crucial to understand how and when to use them. Databases are useful for routine analysis when there is a high degree of match between the analyte and the reference standard. However, when the match quality deteriorates, it is essential to evaluate the accuracy of the database match. In addition, comprehending the fragmentation patterns is vital, particularly when synthesizing new compounds that are not present in published databases, and when there is no reference compound. To correctly identify the composition of an unknown sample, manual interpretation combined with the usage of a library is essential.

4.4 Experimental Part

4.4.1 Analytical conditions on the GC/MS (IT) system

o GLC: Varian 3800 (USA)
o Column   CP-Sil-8: length 30 m, internal diameter 0.25 mm, the thickness of stationary phase film 0.25 mm, CP-index =8
o Overpressure of carrier gas (He)   80 kPa (linear velocity 1.0 ml/min)
o Temperature program   40 ^{0}C – 5 min, 10 ^{0}C/min – 220 ^{0}C – 7 min
o Injector/transfer line temperature   280 ^{0}C / 180 ^{0}C
o Injection volume/split   0.5 μl / spitless.

o Mass spectrometer (MS)   Varian Saturn 2000 (USA)
o EI:
o Mode: Positive (EI-plus; EI$^+$)
o Scan range   11 – 400
o Scan velocity   3 Scan/min (0 - 3 min scanning free area)
o AGC targets   20 000
o Ion trap temperature   150 ^{0}C
o CI:
o Ionization medium   Methanol
o Scan range CI   50 - 400
o Scan velocity   3 Scan. /Min (0 - 3 min scanning free area)

o ARC target   5 000
o Ion trap temperature   150 ^{0}C
o Max. Ionization time   2 000 μs
o Max. Reaction time   40 μs
o Injector temp.   250 °C,

Samples:
#105 = light naphtha 35-85 °C (FT Litvínov)
#106 = benzene fraction 85-110 °C (FT Litvínov)
#107 = heavy naphtha 80-180 °C (FT Litvínov)

Note: Naphtha is a semi-processed substance that serves as a primary input for the petrochemical industry. It is primarily utilized in the production of ethylene, propylene, butylene, and other similar materials. This substance has a distillation range of 300°C to 2100°C or a narrower range. When naphtha is imported for blending, it is recorded as a negative entry on the naphtha side and a positive entry for the corresponding finished product, such as motor gasoline, under the "Transfers of intermediate products" category.

4.4.2 GC/MS Process

Sample Preparation: The first step in GC-MS analysis is sample preparation. The sample, which can be a gas, liquid, or solid, is typically extracted, purified, and concentrated to obtain a representative portion for analysis. This may involve techniques such as solid-phase microextraction (SPME), liquid-liquid extraction (LLE), or solid-phase extraction (SPE), depending on the nature of the sample.

Injection: The prepared sample is then injected into the GC system using an auto-sampler. In GC, the sample is typically vaporized and introduced into the chromatographic column as a discrete plug, known as an "injection." The sample is vaporized by heating in the injector, and the resulting vapor is carried into the column by a carrier gas, such as helium or nitrogen.

Separation: Inside the GC column, the sample components are separated based on their partitioning between the stationary phase (a liquid or solid coating on the column) and the mobile phase (the carrier gas). Each compound has a different affinity for the stationary phase, leading to its differential retention time, which is the time it takes for a compound to travel through the column and reach the detector. This separation process is critical in GC, as it determines the resolution and separation efficiency of the method.

Detection: As the separated compounds elute from the GC column, they pass through a detector, which measures their concentration. The most common detector used in GC-MS is a mass spectrometer, which allows for the identification and quantification of the separated compounds. In the mass spectrometer, the eluting compounds are ionized and fragmented into smaller charged particles, or ions, which are then separated based on their mass-to-charge ratio (m/z) and detected. The resulting mass spectra are unique to each compound and can be used for compound identification by comparing them to a reference library of mass spectra.

Data Analysis: The data obtained from the GC-MS analysis is processed and analyzed using specialized software. The chromatogram, which is a plot of detector response (signal) versus time, provides information on the retention times of the separated compounds. The mass spectra obtained from the mass spectrometer are used for compound identification by comparing them to a reference library of mass spectra. Quantification of the compounds is typically done by measuring the peak areas or heights in the chromatogram and relating them to known calibration standards.

Interpretation: Once the data is processed and analyzed, the results are interpreted to identify the compounds present in the sample and determine their concentrations. This may involve comparing the retention times and mass spectra of the separated compounds with reference standards or databases, as well as considering other factors such as the sample matrix, instrument parameters, and method validation.

GC-MS is a versatile and widely used technique in various fields, including environmental analysis, food and beverage analysis, forensic science, pharmaceutical analysis, and many others. It provides high sensitivity, selectivity, and accuracy in compound identification and quantification, making it a valuable tool in analytical

chemistry. However, it requires skilled operators and proper instrument maintenance to ensure reliable results.

Fundamental of GC-MS
(Diagram)

Regulator

Traps

sample inlet

Transfer line (Interface)

Chromatogram

Detector Amplifier

Column

Ion source

Mass Spectrometer

Detector

Control Electronics

Column Oven

chemwifi.com

vacuum System   Pump

inert Carrier Gas Mobile phase

GC
Stationary phase

MS
Detector

Computer
Data acquisition
+
Data analysis

Gas Cylinder
(He)

www.chemwifi.com
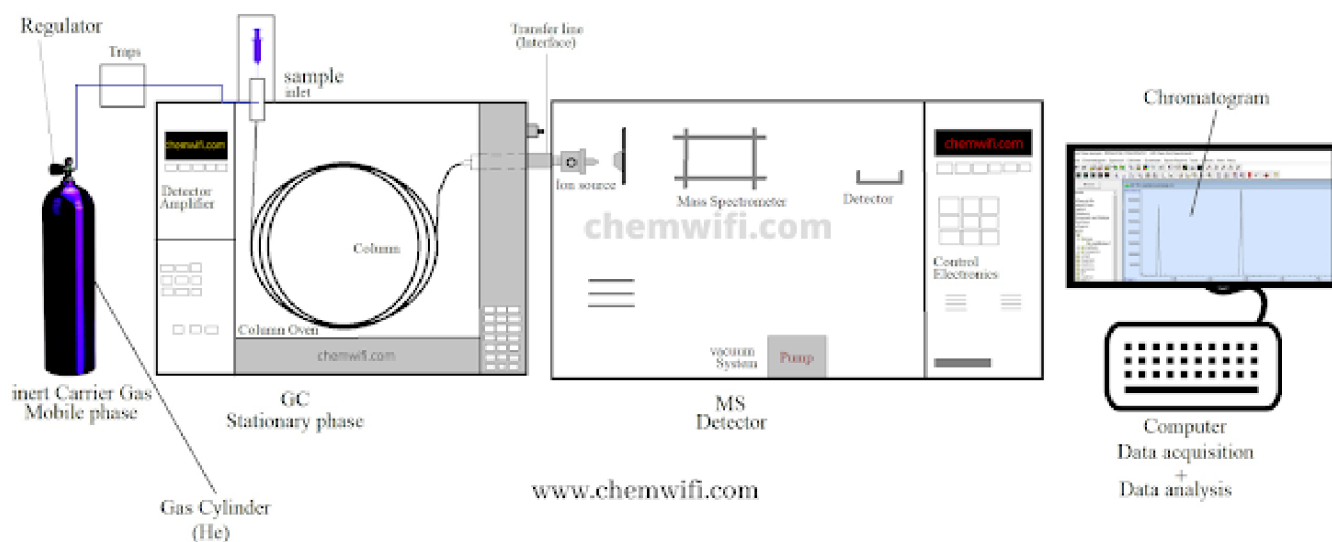
5   Results

GC/MS-Electron Impact (EI), positive mode. Sample #105 = light naphtha 35-85 °C (FT Litvínov)

FID
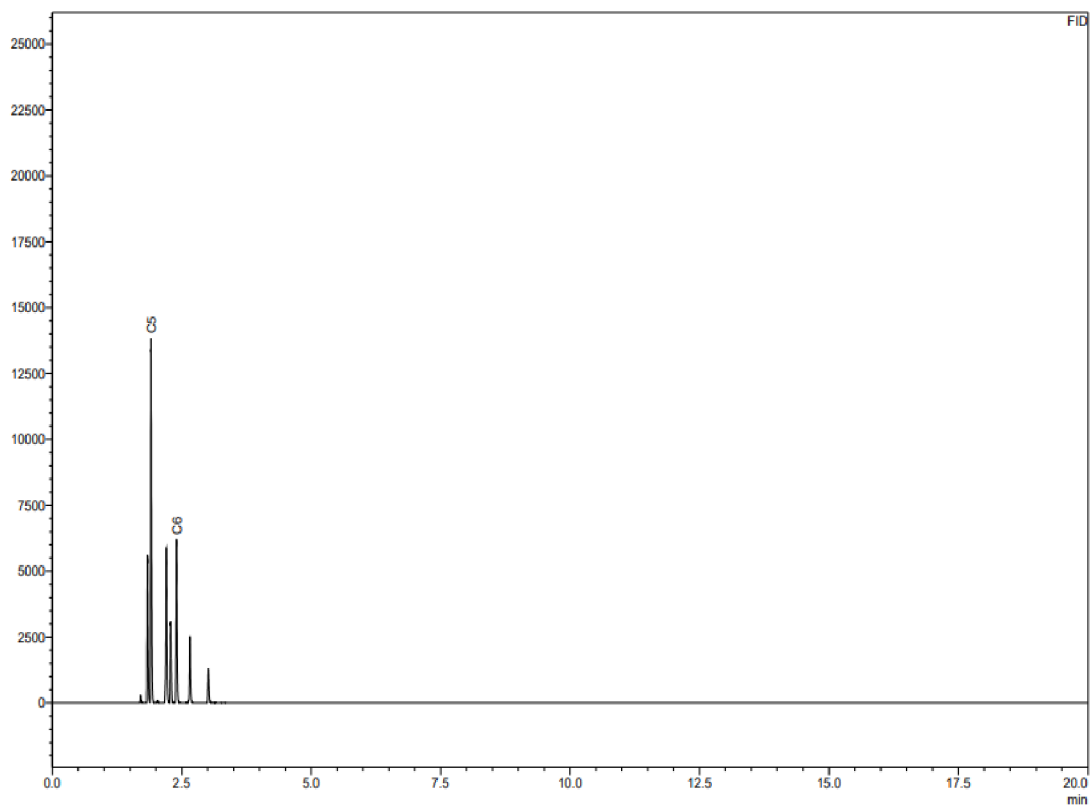
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	1.707	339210	299435	0.670		V	
2	1.835	6566906	5589065	12.974		V	
3	1.904	16662815	13824404	32.920	%	SV	C5
4	2.034	116587	93157	0.230		T	
5	2.199	8606354	5858544	17.003			
6	2.286	4060873	3087809	8.023		V	
7	2.403	8527465	6201234	16.847	%	SV	C6
8	2.585	26353	20180	0.052		T	
9	2.660	3677023	2508164	7.264		SV	
10	3.016	2011791	1289623	3.975			
11	3.142	21448	13352	0.042		V	
Total		50616823	38784968				

Figure1 Chromatogram of the sample #105 = light naphtha 35-85 °C (FT Litvínov)
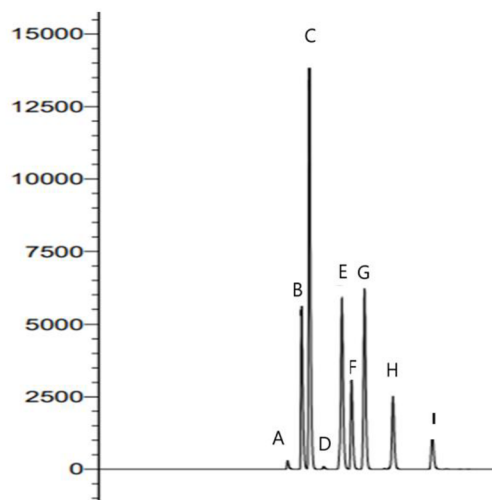
Figure 2 Detail of chromatogram of the sample #105 = light naphtha 35-85 °C (FT Litvínov)

A	**Neo-pentane**	**rt = 1.707 min**	**b.p. 10°C**
B	**2- Methyl butane**	**rt = 1.835 min**	**b.p. 28°C**
C	**Pentane**	**rt = 1.904 min**	**b.p. 37**
D	**Cyclopentane**	**rt = 2.034 min**	**b.p. 49°C**
E	**2-Methylpentane**	**rt = 2.199 min**	**b.p. 60°C**
F	**3-Methylpentane**	**rt = 2.286min**	**b.p. 63°C**
G	**Hexane**	**rt = 2.403 min**	**b.p. 69°C**
H	**Ethanol**	**rt = 2.660 min**	**b.p. 78°C**
I	**Benzene**	**rt = 3.016 min**	**b.p. 80°C**

GC/MS-Chemical Ionization by Methanol (CI)-positive mode of

sample #105 = light naphtha 35-85 °C (FT Litvínov)

		[M+1]$^+$	Mw [g/mol]
A	Methanol	33	32.04
B	2- Methylbutane	73	72.15
C	Pentane	73	72.15
D	1-Methylcyclopentane	85	84.16
E	2-Methylpentane	87	86.18
F	3-Methylpentane	87	86.18
G	Hexane	87	86.18
H	Ethanol	47	46.07
I	Benzene	79	78.11

GC/MS-Electron Impact (EI), positive mode, sample #106 = benzene fraction 85-110 °C (FT Litvínov)

FID
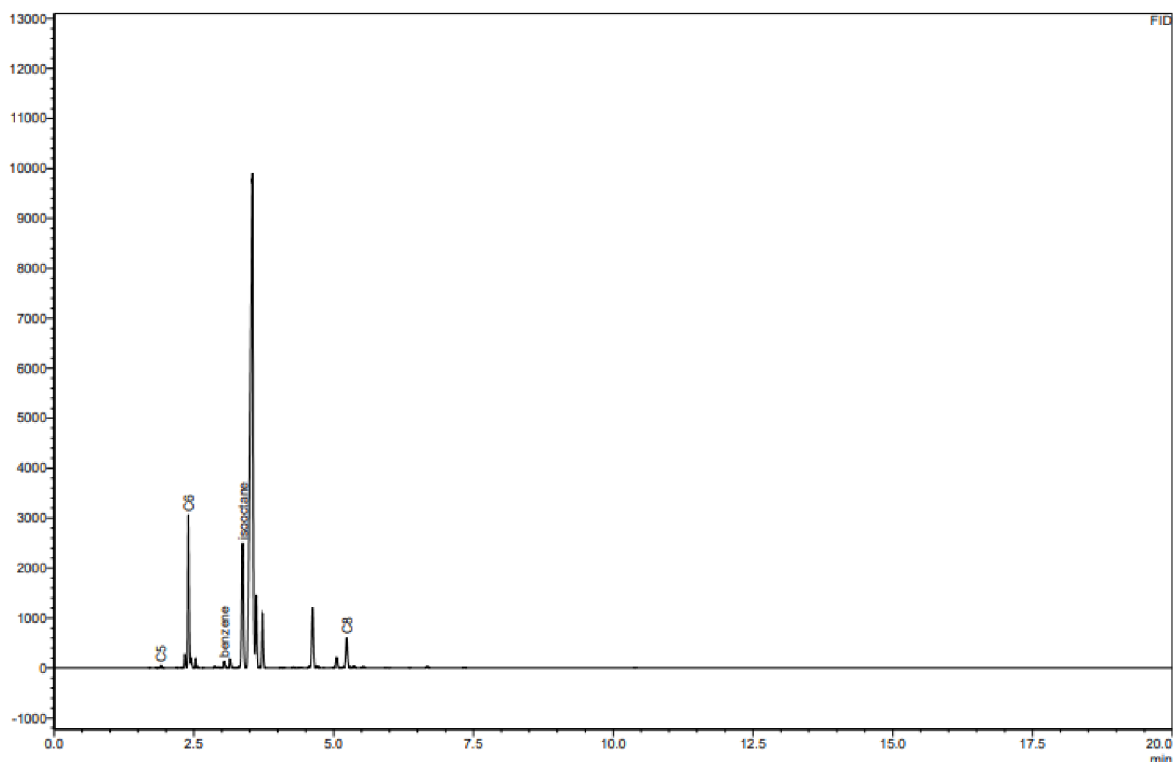
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	1.907	65038	49570	0.119	%	SV	C5
2	2.198	15671	10533	0.029		V	
3	2.287	18791	13970	0.034		V	
4	2.340	379658	276147	0.697		V	
5	2.401	4224628	3052166	7.754	%	V	C6
6	2.452	288234	192649	0.529		V	
7	2.532	280231	193074	0.514		SV	
8	2.874	49545	28273	0.091		V	
9	2.946	29467	15638	0.054		V	
10	3.037	261381	135020	0.480	%	V	benzene
11	3.150	317456	173408	0.583		V	
12	3.230	11131	5694	0.020		V	
13	3.371	5598245	2496545	10.275	%	V	isooctane
14	3.547	33979014	9901386	62.365		V	
15	3.612	2348375	1466770	4.310		SV	
16	3.728	1843550	1092673	3.384		V	
17	4.097	16998	7884	0.031		V	
18	4.280	29053	14779	0.053		V	
19	4.413	28940	9668	0.053		V	
20	4.562	55804	29584	0.102		V	
21	4.624	2519733	1198116	4.625		V	
22	4.707	75167	36463	0.138		V	
23	4.971	12299	5377	0.023		V	
24	5.053	447131	211752	0.821		V	
25	5.168	26967	12643	0.049		V	
26	5.231	1307228	602411	2.399	%	V	C8
27	5.360	89547	41992	0.164		SV	
28	5.528	53372	25369	0.098		V	
29	5.931	12435	5634	0.023			
30	6.672	65279	28668	0.120		SV	
31	7.342	23380	9784	0.043		V	
32	10.395	10596	4469	0.019		V	
Total		54484343	21348108				

Figure 11 Chromatogram of the sample #106 = benzene fraction 85-110 °C (FT Litvínov)
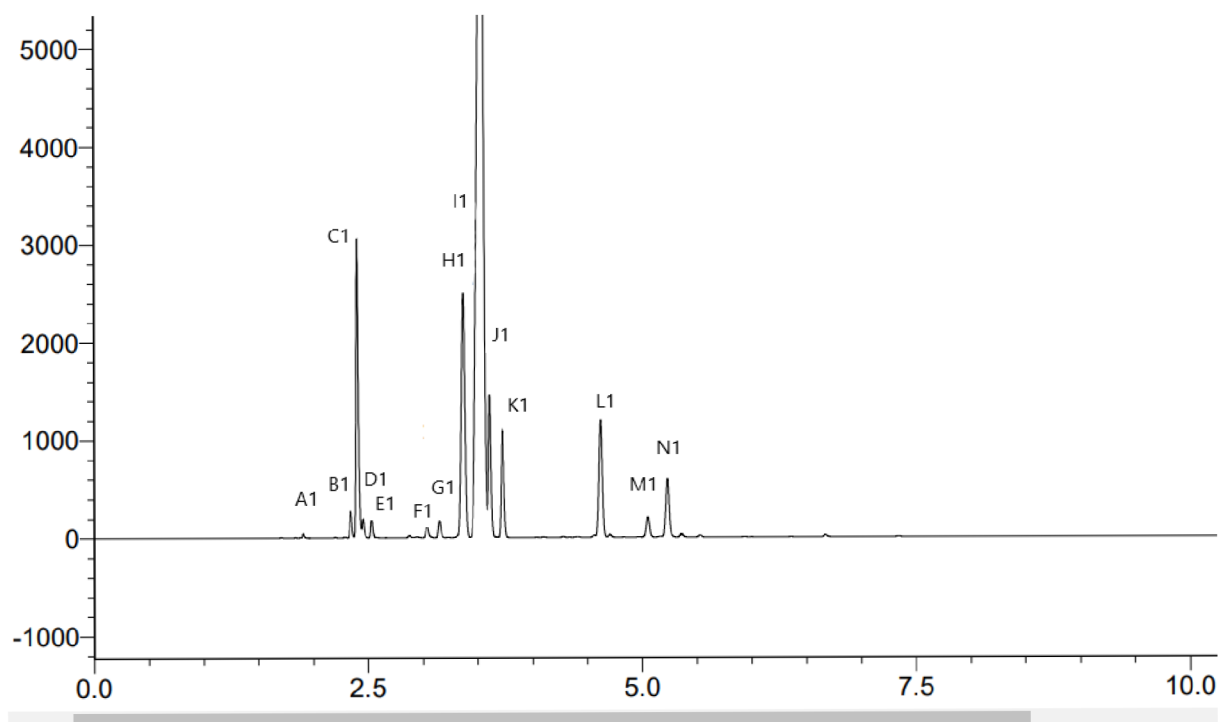
Figure 12   Chromatogram of the sample #106 = benzene fraction 85-110 °C (FT Litvínov)

A1	Methylbutane	rt = 1.907 min	b.p. 28°C
B1	2-Methylpentane	rt = 2.198 min	b.p. 60°C
C1	Hexane	rt = 2.401 min	b.p. 69°C
D1	Methylcyklopentan	rt = 2.452min	b.p. 72°C
E1	Cyklohexan	rt = 2.532 min	b.p. 81°C
F1	Benzene	rt = 3.037 min	b.p. 80°C
G1	Propan-2-ol	rt = 3.150 min	b.p. 83°C
H1	2-Methylhexane	rt = 3.371 min	b.p. 90°C
I1	3-Methylhexane	rt = 3.547 min	b.p. 92°C
J1	Heptane	rt = 3.612 min	b.p. 98°C
K1	Butan-2-ol	rt = 3.728 min	b.p. 100°C
L1	Methylcyclohexane	rt = 4.413 min	b.p. 101°C
M1	2-Methylheptan	rt = 4.624 min	b.p. 117°C
N1	Octane	rt = 5.231 min	b.p. 126°C

GC/MS-Chemical Ionization by Methanol (CI)-positive mode of the

sample #106 = benzene fraction 85-110 °C (FT Litvínov)

|		$[M+1]^+$	Mw [g/mol]
A1	2- Methylbutane	73	72.15
B1	2-Methylpentane	87	86.18
C1	Hexane	87	86.18
D1	2-Methylcyclopentane	85	84.16
E1	Cyclohexane	85	84.16
F1	Benzene	79	78.11
G1	Propan-2-ol	61	60.10
H1	2-Methylhexane	101	100.21
I1	2-Methylhexane	101	100.21
J1	Heptane	101	100.21
K1	Butan-2-ol	75	74.12
L1	Methylcyclohexane	99	98.18
M1	2-Methylheptan	115	114.23
N1	Octane	115	114.23

#107 = heavy naphtha 80-180 °C (FT Litvínov)

FID
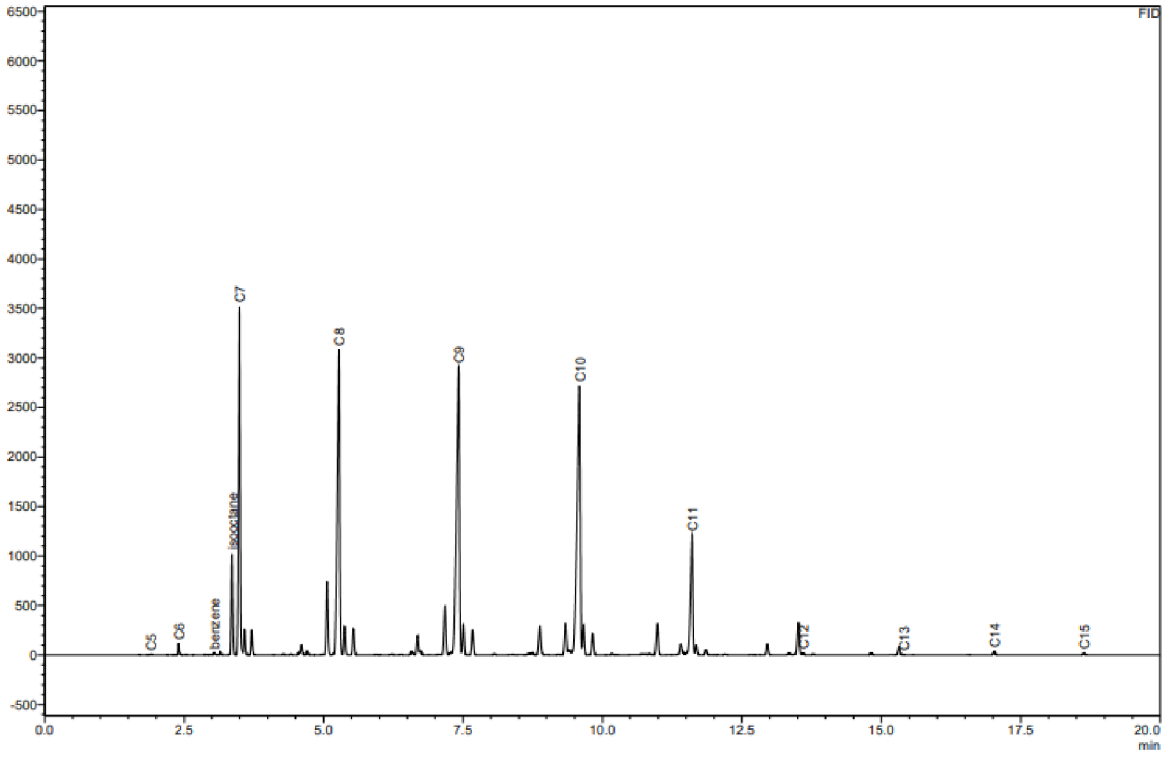
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	1.907	11589	8889	0.020	%	SV	C5
2	2.399	168739	115784	0.294	%	SV	C6
3	2.874	11249	6660	0.020		V	
4	3.036	46147	24897	0.080	%	V	benzene
5	3.148	58364	33731	0.102		V	
6	3.358	1839957	1019351	3.204	%	V	isooctane
7	3.494	7151585	3511558	12.452	%	V	C7
8	3.585	433027	253755	0.754		SV	
9	3.713	439208	251058	0.765		V	
10	4.280	21201	10609	0.037		V	
11	4.414	16287	7124	0.028			
12	4.559	49592	27954	0.086			
13	4.600	204404	101608	0.356		V	
14	4.708	85512	39732	0.149		SV	
15	4.977	14047	6289	0.024			
16	5.064	1666924	741354	2.902		V	
17	5.278	9414853	3087949	16.393	%	V	C8
18	5.374	564172	289467	0.982		V	
19	5.536	534837	264104	0.931		V	
20	5.934	15269	6829	0.027		V	
21	6.230	21972	8091	0.038		V	
22	6.389	18338	5550	0.032		V	
23	6.583	97652	33923	0.170		V	
24	6.685	435397	195134	0.758		V	
25	6.738	88272	41349	0.154		V	
26	7.054	16754	5951	0.029		V	
27	7.176	1254260	493852	2.184		V	
28	7.424	10845048	2903295	18.883	%	V	C9
29	7.506	642535	310605	1.119		V	
30	7.672	550159	251415	0.958			
31	8.058	24540	10557	0.043		V	
32	8.388	14810	5812	0.026		V	
33	8.692	55171	16880	0.096		V	
34	8.747	61249	24611	0.107		V	
35	8.876	752308	291060	1.310		V	
36	9.212	20387	6721	0.035		V	
37	9.337	871934	318024	1.518		V	
38	9.402	142568	46574	0.248		V	
39	9.590	10770325	2715947	18.753	%	V	C10
40	9.659	633999	304415	1.104		V	
41	9.825	479106	211892	0.834			
42	10.171	27391	11649	0.048		V	

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
43	10.261	10221	3490	0.018		V	
44	10.706	27340	10164	0.048		V	
45	10.770	28928	11257	0.050		V	
46	10.842	38355	14532	0.067		V	
47	10.984	781571	315146	1.361		V	
48	11.405	338778	110087	0.590		V	
49	11.607	3596671	1210337	6.262	%	V	C11
50	11.683	215606	96764	0.375		V	
51	11.857	127008	53659	0.221		V	
52	12.191	24865	7584	0.043		SV	
53	12.956	264469	111279	0.460		V	
54	13.347	56798	17282	0.099		V	
55	13.511	835292	325563	1.454		V	
56	13.599	44627	18297	0.078	%	V	C12
57	13.777	25323	10457	0.044		V	
58	14.817	50167	20113	0.087			
59	15.173	12112	3462	0.021		V	
60	15.316	216118	83787	0.376		V	
61	15.400	10403	4138	0.018	%	V	C13
62	17.021	84160	33273	0.147	%	V	C14
63	18.631	42094	15874	0.073	%	SV	C15
64	20.155	19730	7445	0.034		SV	
65	21.600	10643	3950	0.019		S	
Total		57432417	20509946				
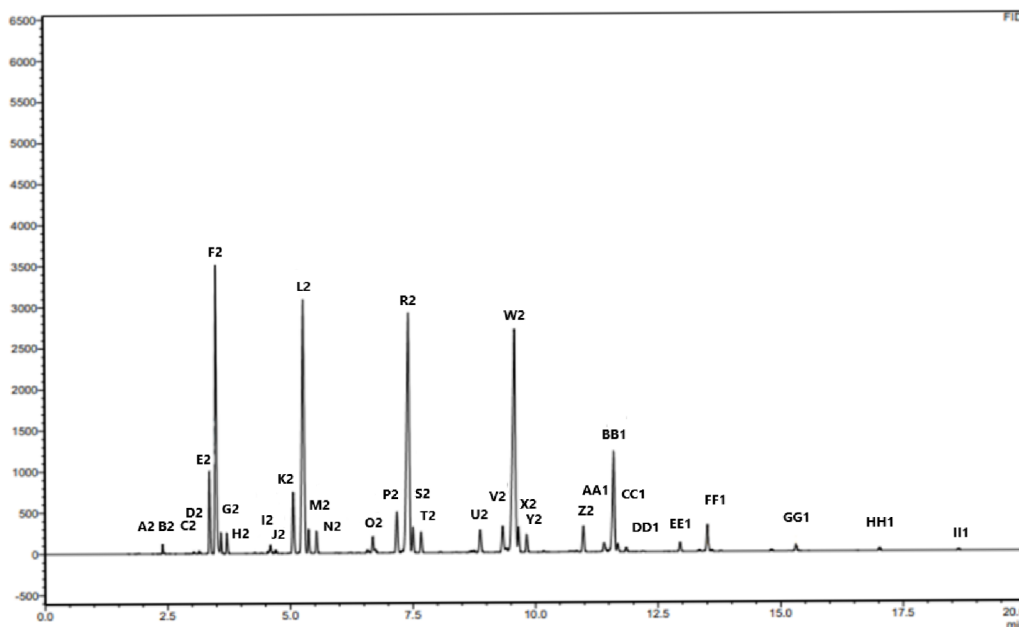
A2	Methylbutane	rt = 1.907 min	b.p. 28°C
B2	2-Methylpentane	rt = 2.399 min	b.p. 60°C
	Ethanol	rt = 2.874 min	b.p. 78°C
C2	Benzene	rt = 3.036 min	b.p. 80°C
D2	Propan-2-ol	rt = 3.150 min	b.p. 83°C
E2	2-Methylhexane	rt = 3.358 min	b.p. 90°C
F2	3-Methylhexane	rt = 3.494 min	b.p. 92°C
G2	Heptane	rt = 3.585 min	b.p. 98°C
H2	Butan-2-ol	rt = 3.713 min	b.p. 108°C
I2	Toluene	rt = 4.280 min	b.p. 110°C
J2	Butan-1-ol ě	rt = 4.559 min	b.p. 116°C
K2	2-Methylheptan	rt = 5.064 min	b.p. 117°C
L2	3-Methylheptan	rt = 5.278 min	b.p. 118°C
M2	Pentan-2-ol	rt = 5.374 min	b.p. 119°C
N2	Octane	rt = 5.536 min	b.p. 126°C
O2	Pentan-1-ol	rt = 6.685 min	b.p. 138°C
P2	2-Methyloctane	rt = 7.176 min	b.p. 142°C
R2	3-Methyloctane	rt = 7.424 min	b.p. 144°C
S2	Nonane	rt = 7.506 min	b.p. 151°C
T2	Hexan-2-ol	rt = 8.876 min	b.p. 136°C
U2	Hexan-1-ol	rt = 9.337 min	b.p. 144°C

6 Discussion

Fischer-Tropsch synthesis for biomass to syngas is a promising technology with the potential to contribute to renewable energy production, reduce greenhouse gas emissions, and promote sustainable use of biomass resources. However, there are several important discussions around its technical feasibility, economic viability, environmental sustainability, fuel quality, and policy frameworks that need to be considered to enable its widespread adoption as a renewable energy solution.

Production of biomass to biofuel has three different fractions and three different samples. There are. Growing boiling point and quality of gasoline compounds we found.

Here we have three samples for GC/MS-Chemical Ionization by Methanol (CI)-positive mode.

light naphtha 35-85 °C, benzene fraction 85-110 °C and heavy naphtha 80-180 °C.

In all the samples we found some liner hydrocarbon, cyclic hydrocarbon, aromatic compound, and alcohol.

Here, we found some liner hydrocarbon Hexane (C_6H_{14}), Benzene (C_6H_6) aromatic hydrocarbon and some alcohol as ethanol (C_2H_5OH) in light Naphtha.

Linear hydrocarbon Hexane(C_6H_{14}),2-Methylhexane(C_7H_{16}), Heptane(C_7H_{16}), 2-Methylheptane (C_8H_{18}), Octane(C_8H_{18}) and Methylcyclopentane(C_6H_{12}), Cyclohexane (C_6H_{12}), Methylcyclohexane(C_7H_{14}) are Cyclic hydrocarbon from Benzene fraction.

Aromatic hydrocarbon Toluene C_7H_8, C_7H_{16} Heptane Liner hydrocarbon form heavy Naphtha.

(FT) synthesis is a catalytic process that converts syngas (a mixture of carbon monoxide and hydrogen) into hydrocarbons, including linear hydrocarbons. The catalyst can be either iron-based or cobalt-based and plays a critical role in determining the selectivity and properties of the hydrocarbon products. Linear hydrocarbons are important in the context of FT synthesis because they have a higher cetane number, which is a measure of their combustion quality in diesel engines. The properties of linear hydrocarbons produced via FT synthesis can be tailored by adjusting the process parameters, such as temperature, pressure, and catalyst composition. FT synthesis has been widely studied and used commercially to produce linear hydrocarbons, which can be further processed and refined to produce a variety of fuels and chemicals. It offers the potential for producing hydrocarbons from a variety of feedstocks, making it a versatile and promising technology for hydrocarbon production.

The production of cyclic hydrocarbons in the FT process can be influenced by various factors, such as process conditions, catalyst properties, and feedstock composition. Properties such as ring size, molecular weight, boiling point, and reactivity can be controlled by adjusting the process parameters and catalyst properties. Cyclic hydrocarbons produced from the FT process have a wide range of potential applications, such as fuels, chemicals, and feedstocks to produce polymers. The ability to produce cyclic hydrocarbons from different feedstocks offers opportunities for the sustainable production of valuable chemicals and fuels from diverse and abundant carbon sources.

FT synthesis typically produces linear and branched hydrocarbons, but aromatic hydrocarbons can be formed as byproducts or minor components. FT synthesis produces aromatic hydrocarbons with molecular weight, boiling point, and reactivity that can be controlled by adjusting process parameters and catalyst properties. These hydrocarbons can be used in the production of chemicals, plastics, and

specialty fuels, but may require additional processing or treatment to meet specific product specifications or regulatory requirements. Research and development efforts are ongoing to optimize FT synthesis to produce aromatic hydrocarbons and other value-added products.

Aromatic hydrocarbons, such as benzene, toluene, and xylene, are used as fuels due to their high energy content and combustion properties.

Cyclic hydrocarbons, such as cyclohexane, cyclopentane, and cyclooctane, are also used as fuels due to their high energy content and desirable combustion properties.

Linear hydrocarbons, such as methane, ethane, propane, and butane, are used as components in natural gas, liquefied petroleum gas (LPG), and as fuels for heating, cooking, and transportation.

7 Conclusion

GC/MS techniques were used to analyze sample #105, which is a light naphtha with a distillation range of 35-85°C (FT Litvínov). The analysis revealed the presence of linear alkanes, a small number of branched alkanes, and a negligible number of cyclic alkanes (specifically, methyl cyclopentane) and aromatic alkanes (benzene). No alkenes or other unsaturated hydrocarbons were detected. However, a small amount of ethanol was detected, but it is likely a contaminant and should be confirmed through further analysis if its presence is significant.

Using GC/MS techniques, a set of substances has been identified in sample #106, which is a benzene fraction with a temperature range of 85-110°C that originated from the FT Litvínov refinery. The substances present in the sample include linear alkanes, some branched alkanes, a small number of cyclic alkanes (specifically, cyclohexane and methylcyclohexane), and an aromatic alkane (benzene). There was no detection of alkenes or other unsaturated hydrocarbons. Additionally, a negligible quantity of alcohols (Propan-2-ol and Butan-2-ol) was found.

By using GC/MS techniques, a series of substances present in sample #107 have been identified, which is a heavy naphtha with a temperature range of 80-180°C that originated from the FT Litvínov refinery. The sample consists of linear alkanes, a certain number of branched alkanes, a small number of cyclic alkanes, and an aromatic alkane (benzene). No detection of alkenes or other unsaturated hydrocarbons has been found. In addition, a certain amount of alcohol has also been detected.

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