Dissertation

Alternative Feedstocks from Waste and Renewable Resources in the FCC Process for a Sustainable Production of Light Olefins and High-Octane Gasoline

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submitted at TU Wien, Faculty of Mechanical and Industrial Engineering, by

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Danksagung

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Abstract

The goal of this work was the assessment of co-feeding of sustainable alternative feedstocks from either waste or renewable sources with vacuum gas oil in a fluid catalytic cracking pilot plant. Multiple studies, outlined below, were conducted to determine the influence of the alternative feedstocks lipstick mass, pyrolysis oils from plastic waste and pyrolysis oils from biomass on the product and the processability of the feedstock combination. Furthermore, studies for the better understanding of the pilot plant as well as a study of different batches of vacuum gas oil were conducted.

Lipstick mass was treated in order to reduce the ash content and afterwards tested as a possible co-feed. This experimental series was done in regard to the recycling of unsold lipstick where lipstick mass accrues as one of the fractions. In this feasibility study treated lipstick mass brought promising results and was confirmed to be a usable co-feed in the fluid catalytic cracking process.

Two distillation fractions of a pyrolysis oil produced from mixed plastic waste were tested as co-feed in the fluid catalytic cracking process. This was done in terms of plastic recycling using the produced light olefins as monomers for plastic production. The lighter fraction, which is called “Heavy SynCrude” amounted in admixtures of 5 wt%, 10 wt% and 20 wt% to nearly the same results as pure vacuum gas oil. The heavier fraction, “Distillation Residue”, caused difficulties at an admixture of 20 wt% due to its high ash content but was processable at an admixture of 10 wt%. The producer strives to increase the quality of Distillation Residue by reducing the ash content as well as the Conradson Carbon Residue value to make it a desirable co-feed.

As part of the project Waste2Road, pyrolysis oils from pine wood, sunflower husks and contaminated wood of different treatment grades were tested for their usability as co-feed, as well as their influence on the products. All in the fluid catalytic cracking pilot plant tested substances caused to a certain degree issues with the feeding system of the pilot plant. Only the pyrolysis oil from sunflower husk was not usable as co-feed in the pilot plant, due to the amount of solids formed when it was combined with vacuum gas oil. None of the other feeds reduced the hydrocarbon gas and gasoline quality of the products compared to the results of hydrogenated vacuum gas oil.

An important comparison done during this thesis was between different vacuum gas oil batches, highlighting the differences in the product spectrum which occur due to the quality of the crude oil used in the refinery at that time.

Zusammenfassung

Das Ziel dieser Arbeit war die Bewertung des Co-Feeding von nachhaltigen alternativen Rohstoffen aus Abfall oder erneuerbaren Quellen mit Vakuumgasöl in einer Fluid Catalytic Cracking Pilotanlage. Ziel war es, den Einfluss der alternativen Einsatzstoffe Lippenstiftmasse und unterschiedlicher Kunststoff- und Biomassepyrolyseöle auf das Produkt und die Verarbeitbarkeit der Einsatzstoffkombination zu ermitteln. Darüber hinaus wurden Studien zum besseren Verständnis der Pilotanlage sowie eine Untersuchung verschiedener Chargen von Vakuumgasöl durchgeführt.

Lippenstiftmasse wurde behandelt, um den Aschegehalt zu reduzieren, und anschließend als möglicher Co-Feed getestet. Diese Versuchsreihe wurde im Hinblick auf das Recycling von unverkauftem Lippenstift durchgeführt, wobei die Lippenstiftmasse als eine der Trennfraktionen anfällt. In dieser Machbarkeitsstudie brachte die behandelte Lippenstiftmasse hervorragende Ergebnisse und kann als brauchbarer Co-Feed im Fluid Catalytic Cracking Prozess angesehen werden.

Zwei Destillationsfraktionen eines aus gemischten Kunststoffabfällen hergestellten Pyrolyseöls wurden als Co-Feed im Fluid Catalytic Cracking Prozess getestet. Dies geschah im Sinne der Entwicklung eines Kunststoffrecyclingverfahrens für gemischte Kunststoffabfälle durch die Verwendung der im FCC-Pozess produzierten leichten Olefine als Monomere für die Kunststoffherstellung. Die leichtere Fraktion, mit dem Namen Heavy SynCrude, erzielte in Beimischungen von 5 wt%, 10 wt% und 20 wt% nahezu die gleichen Ergebnisse wie reines Vakuumgasöl. Die schwerere Fraktion „Distillation Residue“ bereitete bei einer Beimischung von 20 wt% aufgrund ihres hohen Aschegehalts Schwierigkeiten, war aber bei einer Beimischung von 10 m% verarbeitbar. Der Hersteller plant die Qualität von Distillation Residue durch Vorbehandlung weiter zu steigern, indem er den Aschegehalt sowie den Conradson Carbon Residue Wert reduziert, um einen besser geeigneten Co-Feed zu generieren.

Im Rahmen des Projektes Waste2Road wurden Pyrolyseöle aus Kiefernholz, Sonnenblumenresten der Pflanzenölindustrie und kontaminiertem Holz mit unterschiedlichen Behandlungsgraden auf ihre Verwendbarkeit als Co-Feed sowie ihren Einfluss auf die Produkte getestet. Alle getesteten Substanzen verursachten bis zu einem gewissen Grad Probleme mit dem Zuleitungssystem der Pilotanlage. Lediglich das Pyrolyseöl aus Sonnenblumenresten war als Co-Feed in der Pilotanlage nicht verwendbar, wegen der Menge an Feststoff die bei der Vermischung mit Vakuumgasöl entstand. Keine der getesteten Mischungen verringerte die Kohlenwasserstoffgas- und Benzinqualität der Produkte in problematischem Maß im Vergleich zu den Ergebnissen von hydriertem Vakuumgasöl.

Ein wichtiger im Rahmen dieser Arbeit durchgeführter Vergleich war die Gegenüberstellung verschiedener Vakuumgasölchargen, der die Unterschiede im Produktspektrum aufzeigt, die sich aufgrund der Qualitätsunterschiede des zum Produktionszeitpunkt in der Raffinerie verwendeten Rohöls ergeben.

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1 Introduction

So much to do and so little time. This sentiment accompanies us in a lot of aspects of life. But it is also all too fitting to the fight against environmental pollution and climate change. This fight is a protracted one. Since at least the late 1800s countries have negotiated legal agreements addressing environmental problems [1] and now they are already planning ahead for thirty years or more.

To counteract global warming different climate targets were and are set by the EU. A rough summary of the important milestones and agreements concerning Europe is given in chapter 2.2. One of them being the reduction of CO_2-emissions until a net greenhouse gas emission of zero is reached [2], which equals a reduction of CO_2 emissions of at least 105 Mt CO_2 per year [3]. The goal of reaching net zero by 2050 is shared with the US and the UK. Russia and China plan to reach it in 2060 and India in 2070 [3]. Part of the path to this target is the decarbonization of the energy sector through integration of renewable energy sources. One of the interim goals is the reduction of net greenhouse gas emissions by at least 55 % until 2030 in comparison to 1990 [2]. figure 1 shows global CO_2 emissions since 1970 and the needed reductions until 2050 to meet the conditions for 2 °C scenarios (average temperature increases not more than 2 °C) and 1.5 °C scenarios (average temperature increases not more than 1.5 °C). The reduction of CO_2 emissions due to the COVID-19 pandemic can clearly be seen in the figure. The remaining carbon budgets (allowed future emissions to limit anthropogenic global warming) for 1.5 °C scenarios will be used up within 10 years with the current emission trends [3].

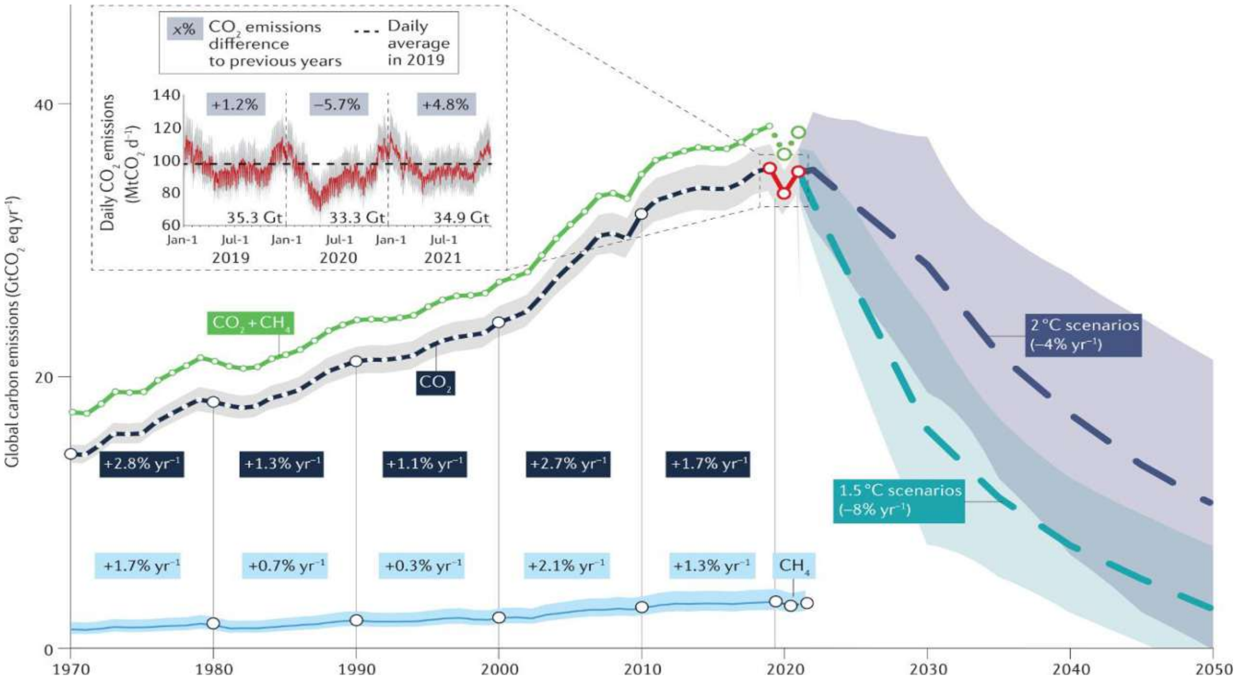


figure 1: Evolution of CO_2 (black blue), near-real-time CO_2 emissions (red), projected CO_2 emission mitigation pathways[1] (dark blue and aqua), and historical fossil CH_4 emissions (light blue). Solid/dashed lines and shading represent the median and range, respectively. Current emission trends will use up the allowed future emissions for limiting anthropogenic warming to 1.5 °C (the remaining carbon budgets) within 10 years. 'Reproduced with permission from Springer Nature' [3]

Austria’s CO_2 equivalent emission in 2021 was 77.5 Mt. Which is a reduction of 1.9 % from the 79.0 Mt emitted in the reference year 1990. The emissions from the sectors, mentioned in the ‘Klimaschutzgesetz’ were slightly higher than the allowed maximum amount from 48.8 Mt. [4]

Biofuel is one of the big buzzwords in discussions over CO_2-emission reduction. There are multiple types of biofuels, which can be differentiated in their application and/or production process. For some applications biomass can be used directly, e.g. wood for heating, but for many other applications it has to be refined, e.g. liquid fuel. There are a variety of different refinement methods for biomass, such as methylation of oils, fermentation to ethanol, gasification to syngas, pyrolysis just to name a few. The advantage of pyrolytic refinement methods is the use of the whole plant as well as the short process times.

Another important thematic for environmental pollution are plastics. For the majority of plastic types there are various environmental issues from cradle to grave, e.g. the descent from fossil oil, the release of micro plastics during use and the release of a variety of pollutants during disposal. According to the OECD in 2019 of 459.7 Mt of plastic that were used globally, 353.3 Mt ended up as waste [5]. Currently a big part of the produced plastic waste is incinerated or landfilled. figure 2 shows the growth trend of plastic production from 1950 to present including a projection of future growth until 2040, which is more than double the amount produced in 2018 [6]. To counteract this development the goal is to use biodegradable plastics and/or have a circular economy in place. As with biomass, pyrolysis offers a versatile possibility to process even highly degenerated and mixed plastic wastes.

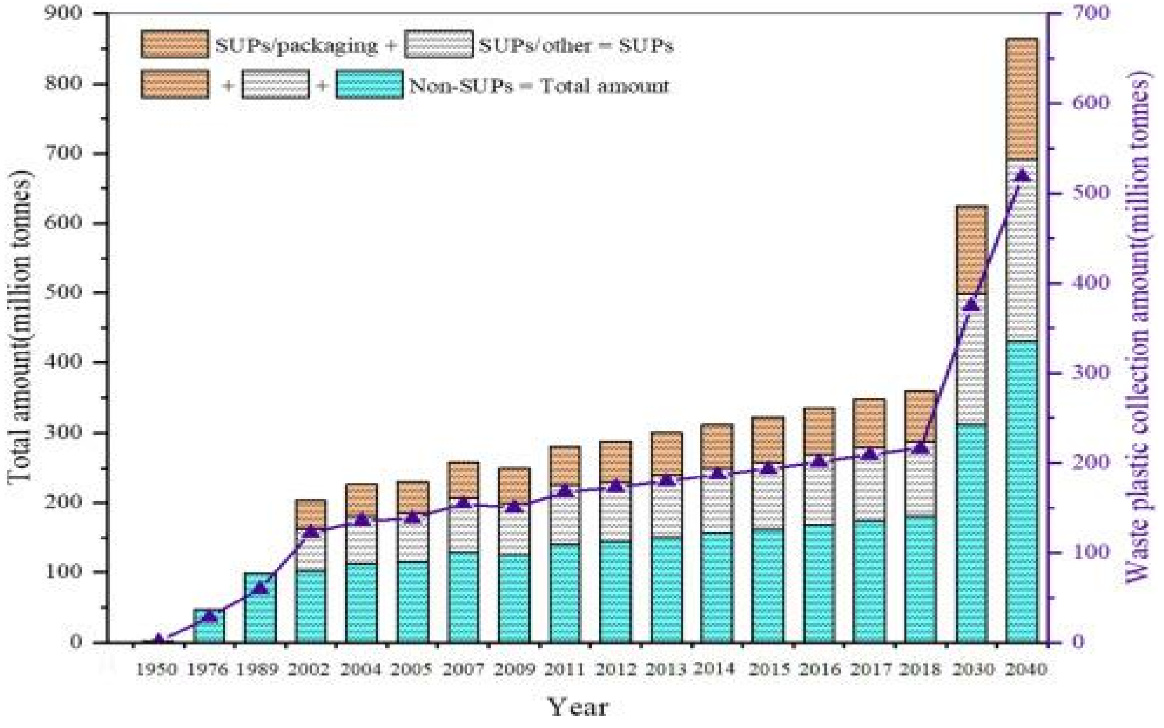


figure 2: Global plastic and single use plastic (SUP) production growth trends; Reprinted from [6] with permission from Elsevier

In order to use pyrolysis oils in high value applications further refinement is needed. Thus, research on pyrolysis oil refinement is in high demand, studies suggest that the typical refinement methods for fossil oil are suitable for pyrolysis oils as well.

The fluid catalytic cracking (FCC) process is one of the most relevant converting processes in petro-chemistry. Its robustness and versatility giving the impetus for the researched topics in this thesis. Over the years the focus of the FCC products has been shifting from gasoline to fine chemicals (e.g. educts for polymer production) [7]. Since more than 20 years, the research group ‘Wirbelschichtsysteme und Raffinerietechnik’ at TU Wien investigates feed alternatives to vacuum gas oil on their FCC pilot plant. As pioneers in their field they were able to publish multiple research on the use of plant oils [8]–[14] and different types of pyrolysis oils[15]–[20] as co-feeds in the FCC process.

It is crucial to understand, that the production of more sustainable fuels and plastics is not only important for the environment, but also gives a form of autonomy since fuels and raw materials can be produced locally. In current times the need for a certain degree of autonomy despite the global economy becomes painfully obvious. SARS CoV2 and the war between Russia and Ukraine have a big impact on the availability of resources like electricity, food, medicines and petrol products just to name a few of the most important ones.

This thesis looks at the role the fluid catalytic cracking process could play in future recycling of various types of waste and its potential contribution to the puzzle which is called sustainable development.

2 Fundamentals

2.1 Definition of Sustainable Development

In 1983, the UN appointed the World Commission on Environment and Development, now known as Brundtland Commission. In 1987, the Brundtland Commission published the report *Our Common Future*. In the report sustainable development is defined as meeting the needs of the present without compromising the ability to meet the needs of the future, with 'needs' being interpreted as the basic needs [21]. Maslow defines the basic needs as physiological and safety needs in his hierarchy of needs, encompassing food, water, warmth, rest, security and safety [22]. Maslow's hierarchy of needs is depicted in figure 3. An important point in guaranteeing sustainable development is the preservation of natural systems and the prevention of overexploiting natural resources.

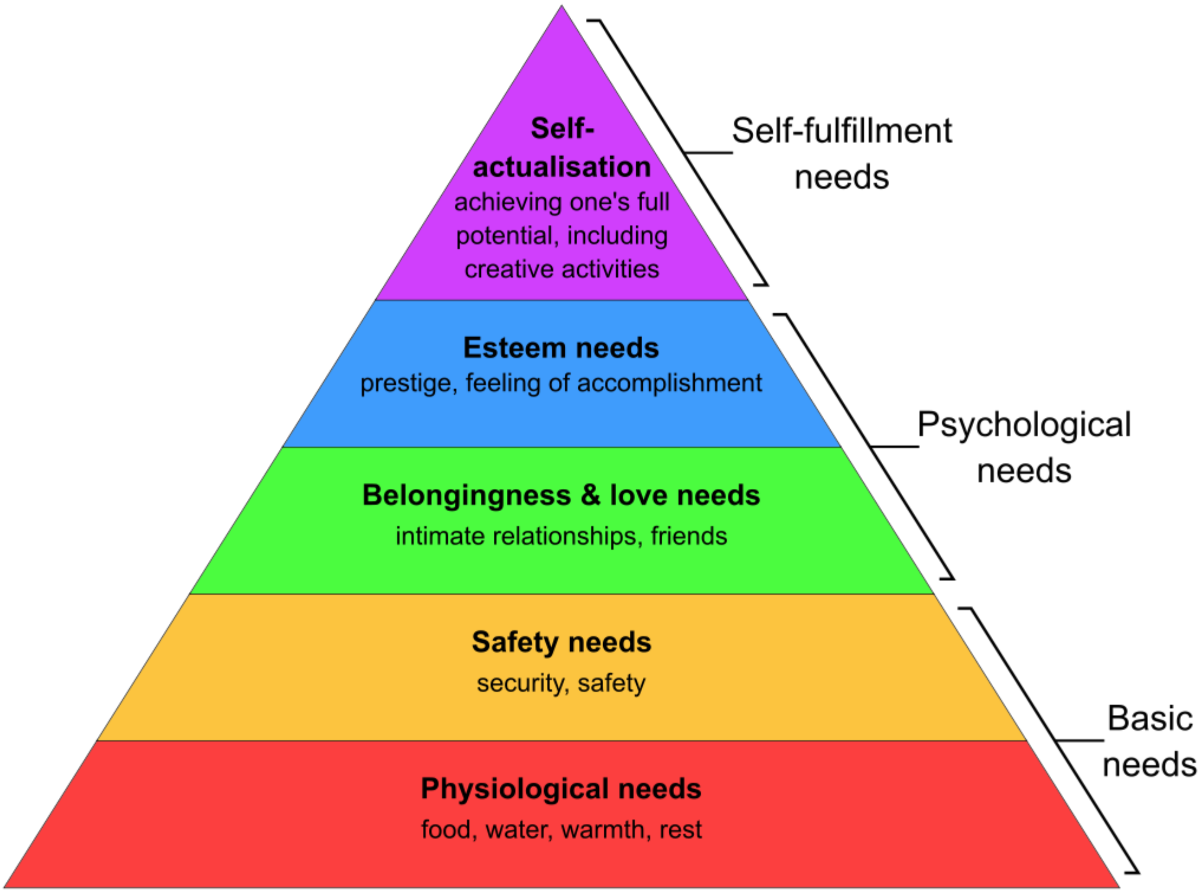


figure 3: Maslow's hierarchy of needs depicted as pyramid [22]

2.2 Europe and Environment

Our planet is one big ecosystem. Local changes can have an impact on the whole ecosystem or at least on big areas of it. This fact makes it so important for countries to pull together in the case of environment preservation. An example for different countries working in unison is the above-mentioned goal of net zero. In this chapter a short summary of the history of endeavors concerning environmental protection within Europe is given. figure 4 gives a graphic timeline for its milestones.

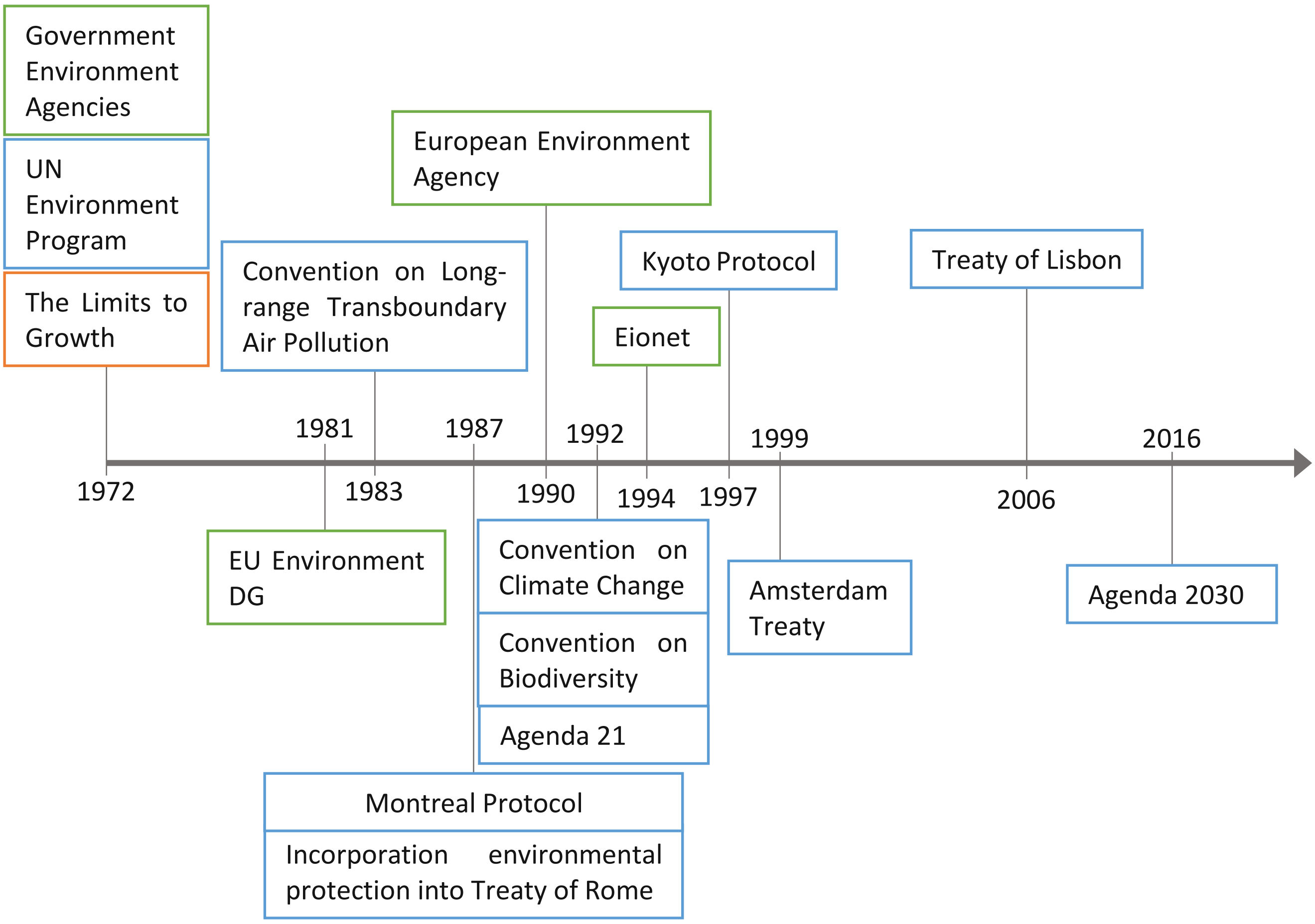


figure 4: Timeline of important milestones of environmental protection within Europe

In 1972, the Club of Rome published 'The Limits to Growth', which stated that the ultimate result of a continued attempt to grow according to the pattern present at the time of publication will be a disastrous collapse [23]. In the same year, the Conference on the Human Environment held by the United Nations (UN) led to the UN Environment Program and the creation of government environment agencies. Furthermore, the European Council founded the European environment policy and the first action program. Currently the EU's 8th Environment Action Programme to 2030 is in force. It was adapted in November 2022.

In 1973, a Standing Committee on the Environment was created in the European Parliament and a small Environment and Consumer Protection Service was attached to the European Commission department for industrial policy. Due to the impact of the Arab-Israeli war on the oil industry and the resulting problems in Europe energy efficiency came into focus.

The body of environmental legislation in the European Economic Community is adapted and expanded continuously. At the first Word Climate Conference in Switzerland, a panel on climate change set up by the National Academy of Sciences in the US pointed out that measures must be taken to avoid significant climate changes. In 1981, the department Environment Directorate-General is introduced. Directorate-General (DG) are departments of the EU government equivalent to ministries at a national level. The DG Environment (DG ENV) is responsible for the environmental policy of the EU.

Two years later, in 1983, the Convention on Long-range Transboundary Air Pollution of the UNECE (United Nations Economic Commission of Europe) entered into force. The convention intends to gradually reduce and prevent long-range transboundary air pollution and air pollution in general. It has since been extended by eight specific protocols, for example the protocol on further reduction of Sulfur emissions. Environmental protection was incorporated into the Treaty of Rome by the single European act in 1987. In the same year, the Montreal Protocol was finalized. It commits to phase out substances that deplete the ozone layer. The 1990 established European Environment Agency and the European environment information and observation network (Eionet, established 1994) were inspired by the Corine program (Coordination of Information on the Environment), which was established in 1985. Eionet is a network across several levels such as regional, national, European, international and civil society. Eionet offers a platform for timely and quality-assured data, information and expertise, by providing it in a common format via shared infrastructure. The Eionet portal hosts publicly accessible information as well as only internally available information[24], [25].

In 1992, at the UN summit on the environment and development in Rio de Janeiro the UN Framework Convention on Climate Change and the Convention on Biodiversity (Agenda 21) were signed. In the same year, the EU's 5th Environment Action Program shifted from regulatory measures to an emphasis on economic and fiscal measures.

The Kyoto Protocol from 1997 has set targets and deadlines for the reduction of global greenhouse gas emissions. In 1999, the EU adopted the Amsterdam Treaty, which states that environmental protection requirements are to be integrated into Community policies and activities. The goal to fight climate change was appointed in the Treaty of Lisbon (2009) [26]. After 24 years Agenda 21 (an action plan with guidelines for a sustainable development established in 1992) was replaced by Agenda 2030 in 2016. Agenda 2030 with the full title "Transforming our world: the 2030 Agenda for Sustainable Development" sets 17 goals, emphasizing the interconnection of different aspects of sustainable development.

2.3 Air Pollutants

Air pollutants are one of farthest-reaching contaminants on earth. They are spread by air movement. Polluted air from Asia can reach Austria within three weeks [27]. This circumstance makes the global observation and reduction of air pollutants especially crucial. Different air pollutants have different negative impacts on the environment and health.

Greenhouse gases (GHG's) absorb and emit radiant energy causing the greenhouse effect, which means they are keeping energy that would otherwise leave the atmosphere and thus heating up the atmosphere. In order to make the impact of different GHG's comparable the typically used method is the Global Warming Potential (GWP). In this method the reference substance chosen is CO_2. If something has a GWP of 20 this means that 1 kg of this substance over the course of its time in the atmosphere, has the same impact as 20 kg of CO_2.

Particulate matter (PM) refers to small particles of solid or liquid matter suspended in the air [28]. PM causes severe respiratory problems. $PM_{2.5}$, particulate matter with a diameter of 2.5 µm or less, count as the most harmful among air pollutants [28].

The air pollutants carbon dioxide, nitrogen oxides and sulfur oxides, which also concern gasoline production and usage, are described in more detail below. Because of that the behavior of nitrogen and sulfur during fluid catalytic cracking will also be addressed in more detail in chapter 2.7.4.

2.3.1 Carbon Dioxide - CO_2

As mentioned above CO_2 is a GHG which is emitted by both natural and anthropogenic sources. The Mauna Loa Observatory (MLO) was the first atmospheric research facility. It has been continuously monitoring the atmospheric CO_2 concentration since the 1950's. In 2021, 37.9 Gt CO_2 were emitted globally and the CO_2 concentration in the atmosphere was at 416.5 ppm which is 136.5 ppm (49 %) higher than pre-industrial levels [29]. In figure 5 the trend of CO_2 concentration in the atmosphere measured at MLO is depicted.

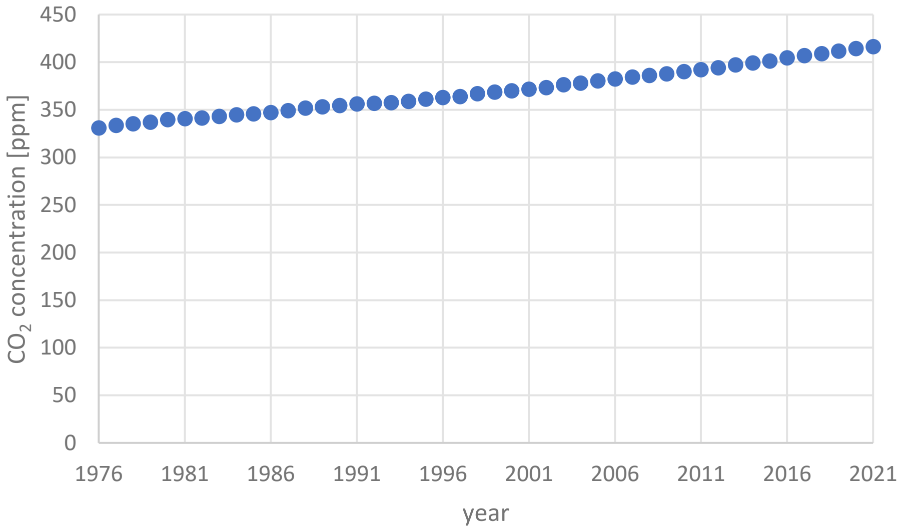


figure 5: CO_2 concentration in the atmosphere since 1976 [30]

In addition to the greenhouse gas effect CO_2 also forms carbonic acid in combination with water and thus it contributes to ocean acidification. Since the industrial revolution the pH of the ocean's surface water has dropped from 8.21 to 8.10 [31] affection maritime flora and fauna.

The European Union set different actions in order to reach climate neutrality by 2050 [32]. The package of proposals 'Fit for 55: delivering the EU's 2030 Climate Target on the way to climate neutrality' calls for a 90 % reduction in overall transport emissions by 2050. An important step in reaching this goal is the replacement of fossil fuel by sustainable fuel. The fluid catalytic cracking of biomass and wastes plays a big role in this endeavor.

2.3.2 Sulfur Oxides - SO_x

SO_2 and SO_3 are precursors for secondary particular matter (PM formed in the atmosphere), they also play an important part in the formation of acid rain (reaction equation (1) to (3)). In the 1980s the phenomenon of forest dieback due to acid rain triggered rigorous efforts to reduce the release of SO_2 and SO_3.

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3 \tag{1}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{3}$$

In 1980, Austria emitted 400 000 tons of SO_2, which was reduced to 91 000 tons in 1990 [33] mainly through implementation of flue gas treatment and reduction of the sulfur content in fossil fuels [34]. The European Community committed to a reduction from 16 436 000 tons in 1990 to 4 059 000 tons in 2010 [33] which amounts to a decrease by 75 %. This goal was reached in 2009 [35]. In 2019, the Austrian emissions of SO_2 amounted to 10 900 tons [34] which is a reduction of 97 % compared to 1980.

2.3.3 Nitrogen Oxides - NO_x

Nitrogen oxides are indirect GHG's since they take part in reactions which create GHG's like tropospheric ozone.

NO either reacts with oxygen in the air to form NO_2 (reaction equation (4)) or forms nitrous acid in water (reaction equation (5)). NO_2 forms nitrous acid and nitric acid (reaction equation (6)).

$$2\ NO + O_2 \rightarrow 2\ NO_2 \tag{4}$$

$$4\ NO + O_2 + 2H_2O \rightarrow 4\ HNO_2 \tag{5}$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{6}$$

Thus, nitrogen oxides, just like sulfur oxides, play a role in acid rain and formation of secondary PM.

The European Community committed in 2003/507/EC [33] to an emission ceiling from 6 671 000 t of NO_x as NO_2 in 2010. This goal was not reached since the emissions amounted to 8 510 000 t. In 2020, the European Union emitted 5 497 000 t of NO2 equivalent [36]. Austria committed to an emission ceiling of 107 000 t in 2010 [33], which was not reached due to an actual emission of over 200 000 t [37]. In 2019, the NO_x emissions of Austria amounted to 144 000 t of NO_2 equivalent [34].

2.4 History of Waste Recovery

The history of waste recovery is as old as the history of humans. Scarcity and poverty have always impelled humankind to reuse and adapt old materials to new ends. Even the humans from the Upper Paleolithic Age put their stone artefacts to multiple uses [38]. Nowadays more matters factor into the reasoning behind waste recovery including resource efficiency and environmental pollution in production and disposal. In this chapter a small overview of the history of waste recovery since industrialization is given. It is supposed to give some background to problems, solutions and desired goals in modern handling of waste.

As production was industrialized, the overall population increased. Cities accumulated more and more citizens and the consumption of resources proliferated. Linked to these changes, the generated waste streams also increased, resulting in local waste disposal problems, threatening human health and the environment. Landfilling, an end-of-pipe solution, should reduce the risk to human health and thus help with this growing problem, initially ignoring the broader environmental impacts and the poor resource efficiency. The first waste incineration plant was built in 1874 in Nottingham (United Kingdom), giving the go-ahead for the implementation of incineration as a tool of waste management. [39] Waste incineration reduces the volume of waste and thus the costs of final disposal. In the 1960s due to events like the foundation of the World Wildlife Fund, the first international environmental Non-Governmental Organization (1961), the publication of Silent Spring by Rachel Carson (1962) and the first supertanker accident, due to which 120000 t of oil leaked into the ocean, society started to focus more on environmental damage caused by humans. This change of attitude heightened the importance of sanitary landfilling, which should further reduce negative impacts of landfilling like odor and the leaching of hazardous pollutants. For example, by burning biodegradable waste in order to prevent methane formation in landfills, which has a higher global warming potential than CO_2.

In the 1970s the term ´recycling´, which originated in the 1920s, was applied to the environmental reprocessing of waste materials [40]. The increasing cost of energy not only encouraged recycling, to reduce the needed energy and the cost of materials, but also the energy production by waste incineration. Since recycling usually saves more energy than which is generated by incineration, it has a higher ranking in the waste management hierarchy [41]. Commonly used metals are a good example for the energy reduction that is enabled due to recycling. Depending on the metal, recycling uses 60 % - 97 % less energy than the production from mined material [42]. Furthermore half of greenhouse gas emissions stem from raw material production, hence recycling represents a great saving potential for greenhouse gas emissions [43].

Following waste management hierarchy is an example for the basis that forms modern waste management policies:

1. Reduce: prevention of waste generation
2. Reuse: reuse of products
3. Recycle: reuse of materials
4. Recover energy: transformation into heat, which can be used in industrial plants or for electricity generation
5. Dispose: sanitary landfilling

The targets of modern waste management not only include public and environmental health, but also sustainability and resource efficiency. The recycling of different waste streams can not only help in reducing the needed energy and raw materials for production, but also improve the security of material supply and helps to slightly increase resource autonomy. D. Dussaux and M. Glachant [44] found in a study including 21 countries that a 10 % growth in metal recovery leads to a 3.3 % decrease in metallic raw material imports. For this comparison it must be kept in mind, that the volume of metal recovery usually is smaller than the use of raw materials. N. Jacobe et. all [45] found that the share of secondary raw materials in processed materials in Austria was 8.5 % for 2014.

In Article 3 (17) of Directive 2008/98/EC [46] **recycling** is defined as: "*any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations*".

Recycling is usually practiced when it is technically possible, saves energy, emissions and/or money or if the primary raw material is scarce. **Downcycling**, is a form of recycling that refers to using the unwanted material in an application of less value than it was used before. Although downcycling is less favorable than recycling, it is more favorable than incineration and landfilling, when energy can be preserved or the impact on the environment can be reduced.

In 2012, the average person in Europe used 16 tons of materials. Only 40 % of the discarded material was recycled, leaving 60 % for incineration and landfilling [47]. In 2020, Europe landfilled 23 %, incinerated 27 %, recycled 30 % and composted 18 % (the remaining 2 % fall into the category other) of the 225.73 Mt municipal waste generated [48]. This is an increase of the recycling rate of almost 80 % and reduced the waste sent to landfills by more than 50 % since 2000 [48].Within the EU recycling rates still vary dramatically, from a high in Germany (45% of waste treated) to lows in the single digits (e.g. 1% in Romania, and 4% in Slovakia) [39].

Two other important terms related to waste management are sustainable materials management and Circular Economy. **Sustainable materials management (SMM)** is a multifaceted approach to efficient use of resources and materials linked with a reduction of environmental impact not only in production but throughout the whole life cycle of a product while taking economic efficiency and social equity into account [49]. There are different areas in which policies can be used to exert positive influence on the environment for the purpose of sustainable materials management. The main areas being handling of natural resources (decoupling their consumption from economic growth), product life cycles and waste management. The Council of the European Union adopted the SMM approach at the 3061st Environment Council meeting in 2010 [50]. **Circular Economy** is a concept with recycling at its core that fits seamless into the ideas of SMM. Circular Economy not only focuses on how to recycle existing waste streams, but also on how to redesign processes and products to reduce waste and produce waste that is easier to recycle[51].

Important goals concerning waste treatment set by the EU are given below [52]:

- Until 2030:
  - recycle rate for packaging of at least 70 %
- Until 2035:
  - Landfilling rate of maximum 10 %
  - Recycling rate for municipal waste of at least 65 %

Being able to utilize the FCC process for waste treatment will open a new pathway to further reduce incineration and landfilling. Especially for plastic wastes since recycling of mixed plastics with high quality of the product is not yet commercially available. This topic is further discussed in chapter 2.6.2.

2.5 Environmental Impact of Fossil Fuel

In 2008, the overall fossil fuel consumption produced nearly 30 Gt of CO_2 [53]. The biggest Greenhouse gas emission contributor of mankind, with 68 % (62 % from fossil fuel; 6 % from CH_4), is energy production [53]. 23 % of those energy-related emissions are produced by transport [54].

In 2006, global transport used 93,14 TJ equaling 5,47 Gt [55] of CO2 eq. [56]. In 2021, global transport CO_2 emissions reached nearly 7.7 Gt [57]. In April 2022 the average global consumption of liquid fuel is estimated to be 97.4 million barrels per day [58] (≈13.4 Mt per day).

The EU member states committed to reach an overall minimum target share of 40 % renewable energy [32] and an increase of renewable energy of 14 % [59] in transport by 2030 in order to reduce the consumption of fossil fuel. The package of proposals 'Fit for 55: delivering the EU's 2030 Climate Target on the way to climate neutrality' calls for a 90 % reduction in overall transport emissions by 2050 in order to reach the goal of climate neutrality [32].

In 2019, the gasoline consumption of the EU Member States amounted to 74 Mt [60]. Since around 20 - 40 % of the gasoline blend [7], [61]–[64] produced in refineries stems from the FCC process, one of the driving factors for the application of alternative co-feeds in the FCC process is the reduction of carbon content originating from fossil sources. A more detailed account of the role gasoline plays in transport is given in chapter 2.5.1.

The use of fossil fuel not only has an impact on climate change and CO_2 emissions but also goes hand in hand with the release of other pollutants which can cause health issues or damage to buildings and plant life. Devices with a small consumption of fossil fuel, like vehicles and heaters, have a high impact on health and local damage cost. Which is due to the release within a small area resulting in high exposure levels [65]. In figure 6 different environmental impacts of automotive fuels are compared such as greenhouse effect, ecotoxicity, Carcinogenic effects. The effect of biodiesel is mostly lower than these of petrol and diesel, expect for inorganic respiratory effects and ecotoxicity. Biodiesel has the highest inorganic respiratory effects out of the three fuels and its ecotoxicity is worse than that of diesel, but better than petrol.

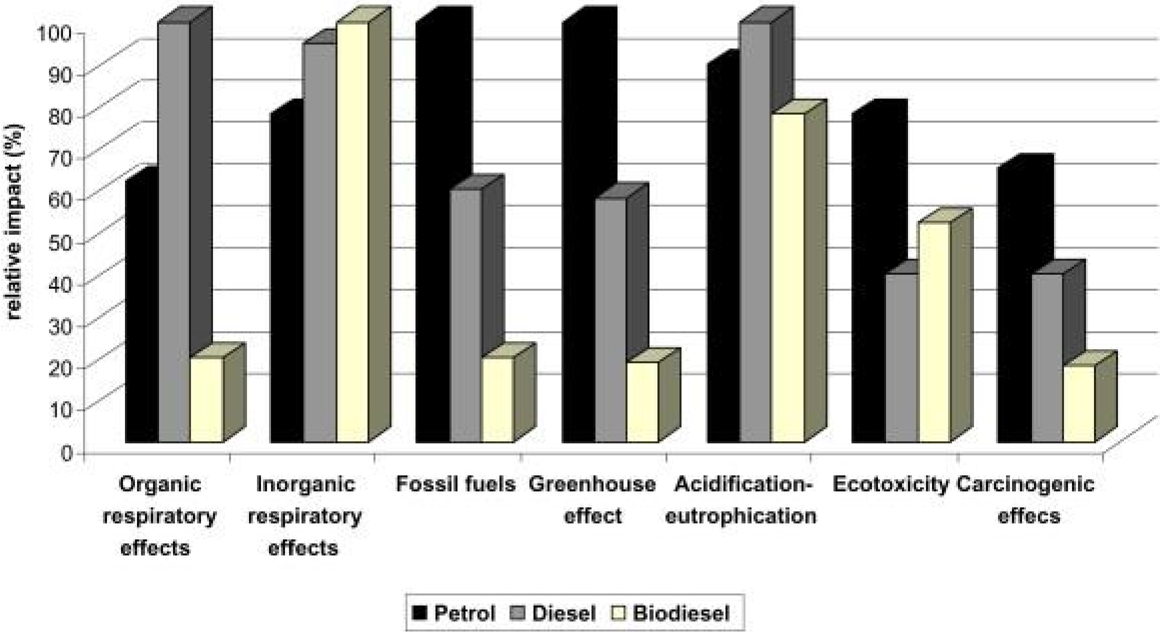


figure 6: Comparison of the environmental impacts of the automotive fuels *Reprinted from [66] with permission from Elsevier*

Between 2005 and 2017 the use of fossil fuel in the primary energy consumption of the European Union decreased by 6.5 % from 76.9 % to 70.4 % translating to a decrease of absolute consumption of 27 % for solid fossil fuels, 15 % for liquid fossil fuels and 11 % for gaseous fossil fuels [67]. The percentage of fossil fuel in energy consumption in Austria for 2015 amounted to 65.7 %. In figure 7 the decreasing trend of the share of energy from fossil fuel between 1960 and 2015 in Austria can be seen. F. Martins et al. [68] concluded that 24 of 29 analyzed European countries have fossil fuel energy consumption values over 60 % showing that they still depend heavily on fossil fuel (including Austria). In 2014, 68 % of the net physical import of processed materials (=import - export) in Austria were fossil energy carriers [45], showing a strong dependency on oil producing countries.

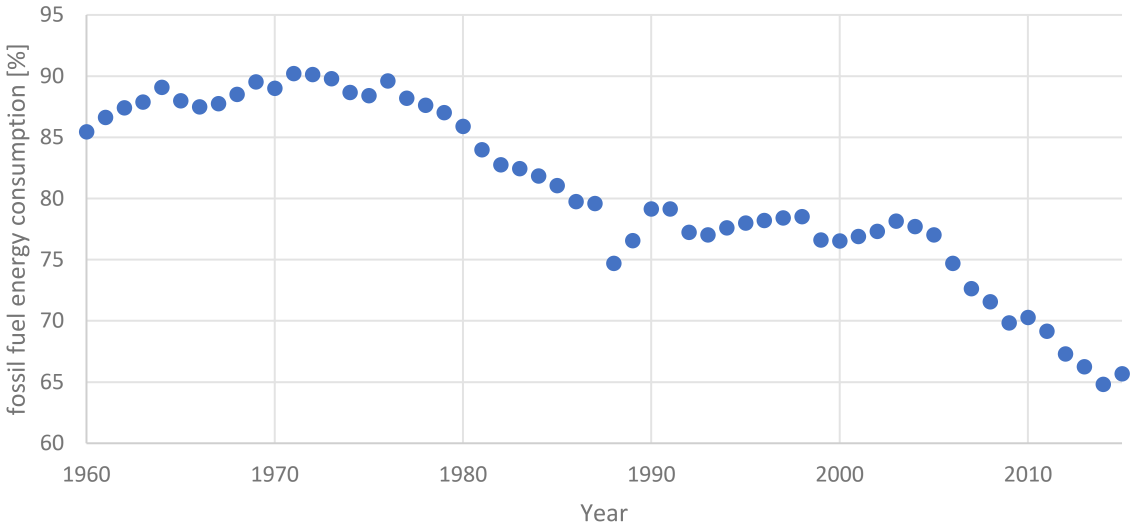


figure 7: Trend of fossil fuel share in energy consumption in Austria between 1960 and 2015. Data from [69]

Although, the share of fossil fuel use for primary energy in the European Union is decreasing, the global total use of fossil fuel e.g. in transportation is increasing as can be seen in figure 8 where the trend of CO_2- emissions of transportation is depicted.

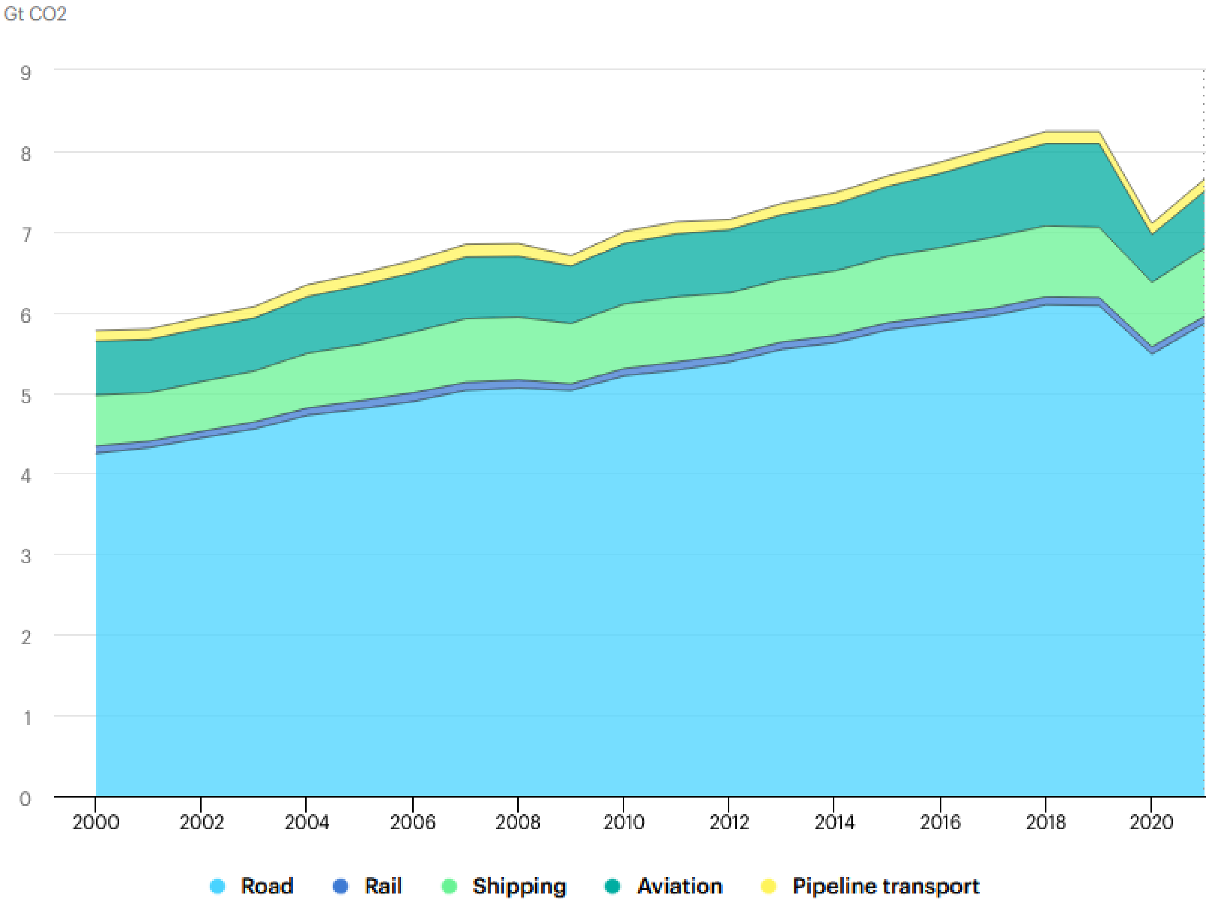


figure 8: Global CO2 emissions from transport by sub-sector 2000-2021 [37]

2.5.1 Environmental Impact of Gasoline and Transportation

In the US 63 % of the fossil oil consumed is used to produce energy for transportation [70]. About 17.3 % of the world energy related GHG emissions in 2004 are attributed to road vehicles, which relates to 4.7 Gt of CO_2 equivalent emissions. [56]. In this calculation, other pollutants e.g. CH_4, N_2O and fluorinated gases which are also emitted by the transport sector are included as well [71]. In 2021, global transport CO_2 emissions reached nearly 7.7 Gt [57]. The EU set a mandatory goal for its member states to reach a minimum share of 10 % biofuel in transport petrol and diesel consumption by 2020 [72].

The CO_2 emissions during combustion of gasoline originating from fossil oil are assumed to be (depending on the source) between 67.5-73.3 g CO_2/MJ [54], [73]–[75]. Which roughly equates to 86 % of the CO_2 equivalent emitted during the life cycle of gasoline (well-to-wheel (WTW)) [73]. The combustion of bio-fuel does not produce GHG-emissions per definition, since all the CO_2 released was in the atmosphere before being converted into biomass. However, this assumption does not factor in the GHG released during growth (e.g. due to fertilizer usage) and processing of the biomass. In figure 9 the estimated GHG emissions in CO_2 eq. per liter of gasoline equivalent for different fuels are compared. In order to take the GHG emissions during production into account the emissions are estimated for well to tank (WTT) and tank to wheel (TTW) and the WTW calculated from them. Here it can be seen that even bio-fuels produce a certain amount of CO_2 eq. [55].

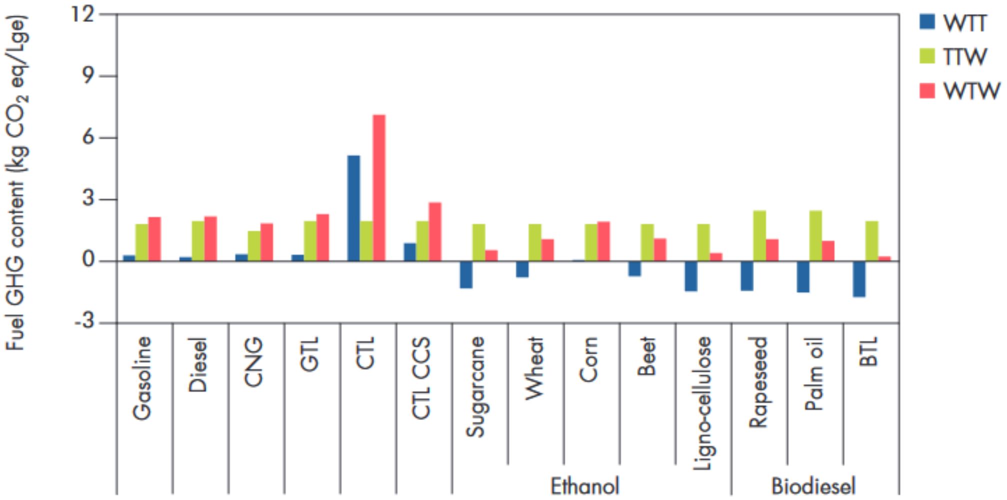


figure 9: Estimated GHG emissions per liter of gasoline equivalent for different fuels; originally published in [55] under CC BY 4.0 license

In 2019 the emission contribution of traffic to the total emissions from Austria were 2.9 % SO_2, 55 % NO_x, 5,2 % NMVOC, 13 % CO, 16 % PM_{10}, 21 % $PM_{2.5}$, 24 % Pb and 5.4 % PAH [76]. Thanks to the policies on sulfur content of fuels, the emission of SO_2 via traffic in 2019 could be reduced by 94 % in comparison to 1990 amounting to nearly 320 tons [34]. The main contributor to sulfur in gasoline is the FCC gasoline, thus alternative feeds for the FCC should not increase, in the best case even reduce, the sulfur content of the FCC gasoline in order to maintain its quality. Sulfur compounds in the flue gas resulting from combustion of fuels with sulfur contend reduce the efficiency of the three-way catalytic converter located at the exhaust of internal combustion engines due to their poisonous behavior [77]–[79]. Thanks to the three-way catalytic converter, the NO_x emissions of gasoline cars decreased to negligible values. The emissions of NO_x from traffic decreased by 34 % from 1990 to 2019 [34].

Problematic organic compounds in gasoline are aromatics and olefins. The concentration of aromatics in gasoline has a significant negative impact on the formation of secondary organic aerosols (SOA), VOC, CO and PM2.5 [80]–[83].

Olefins are one of the precursors for volatile organic compounds (VOCs), NOx and toxic air pollutants (TAPs) and are thus used in models to predict their emissions [79]. Because of that, there are regulations for the olefin content in gasoline. Fluid catalytic cracking catalysts that reduce the olefin content in gasoline exist, but one particular challenge for those catalysts is maintaining the yield of light olefins in the gas fraction.

2.6 Fast Pyrolysis

Fast pyrolysis is a versatile liquefaction treatment of solid organic matter, allowing it to be used in different applications. Pyrolysis is the decomposition of hydrocarbons in the absence of oxygen at elevated temperatures (400-600 °C). The term fast pyrolysis is a bit arbitrary with no precise definition of reaction time and heating rate. The goal of fast pyrolysis is the production of mostly liquid product with only a small amount of char and non-condensable gases formed. First experiments were done in the 1970s [84]. The short reaction time prevents over-cracking of vapors and polymerization. Pyrolysis oil can be used as boiler fuel or serve as a precursor for transportation fuel or chemicals [85], [86]. It could also fit well in the petrochemical refinery process. Formed char and non-condensable gases can be used as source for thermal energy for the process.

Inorganic elements contained in the educts can be transferred into the pyrolysis oil during its production. These can lead to complications if the pyrolysis oil is designated to further upgrading. The carry over into the pyrolysis oil can happen due to entrainment of particles or due to the formation of volatile substances. Alkali earth metals, transition metals, post transition metals and phosphorus are mainly transferred via char entrainment. Less than 5 wt% of inorganics in the feed transfer to the pyrolysis oil [87]. The various forms of inorganics present in the popular feeds studied for fast pyrolysis (biomass and wastes) make a prevention of transfer into the pyrolysis oil unlikely [87].

The pyrolysis process can be summarized in the following steps [70]:

- Heating of the feed
- Primary pyrolysis reactions where volatiles are released and char is formed
- Autocatalytic secondary pyrolysis reaction
- Secondary reactions and further thermal decomposition, reforming, water gas shift reactions, radical recombination and dehydration

As mentioned in chapter 1 one of the problems of fast pyrolysis in the aspect of biomass and waste utilization is the fact that pyrolysis oils usually are used in low value applications (e.g.

boiler fuel), making it difficult to operate economically profitable. Thus, research on pyrolysis oil refinement is in high demand. The refinement methods for fossil oil being suitable for pyrolysis oils as well gives the impetus to this thesis aiming at the utilization of pyrolysis oils in the fluid catalytic cracking process.

In figure 10 different uses and products for pyrolysis oils are depicted. The here mentioned up-grading method is hydrogenation, which reduces oxygen, nitrogen and sulfur content. The following reactions ((7),(8),(9)) are possible [88]:

$$C_xH_yO_z \rightarrow C_xH_y + H_2 0 \tag{7}$$

$$C_xH_yN_z \rightarrow C_xH_y + NH_3 \tag{8}$$

$$C_xH_yS_z \rightarrow C_xH_y + H_2S \tag{9}$$

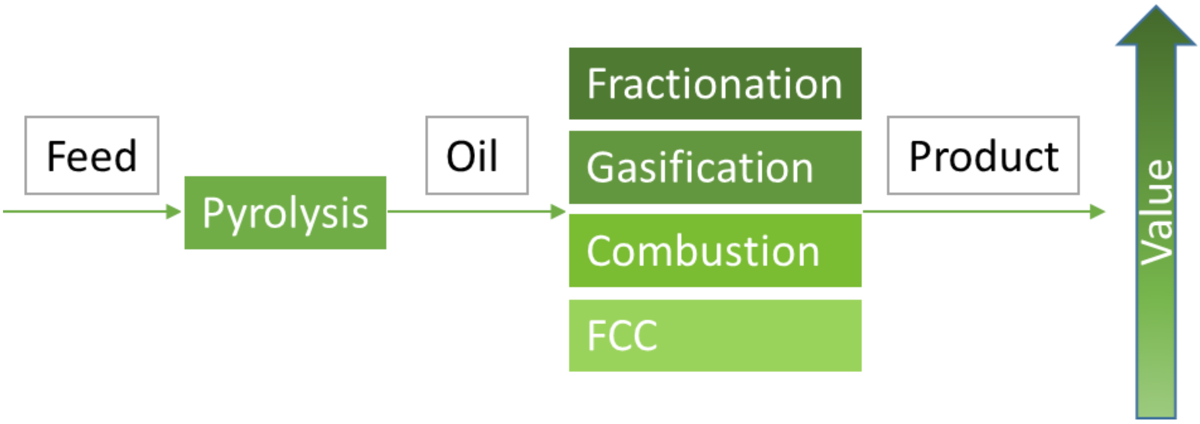


figure 10: Possible uses of pyrolysis oils [85]

2.6.1 Pyrolysis of Biomass

The fast pyrolysis of biomass has the potential to enable the use of renewable resources in chemical processes such as in petrochemistry. Currently there are commercially used fast pyrolysis plants producing bio-liquids from biomass (e.g. Ensyn, BTL). For a description of different biomass fast pyrolysis plants *“Fast Pyrolysis Processes for Biomass”* [84] and *“Fast Pyrolysis of Biomass for Energy and Chemicals: Technologies at Various Scales”* [89] are recommended as supplementary literature. Continuously operated pilot plant reach yields of 60 - 80 wt% (dry feed basis) for woody feedstocks [70], [84], [85], [89].

It is assumed that the char produced by fast pyrolysis from woody biomass derives mainly from lignin, which also produces the largest fraction of CH_4. Hemicellulose produces mainly CO_2 and smaller components. The main product of cellulose pyrolysis are dehydrated carbohydrates.

Pyrolysis oils from biomass, also called bio-oil, bio-crude and bio-liquid comprise a range of oxygenated compounds and tend to instability since they can contain many highly reactive components. Adverse properties of bio-oils in comparison to fossil products are the high water and oxygen content, high acidity (neutralization leads to polymerization [84]), a lower heating value and the aforementioned lower stability. Nevertheless, bio-oil has its advantages over fossil fuel, the most important one being that they count as GHG neutral. Furthermore, it can be produced when biomass is available, reducing the dependency of countries without oil deposits.

Due to the vast collection of different substances, fractionating the bio-oil into single components is not feasible. Present substances are guaiacols, catecols, syringols, vanillins, furan carboxy aldehydes, isoeugenol, pyrones, carboxylic acids, hydroxylaldehydes, hydroxyketones, sugars, dehydrosugars, ethylenglycol, levoglucosan, glyoxal and phenolic compounds [70], [89]–[92].

Acidic acid and methanol are currently the only components that can be isolated on a nearly commercial scale. Bio-oil is sensitive to higher temperatures and thus cannot be distilled [84]. Besides being used as fuel oil, the product from wood pyrolysis oil with the highest commercial use is a food flavoring called liquid smoke [91]. A good compromise is the separation of the liquid on basis of functionality of the components. R.H. Venderbosch [85] suggests the differentiation of three product streams, namely pyrolytic lignin, pyrolytic sugars and a watery phase.

- Pyrolytic lignin can be used to substitute up to 75 wt% of fossil phenol in phenol/formaldehyde resins, bitumen in e.g. for asphalt and roofing materials or as feed for the production of phenolic derivatives [85], [91], [93], [94]. Phenolic compounds present in bio-pyrolysis oil are phenol, cresols, acetophenon, dimethylphenol, ethylphenol, trimethylphenol, ethylmethylphenol and phenol-3(1-methylethyl) [88].
- Experiments indicate that the pyrolytic sugars can be converted to fermentable sugars making it a potential source for the production of bio-ethanol, levulinic acid, polyols etc. [85], [86].
- The organic acids contained in the water phase are extractable as carboxylate salts [85].

Other possible up-grading methods that are more specific for bio-oil, additionally, to the ones depicted in figure 10 are added in figure 11. Whether the different up-grading methods/ chains are economically feasible is strongly dependent on the market. Thus, the big advantage of using processes already established at an industry level is that there are no acquisition costs for new units.

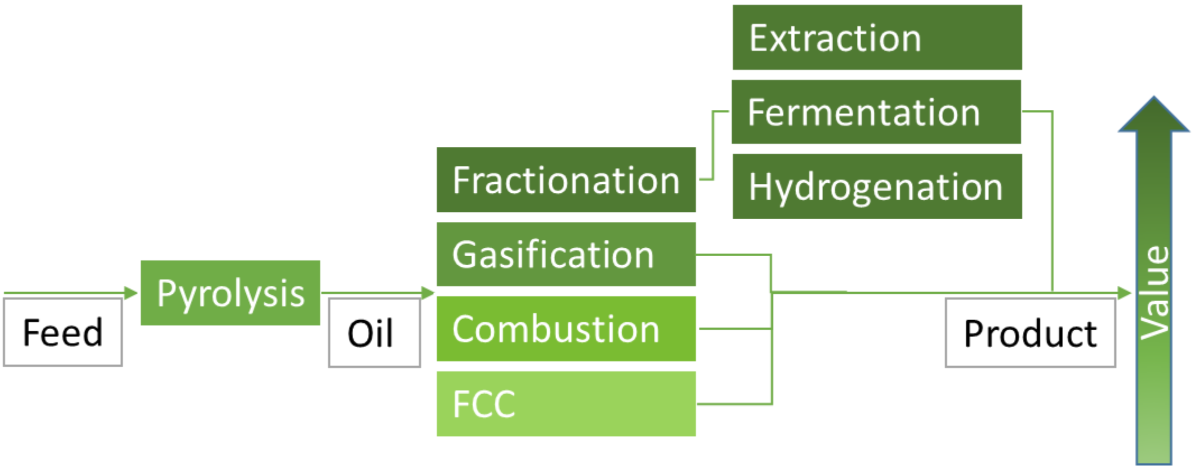


figure 11: Possible uses of pyrolysis oil from biomass [85]

2.6.2 Pyrolysis of Plastics

In addition to making renewable resources available to petrochemistry, fast pyrolysis also provides a more environmentally friendly way to handle plastic wastes compared to incineration and land filling, due to its lower carbon foot print [95], [96]. Most plastic species don't decompose for decades or even centuries. The different biodegradable plastics currently available are not able to replace non-biodegradable plastics in every application. Due to this and the fact that plastics have a low density they fill up landfills pretty fast. There, depending on the conditions in which they are stored, leaching of toxic or otherwise problematic substances can happen. The incineration of plastic waste, as an energetically attractive alternative to landfilling, is especially grave if there is no sufficient flue gas treatment present, due to the release of pollutants e.g. dioxins and furans [97]. The different challenges associated with the direct recycling of plastic waste make a lot of it unfit for recycling. A lot of recycling processes for plastics are specific for one type of plastic and have a sensitivity to the presence of other types. Currently less than 10 % of plastic waste is recycled [98]. The challenge of increasing the recycling rate of plastics is not only the increased need for varietal purity but also the shear amount of produced plastic types. Although 60 types of plastic are the most popular, over 300 types of plastic are produced [6]. The robustness, flexibility and versatility of the fast pyrolysis process complements the specific needs of the direct recycling of plastics perfectly. Any plastic waste not fit for direct recycling even if highly degenerated can be pyrolyzed. Anuar Sharuddin et. al. [99] concluded, that plastics have a high potential to produce liquid oil during pyrolysis. The resulting gaseous and solid products can be burned to provide heat and the liquid product can be further processed e.g. into fuel or monomers [100].

Different reactor types may be used for plastic waste pyrolysis such as fixed bed, fluidized bed, rotary kiln, melting vessels, tubular reactors or extruders. But pyrolysis processes for plastics differ not only in the used reactor but also whether catalysts and/or solvent are used in the process.

In the following the concept of a tubular reactor that uses a solvent will be described since the pyrolysis oil from plastic waste used in the studies detailed in this thesis was produced in one.

The shredded and pre-treated plastic waste is molten under nitrogen atmosphere and afterwards mixed with the solvent. The concentration of plastics is 10-20 % for this case [personal communications]. The mixture is then thermally depolymerized in a tube reactor, followed by fractionating. The flowchart for this process is depicted in figure 12.

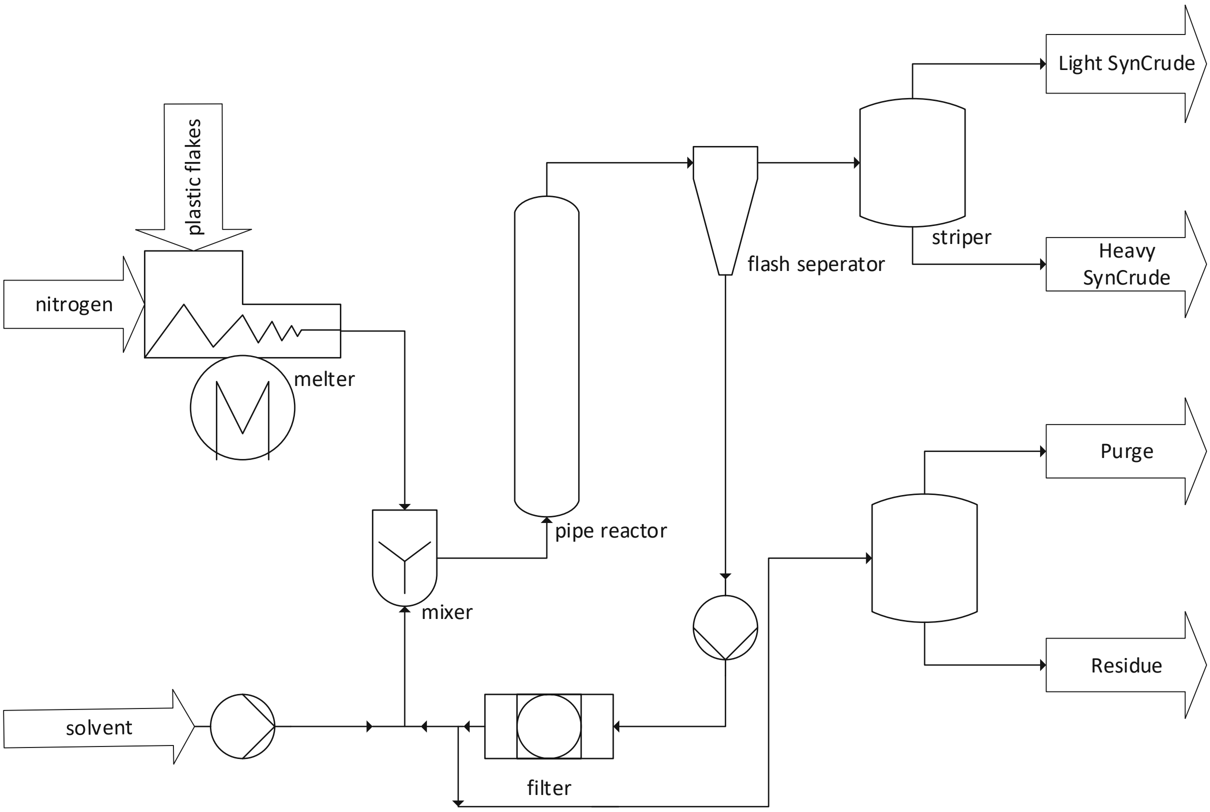


figure 12: Flowchart of a plastic pyrolysis unit with solvent use and a tube reactor [101]

Due to the big differences in the molecular structure of different plastics the pyrolytic oil yield can vary strongly. In literature yields from 37 wt% - 95 wt% can be found [98], [102], [103]. The plastic types present also greatly influence the composition of the pyrolytic oils [95]. For example PET content in the feedstock for fast pyrolysis leads to large amounts of benzoic acid in the pyrolysis oil [99].

The highest yields are accomplished with virgin materials. The presence of foreign materials like colorants, plasticizers, stabilizers or pollutants from past uses hampers the degradation process [102]. A by-product of plastic waste pyrolysis is HCl [98], [100], which, depending on the plastics pyrolyzed (with PVC being one of the main contributors), can be produced in substantial amounts and causes corrosion in the plant. Scott et.al. [100] report about a two-step pyrolysis concept from Matsumoto et.al. with a preliminary low-temperature pyrolysis in which a dehydrochlorination takes place. This concept was presented at a conference in Montreux in 1975 [104].

Williams and Slaney [103] conducted extensive research on the products yielded by different plastic types via fast pyrolysis. E.g. the difference between production of n-alkane and alk-1-ene for different feeds was up to five times. In figure 13 the results for the produced alkanes, alkenes and aromatics from pyrolysis of different plastic mixtures are presented. It is a good example to underline the strong dependency of the product composition on the used plastics.

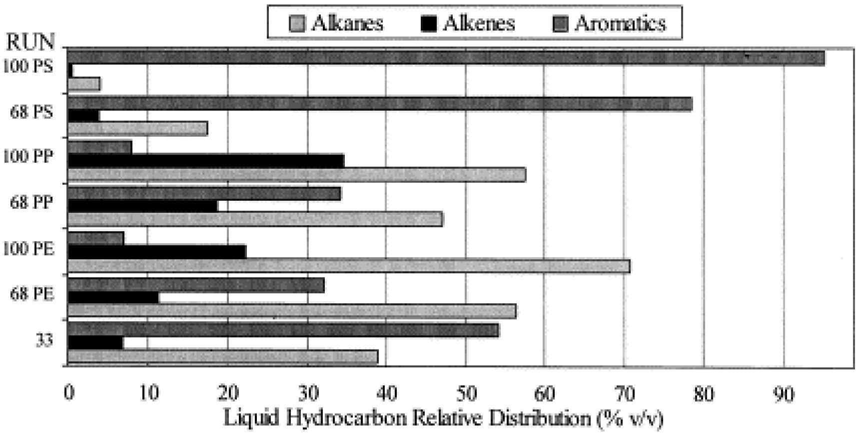


figure 13: Results from pyrolysis of different mixtures of PS, PP and PE. The numbers before the abbreviation is the content of the main plastic type, the rest of the admixture are the other plastic types in equal measures. 33 stands for equal parts of each plastic; reprinted from [105] with permission from Elsevier

Although the products of plastic types differ, the results of the pyrolysis of mixed plastics can be predicted from the knowledge of the behavior of the used plastics [100], [103]. Furthermore, Xue et.al. [106] showed that the co-pyrolysis of plastics and biomass can result in positive synergetic effects.

2.7 Catalytic Cracking

Catalytic cracking is one of the conversion methods used in oil refineries that enables them to utilize heavier feedstock and produce more valuable products (e.g. high octane gasoline and light olefins) as well as better cater to the demands of the global market for different products [107]. Catalytic cracking evolved from thermal cracking, utilizing catalysts to make the process more selective and efficient, since the catalyst decreases the activation energy for breaking the C-C bonds. The first units were fixed bed reactors which are nowadays replaced by fluidized bed reactors, due to their better transfer of heat and catalyst [108]. For an overview of the history of catalytic cracking following literature can be recommended '*Handbook of Petroleum Processing*' [108] and the dissertation of Marco Büchele [17].

Worldwide fluid catalytic cracking units have a capacity of more than 500 Mt per year [77], according to Sadeghbeigi [107] even over 700 Mt per year. Around one third of the crude oil a refinery processes goes into an FCC unit [108]. In the flow chart of a high conversion refinery depicted in figure 14 the place of fluid catalytic cracking within the crude oil refinery process can be seen.

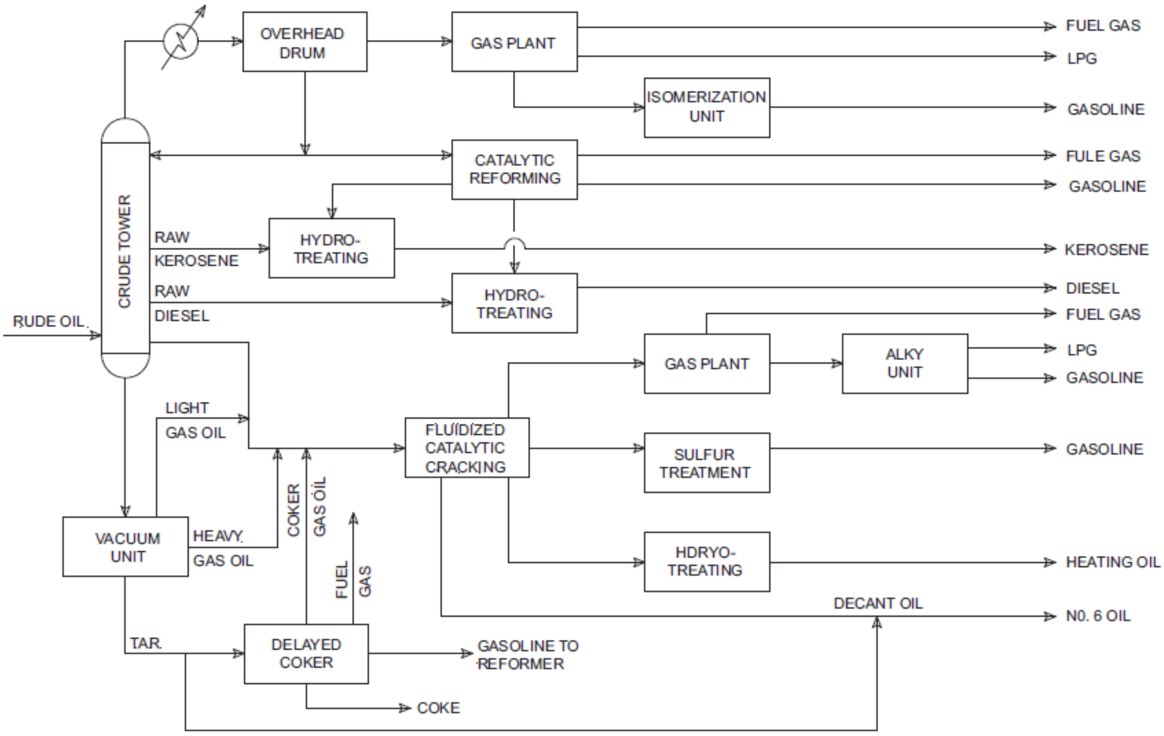


figure 14: Flow chart of a typical high conversion refinery; reprinted from [107] with permission from Elsevier

2.7.1 Fluidized Bed

In order to form a fluidized bed a gaseous medium must flow through a fixed bed at a velocity that lifts up the particles giving the fluidized bed the characteristics of a fluid. This velocity is called minimum fluidization velocity. The difference between fixed bed and fluidized bed can be seen in the pressure loss as function of the velocity. During the state of fixed bed the pressure loss increases with the velocity whereas the pressure loss during the state of fluidized bed stays roughly the same for different velocities. If the fluidization velocity is further increased so that it is higher than the rate of descent the state of pneumatic transport is reached. Here, the pressure loss increases again with the velocity of the gas. In figure 15 the trend of the pressure loss is portrayed.

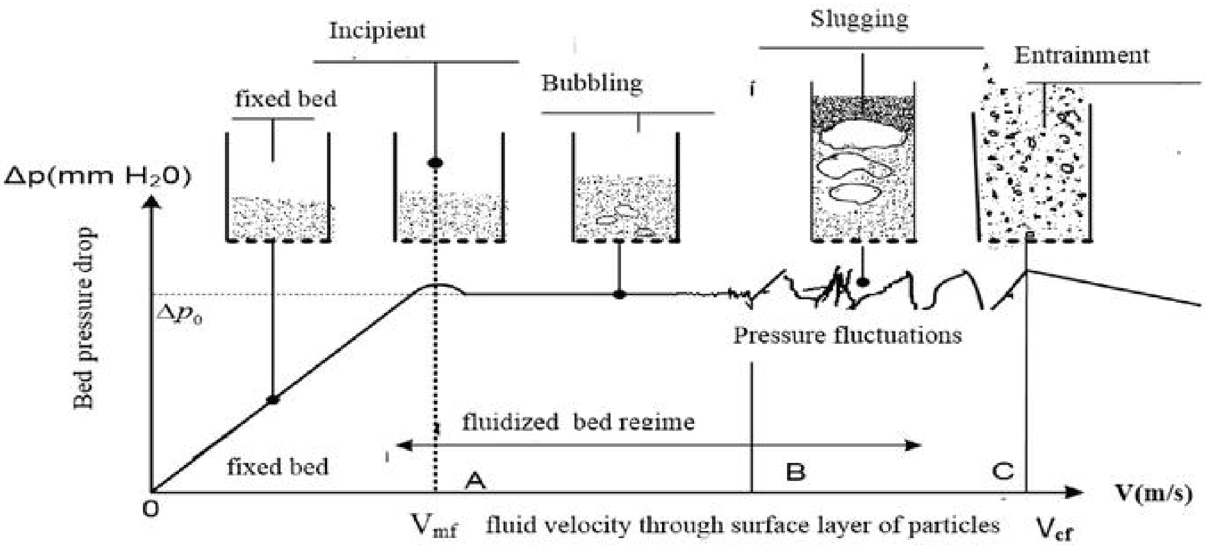


figure 15: Schematic of the pressure loss curve in a particle bed in relation to velocity originally published in[109] under CC BY 4.0 license

A schematic of an industrial FCC plant is depicted in figure 16. The cracking of the feed takes place in the riser/reactor whereas the produced coke is burned of the catalyst to reactivate it in the regenerator. In the beginning both regenerator and reactor were typical fluidized-bed reactors but with the evolution of catalysts the residence time in the reactor had to decrease enforcing the use of up-flowing transported beds in the reactor also called riser [7]. Another fluidized bed is utilized in the stripper, where entrained hydrocarbons are desorbed from the catalyst [7].

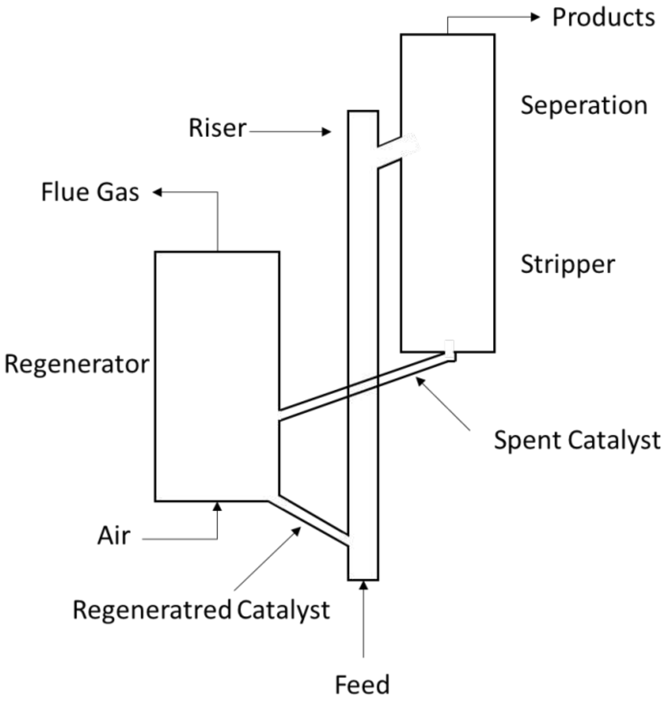


figure 16: Schematic of an industrial FCC unit

2.7.2 Reactions taking place during Fluid Catalytic Cracking

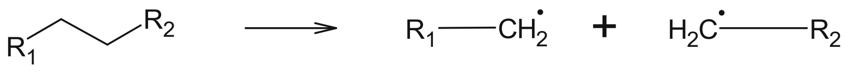
There are two principals for cracking reactions happening in a fluid catalytic cracking reactor:

- thermal cracking / radical reaction mechanism
- catalytic cracking / ionic reaction mechanism

The catalytic cracking in a fluidized bed happens in two time-frames. In the first 50 ms, the *initial time-frame*, radical reactions play an important role. Radical reactions are the main cracking reactions predominantly present in thermal cracking of hydrocarbons. Afterwards in the *steady-state time-frame* of the catalytic cracking, radical reactions can be neglected [77], [110]. Causes for thermal cracking during catalytic cracking processes are non-ideal mixing and poor separation of products [111]. The reactions taking place in FCC-units can be divided into two categories, the primary cracking and the secondary cracking of products of the former and secondary rearrangement. These will be described below. Aromatics are considered uncrackable under FCC-conditions [77].

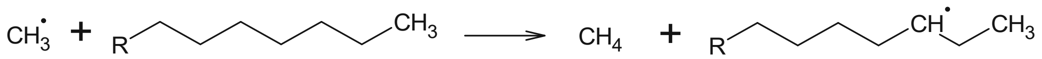
2.7.2.1 Thermal Cracking Reactions

In the fluid catalytic cracking process thermal cracking reactions are considered undesirable side reactions, which cannot be completely prevented. These thermal cracking reactions occur in hydrocarbons at elevated temperatures. The high temperature provides the energy needed for initial hydrocarbon rupture to occur (10) creating free radicals and thus starting the radical chain reaction [112].



(10)

Those radicals are highly reactive and take part in reactions with hydrocarbons (11), α-scission (12), β-scission (13) and polymerization reactions (*14*).



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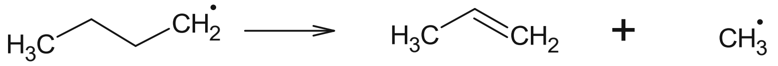

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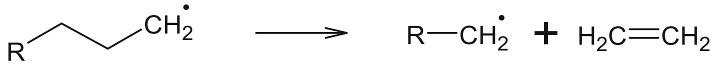

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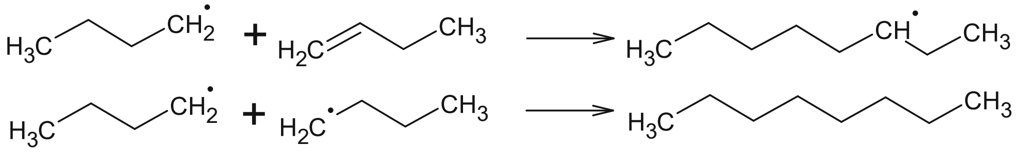
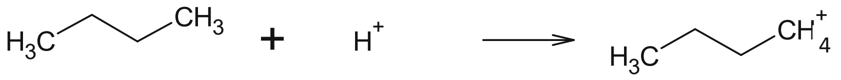


(14)

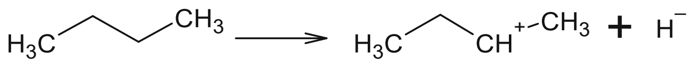
2.7.2.2 Catalytic Cracking Reactions

In comparison to the radical reaction mechanism of thermal cracking, catalytic cracking takes place via an ionic reaction mechanism. Due to the reaction on the catalyst’s active sides Carbocations are formed. Carbocations can be carbonium ions (a positively charged hydrogen ion is added to a paraffin (15)) or carbenium ions. During the FCC process primarily carbenium ions are formed. Their formation takes place at Brønsted acid sites where a hydrogen ion is added to an olefin (16) or at a Lewis acid site a hydride ion is subtracted from a paraffin (17).



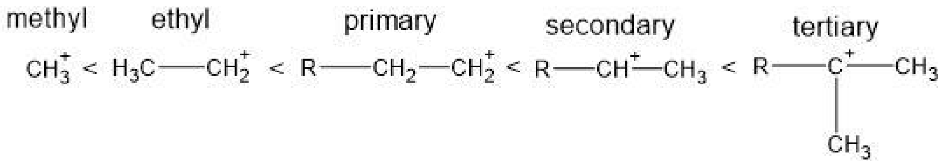
(15)

$$H_2C{=}CH_2 + H^+ \longrightarrow H_3C{-}CH_2^+ \qquad (16)$$



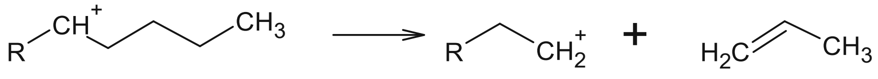
(17)

Carbenium ions are stabilized by positive inductive effects of alkyl chains bound to the charged carbon atom, resulting in the following listing of increasing stability of the different Carbenium ion types:



$$CH_3^+ < H_3C{-}CH_2^+ < R{-}CH_2{-}CH_2^+ < R{-}CH^+{-}CH_3 < R{-}\underset{\displaystyle CH_3}{\overset{+}{C}}{-}CH_3$$

Like radicals, Carbenium ions can undergo β-scission (18), forming a shorter Carbenium ion and an olefin with the smallest one possible being propylene.



(18)

Following there is a short summary of primary cracking reactions taking place [7], [111]:

paraffin → paraffin + olefin (19)

alkyl naphthene → naphthene + olefin (20)

alkyl aromatic → aromatic + olefin (21)

olefin → paraffin + olefin (22)

2.7.2.3 Secondary reactions

Beside the cracking reactions secondary reactions also take place. Important secondary reactions of the FCC process are isomerization, hydrogen transfer, transalkylation, cyclization, low olefin disproportion and dealkylation reactions [7], [111].

Isomerization: carbeniumions transforming into more stable forms

- Bond shift in olefins
- Formation of iso-olefins from n-olefins
- Formation of iso-paraffins from n-paraffins

Hydrogen transfer: transfer from hydrogen between two molecules

- from naphthene to olefin forming aromatic and paraffin
- Cycloaromatization from Cycloalkane and olefins to aromatic and paraffins

Transalkylation: transfer of alkyl groups

Cyclization:

- of olefins to naphthenes
- of naphthenes into coke

Olefin disproportion: exchange of substitutes between olefins

Dealkylation: removal of an alkyl group

- Iso-paraffin to olefin and paraffin
- Alkylaromat to aromat and olefin

Further reactions are dehydrogenation (23) and coking which are important for the FCC unit operation [111], whereas dehydrogenation should not take place under ideal conditions. It is a sign for catalyst poisoning and promotes coke formation. Coke is burned in the regenerator supplying necessary heat to the process, but the formation of coke reduces the yield of the FCC process. Additionally it is also an important factor of temporary catalyst deactivation, due to its deposition blocking the access to reactive sides. Around 0.5 - 1.3 wt% of the solid reaching the regenerator is coke [113]. Nonetheless, coke formation is important to ensure the autothermal nature of the FCC-process.

$$C_8H_{18} \longrightarrow C_8H_{16} + H_2 \qquad (23)$$

2.7.3 Emissions of the Fluid Catalytic Cracking Process

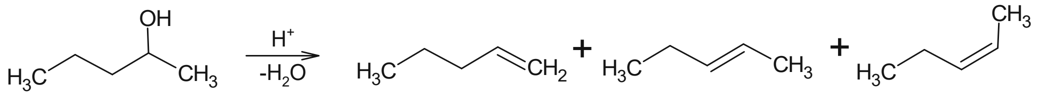
In the regenerator several atmospheric pollutants like carbon monoxide, sulfur oxides, particulate matter, nitrogen oxides and nickel compounds are potentially produced. Optimized air/catalyst distribution in the regenerator, the correct performance and activity of the catalyst are important for the prevention of increased formation of these pollutants [113].

- The carbon monoxide concentration in the flue gas is highly dependent on the operation method. “Partial burn”, where oxygen is the limiting reaction component, produces high amounts of carbon monoxide that require post treatment (CO combustor) [7].
- Depending on feed and regulations a flue gas scrubbing for the removal of sulfur oxides can be necessary.
- Residual particles in the flue gas are further reduced in a tertiary separation device in about 90 % of FCC units [113].
- In full combustion 5 % of N in the regenerator form NO_x of which 90 % is present as NO [113]. The rest is made up of NO_2 and N_2O. In partial burn mode intermediate nitrogen compounds (e.g. ammonia and hydrogen cyanide [113]) are present due to the absence of excess oxygen. Flue gas treatment for nitrogen compounds which are not N_2 is necessary.

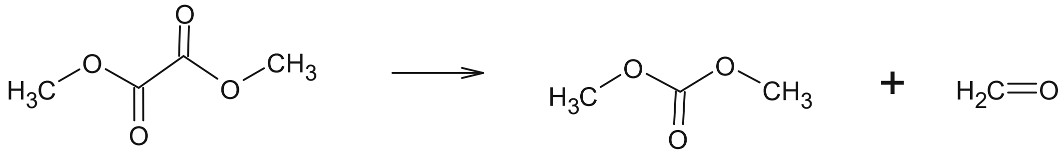
2.7.4 Catalytic Cracking and Pollutants

2.7.4.1 *Oxygen*

The deoxygenation processes occurring during cracking are dehydration (24), decarbonylation (25) and decarboxylation (26) [114].



(24)



(25)

(26)

Fogassy et al. [115] and Schuurman et al. [116] found that the formation of olefinic products is promoted by the presence of oxygenated components due to the consumption of hydrogen in dehydration reactions.

2.7.4.2 *Sulfur*

During the FCC process 30 - 55 % [61], [107], [117], [118] of the sulfur content in the feed is converted into H_2S. Hydrotreatment of the feedstock reduces the amount of produced H_2S since compounds that would form H_2S in the FCC process are removed. It also increases the amount of sulfur in slurry and coke [107]. The sulfur in the coke is burned in the Regenerator and forms SO_2 (more than 90 %) and SO_3 [107], [113].

In theory, it makes no difference for the cracking process itself if a compound contains sulfur or not [77]. The occurring reactions of compounds with sulfur can be summarized as follows [61], [117], [119]:

sulfide ⇌ mercaptan + alkene (27)

mercaptan ⇌ hydrogen sulfide + alkene (28)

Cyclic compounds are more stable than aliphatic compounds and less stable than thiophene and its derivatives. In figure 17 a schematic of the different conversions of sulfur species taking place during fluid catalytic cracking is depicted.

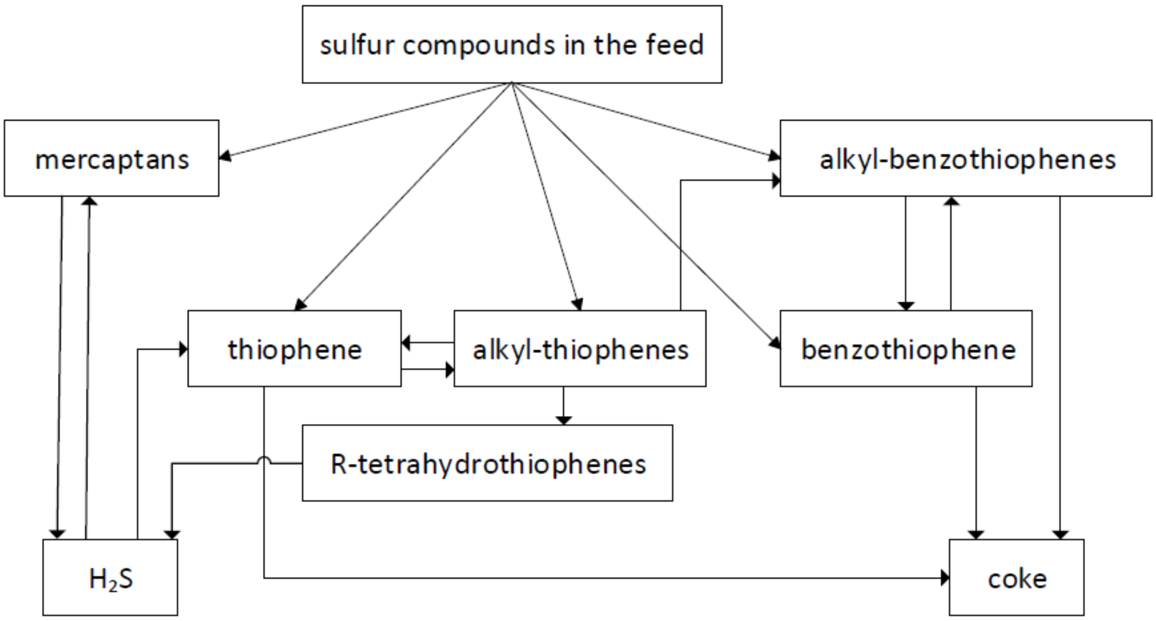


figure 17: Schematic of different conversions of sulfur species in fluid catalytic cracking (redrawn from [119])

Sulfur species in FCC gasoline are mercaptans, thiophene, alkylthiophenes and benzothiophene [118]. Thiophenic sulfur species make up around 50 - 60 % of sulfur content in FCC gasoline [118], [119]. They are aromatic and thus do not crack in the FCC process [77], [78]. Furthermore, there are two possible mechanisms responsible for their formation mentioned by P. Ø. Vistisen and P. Zeuthen [61], one being the cracking of alkylthiophenes, alkylbenzothiophenes and other heavy sulfur containing molecules or the reaction of formed H_2S with olefins. Mercaptan sulfur in the gasoline fraction can be removed via a caustic extraction process [107]. Despite the fact that only 3 - 10 % [107], [117], [118] of the sulfur contained in the feed ends up in the gasoline, the sulfur content of FCC gasoline is higher than the sulfur content of gasolines from other processes in a refinery. 80 - 95 wt% [61]–[63], [78] of the total sulfur content of gasoline blends produced in refineries stem from FCC gasoline despite the fact that FCC gasoline only makes up around 20 - 40 % of the blend [7], [61]–[64].

Sulfur as well as nitrogen have a negative influence on the kinetic constant of gasoline formation, with the influence of sulfur being stronger than the one of nitrogen [120]. The sulfur concentration in the gasoline does not depend on the cracking conditions like temperature or catalyst to oil ratio (C/O) but on the residence time in the reactor, showing a maximum as function of conversion. Gasoline and diesel sulfur specifications cannot be met by FCC products, irrespective of the cracking severity [77], [79], although a reduction by advancing catalyst technology is possible [78], [79], [121], [122]. In literature additional sulfur content reduction in FCC gasoline between 14 - 30 wt% is found [78], [118], [121], [123].

2.7.4.3 Nitrogen

While most research points towards organic nitrogen compounds poisoning FCC catalysts by chemisorption on active sites, deactivating them irreversibly and thus, severely affecting the catalyst activity [117], [124]–[127], while Sadeghbeigi [107] mentions it as a temporary poison, since the compounds are burned-off in the regenerator hence the activity being restored. Ho et al. [125] reported that the passivation capacity of basic nitrogen compounds increase with their proton affinity.

The nitrogen compounds in the typical FCC feed can be divided into basic and non-basic whereas the basic nitrogen makes up around 25 - 50 % of the total nitrogen [107], [128], [129]. Pyridines, quinolones and related molecules make up the basic nitrogen compounds, whereas the non-basic components are made up of pyrroles, indoles and carbazoles.

During the FCC process the alkyl side chains of basic nitrogen compounds break, but the unsaturated rings containing nitrogen do not crack and form compounds with higher degree of condensation. Similar reactions take place with the non-basic nitrogen compounds [127]. Furthermore, Vistisen et al. [61] suggest that the formed NH_3, similar to H_2S, reacts with olefins or diolefins which are also products by the cracking reactions. Hydrogen cyanide is also formed during the cracking reactions, which accelerates corrosion of the FCC unit [107]. The nitrogen species with the highest relative abundance in the liquid product are deemed most likely to be cycloalkyl-acridines, azapyrene, and benzo-acridines, respectively [127].

50-60 % of the nitrogen contained in the feed ends up in the coke [107], [127]. During the regeneration 95 % contained in the coke is converted to elemental nitrogen, whereas the remaining 5 % are converted to nitrogen oxides (NOx) [107].

2.7.4.4 Chloride

Depending whether the Feed contains Cl components or not HCl is formed during the process. HCl and present NH_3 will react to the hygroscopic salt NH_4Cl. The hydrolysis of deposited NH_4Cl promotes corrosion in the steel parts of the plant [130].

2.7.4.5 Sodium and Heavy Metals

Metals permanently poison the catalyst herby reducing its ability to form the desired products [107]. Ni, V, Cu and Fe deposit on the catalyst particles as metals or sulfides [117] poisoning the catalyst leading to a reduction of the conversion rate. The competing catalytic activity of Ni leads to an increase of coke formation and other unwanted reactions [79], [117].

While sodium reduces the stability and activity of the catalyst due to neutralization of a portion of the active sites. It also promotes the sintering of the catalyst (reduction of thermal stability [107]) and thus a closing of the pores [117].

2.7.4.6 Aromatic compounds

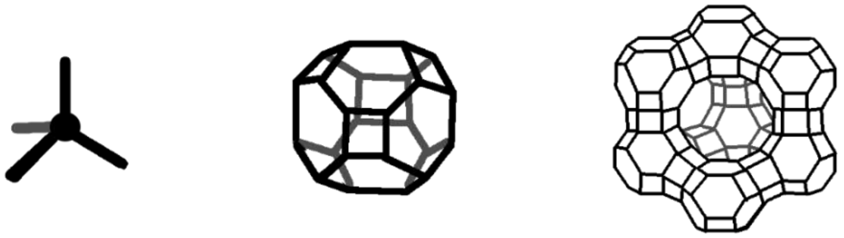
Aromatic compounds are usually not seen as pollutants in the catalytic cracking process. Due to their negative influence on the cracking process, they are still given a paragraph in this chapter. Side chains undergo breaking whereas the aromatic rings are stable and no ring breaking occurs. Although the aromatics do not react further in the cracking process they still can participate in condensation reactions forming slurry product or coke [107]. Coke is a reversible catalyst poison, inactivating the catalyst until it's combustion in the regenerator.

2.7.5 Catalyst

Typical FCC catalysts have four major components:

- Zeolite
- Matrix
- Filler
- Binder

The Zeolite provides the major part of the catalytic activity and the product selectivity [107], [117], [131]. Commercial FCC catalysts usually contain 15-40 % zeolite [132]. Although zeolite X can be used, mainly zeolite faujasite Y is used in cracking catalysts due to its superior stability. The basic structure are tetrahedrons with oxygen occupying the vertexes and aluminum or silicon their centers. The tetrahedrons form stumped octahedrons also called a sodalite cage. The basic element of faujasite is formed of six sodalite structures joined by prisms. Depictions of these three levels of zeolite structure can be found in figure 18. The raw formula of an elementary cell can be written as $Na_n[(Al_2O_3)_n(SiO_2)_{192-n}] \cdot m\ H_2O$ with approximate values of 250-260 for m and 48-67 for n [117].



$SiO_{4/2}$ or $AlO^-_{4/2}$ tetrahedron

sodalite cage

basic faujasite element

figure 18: Different levels of zeolite structure

Zeolite have both Brønsted and Lewis acid sites, of which the Brønsted acid sites can be exchanged with rare earth metals (e.g. La and Ce) enhancing thermal stability of the acid sides and thus their activity because they enable a higher UCS (Unit cell size) level. UCS is a measure of the total potential active acid sites per unit cell and is related to the number of aluminum atoms. Y Zeolites without rare earth metals are called USY (ultrastable Y), they have a lower UCS and thus a lower activity [7], [131]. But they are more stable under severe thermal and hydrothermal treatments.

The matrix increases the resistance to attrition of the catalyst and helps dilute the active sites of the zeolite which in its pure form would be too reactive for common FCC plants. If the matrix consists of components with catalytic activity aside from the zeolite [107], [117], [131, p. 4] it is called active matrix. It provides the primary cracking site, reducing the size of big molecules so they can enter the pores of the zeolite. It also poses as a trap for catalyst poisons.

Filler and Binder are means for enhanced physical integrity, mechanical strength and activity dilution, to prevent over-cracking.

Catalysts are trimmed to certain results like maximum gasoline yield, gasoline with high octane numbers or for the treatment of residues. As the FCC process is undergoing a shift from the main product being gasoline to increasing importance of light olefins, catalysts that boost propylene or butylene production are also gaining importance. For example the additive HZSM-5 and its variations crack gasoline range olefins to light olefins [133]. In more than 30 % of FCC Units a catalyst with HZM-5 additives is in use [134]. HZSM-5 is a protonated zeolite socony mobil-5 (ZSM-5) which is a zeolite that is formed of pentasil units. As can be seen in figure 19 a pentasil unit consists of eight five-membered rings. It helps form olefins from the primary cracking products of the zeolite Y and thus prevents the carbenium ions to take part in hydrogen transfer reactions [134].

figure 19: Pentasil unit

3 Feedstocks and Catalyst

In the following chapters the utilized feedstocks and catalyst are described.

3.1 Catalyst

The demand for light olefins has an upward trend which is also noticeable in the product demand of the FCC process. In this thesis an equilibrium catalyst (E-cat) which is a mixture of 30 % propylene boosting catalyst and 70 % of an LPG boosting catalyst was used. To ensure that the amount and activity of catalyst in an industrial FCC plant always stays the same there is a continuous exchange of fresh and used catalyst. The resulting catalyst mixture in the plant is called equilibrium catalyst. The use of equilibrium catalysts in experiments like these is especially important in order to have realistic industrial conditions. Fresh catalysts are too active to be compared to the equilibrium catalyst which is standard in the industry. In table 1 parameters of the used e-cat are given.

table 1: Parameters of the e-cat used

parameter	E-cat	unit
total surface area	173	m^2/g
unit cell size	24.29	Å
average bulk density	0.84	g/cm^3
pore volume	0.39	cm^3/g
nickel	609	ppm
vanadium	105	ppm
sodium	0.22	wt%
iron	0.3	wt%
rare earth oxides (RE_2O_3)	1.75	wt%
aluminium oxide (Al_2O_3)	47.70	wt%
phosphor pentoxide (P_2O_5)	2.52	wt%
Sauter diameter d_{sv}	67.49	µm

3.2 Different Vacuum Gas Oils

Different batches of Vacuum Gas Oil (VGO) were used over the course of this thesis. Their parameters are summarized in table 2. VGO is the head product of the vacuum distillation of crude oil and is an intermediate product with a boiling range from 350 - 560 °C. All of them came from the same provider and were hydrogenated after distillation to reduce the sulfur content. The boiling curve of VGO_3 is depicted in figure 20 as an example.

*table 2: Comparison of the different batches of VGO; values marked with * were measured at TU Wien*

	S	**N**	**Ash**	**CCR**
VGO_1	291 ppm	275 ppm	<0.001 *	0.202 ± 0.020*
VGO_2	-	-	0.008 ± 0.006 *	0.376 ± 0.027 *
VGO_3	319 ppm	284.7 ppm	0.0080 ± 0.014 *	0.38 ± 0.065 *
VGO_4	-	-	<0.001 *	0.16 *

3.3 Lipstick Mass

The Lipstick mass (LS) used for the experiments was obtained as fresh product directly from the factory. But the experiment was conducted, with the recycling of unsold lipsticks in mind. Since the recycling rate of packaging is supposed to reach 70 %, since the lipstick mass will make up one of the fractions won during the recycling process of lipstick the manufacturer wants to take it a step further and not only recycle the packaging fractions but all recovered fractions.

Besides a variety of different organic compounds, the lipstick mass also contains calcium sodium borosilicate, tin oxide, alumina and different inorganic pigments. Since these can cause issues in the pilot plant, several batches of lipstick mass were heated to 100 °C in a drying cabinet and left for sedimentation for 48 h. Afterwards, the top phase (LST) was collected and used in the experiment. A hotplate is not recommended for the sedimentation since the movement in the mixture caused by the temperature differences keeps most of the particles suspended.

3.4 Pyrolysis Oil of Plastics

The plastic derived pyrolysis oils used in this thesis were obtained from a process similar to the one described in chapter 2.6.2. As feed for the pyrolysis shredded and cleaned mixed municipal plastic waste was used. Thus the exact composition of the feed is not known. The liquid product of the pyrolysis was fractionated via distillation. The fractions ‘Heavy SynCrude’ (HSyn) and the bottom product of the distillation (DiRe) were tested as co-feeds in the FCC pilot plant. Details to the feeds can be seen in table 5. The boiling curves of Heavy SynCrude, Distillation Residue and VGO_3 are depicted in figure 20.

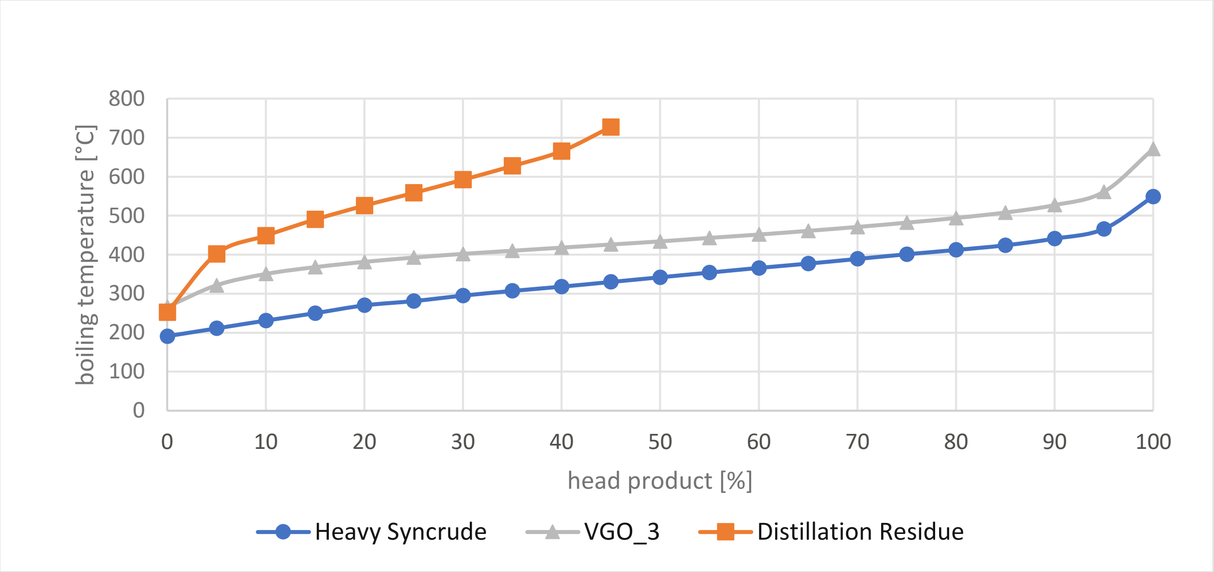


figure 20: Comparison of the boiling curves from Heavy SynCrude, Distillation Residue and VGO_3

3.5 Pyrolysis Oil of Biomass

Five different pyrolysis oils form biomass were part of this thesis and also of the Horizon 2020 Project Waste2Road. They were produced by the company BTG-BTL using the steps shown in figure 21 using the condition listed in table 3. In table 4 the information of the oils like feed, treatment and the abbreviations used in this work are given.

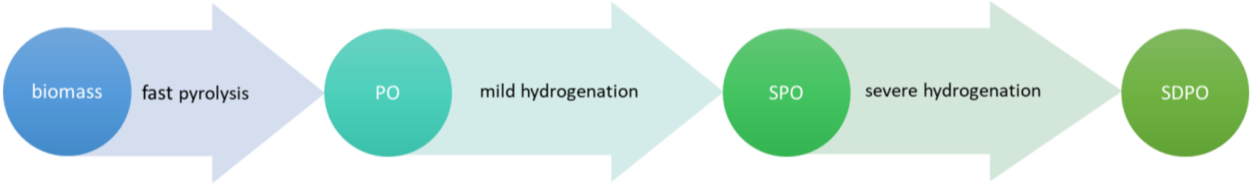


figure 21: Schematic of the processing steps from biomass to stabilized deoxygenated pyrolysis oil

table 3: Hydrotreatment conditions for the refinement of pyrolysis oil from biomass

	Catalyst **-**	**Temperature** **[°C]**	**Pressure** **[bar]**
mild hydrogenation	Picula^{TM}	80-250	200
severe hydrogenation	CoMo/NiMo	>300	200

table 4: Information of the used bio-oils

	Abbreviation	**Feed for production**	**Treatment**
Pyrolysis oil from clean wood	PO	clean pine wood	untreated
Stabilized pyrolysis oil from clean wood	SPO	clean pine wood	Stabilized via hydrogenation
Stabilized pyrolysis oil from contaminated wood	SPOcw	contaminated wood / scrap wood	Stabilized via hydrogenation
Stabilized deoxygenated pyrolysis oil from contaminated wood	SDPOcw	contaminated wood / scrap wood	first stabilized and afterwards deoxygenated via hydrogenation
Stabilized deoxygenated pyrolysis oil from sun flowers	SDPOsun	Sun flower plant parts that accumulate during sun flower oil production	first stabilized and afterwards deoxygenated via hydrogenation

There is no detailed analysis of the contamination from the contaminated wood since scrap wood was used. As a rule of thumb the use of untreated feeds is preferred if possible but the untreated pyrolysis oils from contaminated wood and sun flowers as well as the stabilized pyrolysis oil from sun flowers had such a poor quality for their potential as FCC co-feed that co-feeding experiments were not attempted.

3.6 Compilation of Feedstock Characteristics

The results of the feed measurements conducted in the course of this thesis are brought forward in order to have all the information in one place. The measurement methods for the Conradson Carbon Residue (CCR) value and ash content will be portrayed in more detail below. As will be mentioned in chapter 4.5.1 these analyses are important to predict certain problematic behaviors of different feeds. For the CCR value of the lipstick mass samples the ash content was subtracted to have a more accurate “carbon residue only” value. In table 5 the characteristics of the different tested co-feeds/alternative feeds are summarized.

*table 5: Comparison of the different co-feeds utilized in this thesis; values marked with * were measured at TU Wien, values marked with ° were measured by the Mikroanalytisches Laboratorium of Universität Wien*

feedstock	**C content [wt%]**	**H content [wt%]**	**S content ppm**	**N content [wt%]**	**O content [wt%]**	**ash content [wt%]**	**CCR [wt%]**	**Water content [wt%]**
HSyn	85.5	13.9	90.4	74.1 ppm	0.229	0.010 ± 0.019 *	0.04 ± 0.025 *	160 ppm
DiRe	80.40	10.20	-	160 ppm	1.9	10.49 ± 0.96*	43.49 ± 0.665 *	-
PO	43.9	7.9	-	-	48.2	0.083 ± 0.000 *	20.459 ± 0.980*	20.5
SPOcw	54.66	8.1	-	0.48	36.76	0.091 ± 0.000 *	20.504 ±1.404*	12.85
SDPOcw	77.6	10.47	-	0.93	11	0.003 ± 0.000 *	4,722 ± 0,029*	5.31
SDPOsun	72.65	10.45	-	1.43	15.47	0.076 ± 0.000 *	5.068 ± 0.023*	33.42
LS	67.43 ± 0.41 °	12.18 ± 0.13 °	<0.02 °	0.113 ± 0.017°	10.04 ± 0.12 °	16.5 ± 0.3*	0.487 *	-
LST	-	-	-	-	-	0.623 ±0.029*	0.295 *	-

3.7 Miscibility of Alternative Feeds with VGO

LST, HSyn and DiRe could be easily mixed with VGO, while PO, SPO and SPOcw were unmixable with VGO.

SDPOcw and SDPOsun when mixed with VGO formed solids. Pictures of the formed solids can be seen in figure 22. In both cases the solids were sticky. SDPOsun produced more solids than SDPOcw.

figure 22: Pictures of the solids formed when SDPOcw, SDPOsun respectively are mixed with VGO (admixture 10 %). Left: thermometer that was in 4000 mL of a 10 % admixture SDPOcw; Right: wire that was in 100 mL of a 10 % admixture SDPOsun

To determine the amount of formed solids experiments with SDPOcw 5 wt% and 10 wt% admixed to VGO were conducted. The results are presented in table 6. It is assumed that all solids formed stem solely from the admixed SDPOcw, because of that the percentage of solids based on the amount of SDPOcw as well as the amount of SDPOcw remaining in the liquid are calculated. It can be seen that roughly ¼ of the SDPOcw solidifies in both cases.

table 6: Results of the admixture experiments with SDPOcw and VGO

SDPOcw admixture	solid amount mixture based	Solid amount SDPOcw based	SDPOcw remaining in liquid
5.15%	1.35%	26.2%	3.80%
10.34%	2.66%	25.7%	7.68%

Furthermore, miscibility experiments with admixtures of SPOcw, SDPOcw and VGO were also carried out. The pictures of the experiments are shown in figure 23. The admixture of 4 % SPOcw, 6 % SDPOcw and 90 % VGO was the first admixture that didn't form solids. From a concentration of 2 % SPOcw, 8 % SDPOcw and 90 % VGO the formation of two liquid phases could be observed.

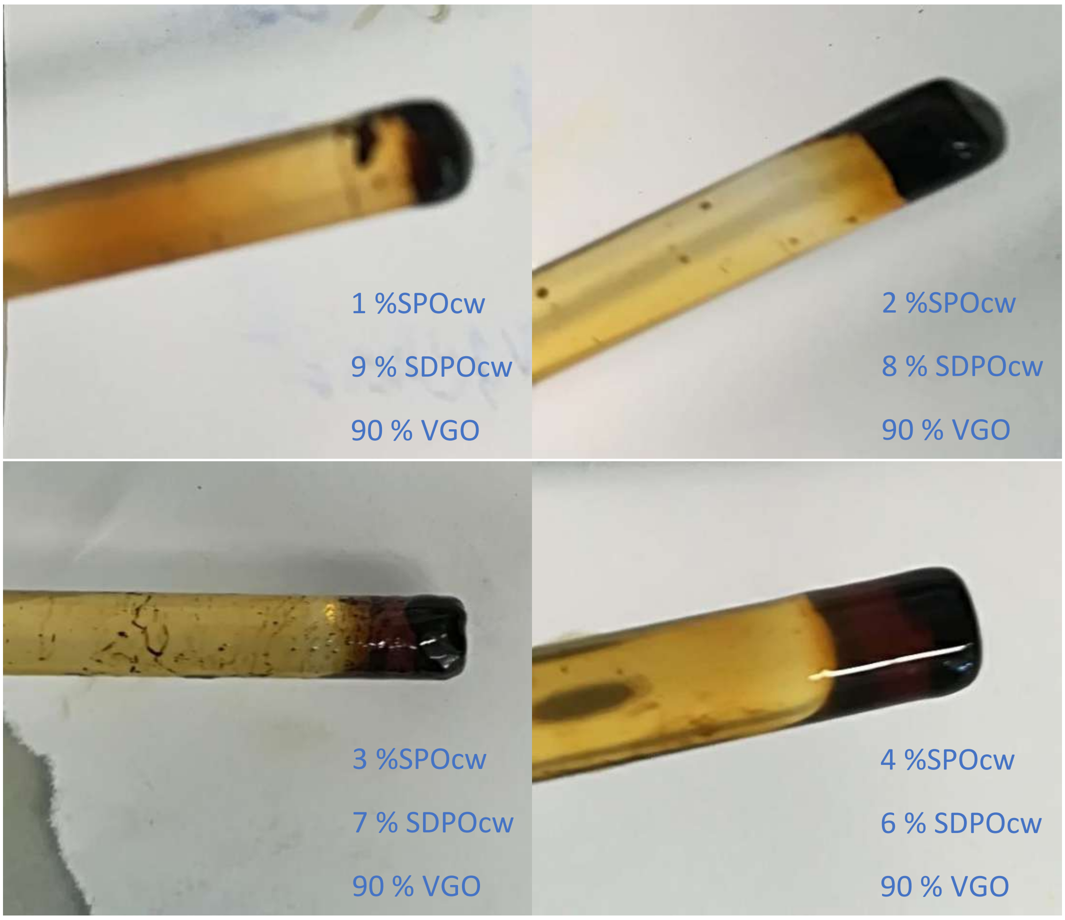


figure 23: Pictures of glass rods that were used to stir the different admixtures of SPOcw, SDPOcw and VGO

For feeds which caused problems during feeding, different modifications of the feeding system were tested. The different modifications are described in chapter 4.1.

4 Fluid Catalytic Cracking Pilot Plant

Besides the size, there is one important difference of the FCC pilot plant compared to industrial plants. In contrast to the typical externally circulating fluidized bed used in commercial applications the FCC pilot plant is built as an internally circulating fluidized bed. Disadvantages of the internally circulating fluidized bed concept are the hard accessibility for maintenance and the coupling of the temperatures of Regenerator and Riser. The coupling of the temperatures is solved via cooling which enables the variation of the riser temperature when needed. The main advantage is the reduction of occupied space and removal of a possible need for heating elements for the riser. A schematic of the pilot plant is depicted in figure 24 with parameters listed in table 7. The catalyst cycle is described in more detail in figure 25. The fluidization regimes utilized in the different sections of the pilot plant are listed in table 8.

Büchele [17] investigated the comparability of the FCC pilot plant located at TU Wien with an industrial plant. The biggest deviation of the results was the amount of coke produced with a difference of 1.6 wt%. The operation parameter that had the most significant difference was the catalyst to oil ratio. Nonetheless, the comparability is satisfactory not least because the high catalyst to oil ratio is offset by the short contact time which is due to the smaller construction size of the pilot plant compared to the industrial counterpart.

table 7: Important parameters of the FCC pilot plant at TU Wien

parameter	**value**	**unit**
total height	3.2	m
riser length	2.5	m
riser diameter	0.0215	m
regenerator diameter	0.33	m
regenerator temperature	610 - 620	°C
riser temperature	525 - 555	°C
pressure	ambient	-
residence time in riser	≈ 1	s
catalyst mass	50 - 70	kg
feed rate	1.5 - 2.5	kg h^{-1}
bottom fluidization (N_2)	4	NL min^{-1}
riser auxiliary fluidization (N_2)	0.1 - 5	NL min^{-1}
syphon fluidization (N_2)	12 - 15	NL min^{-1}
cooler fluidization (air)	10	NL min^{-1}
regenerator fluidization (air)	25 - 33	NL min^{-1}

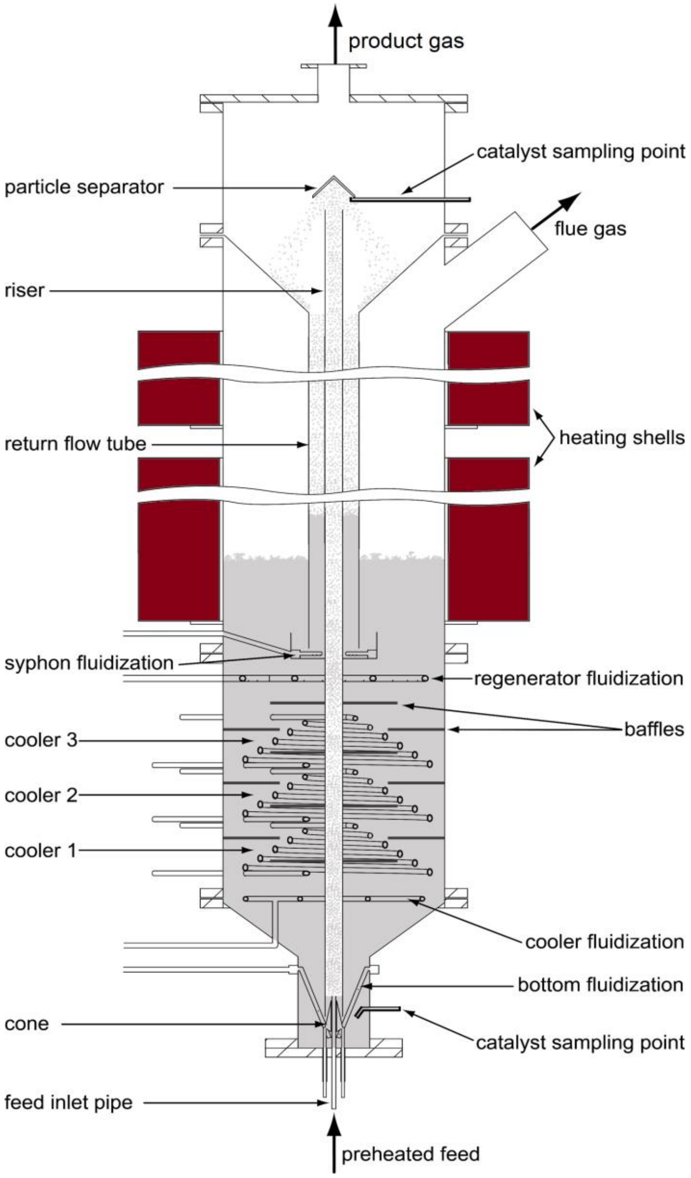


figure 24: Schematic of the pilot plant adapted from [135] by [17]

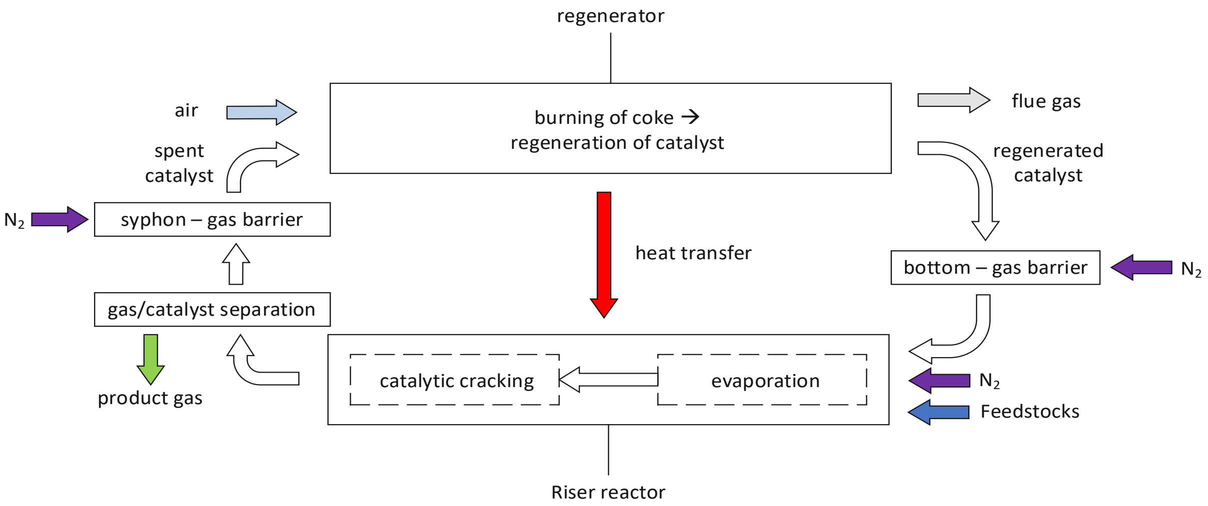


figure 25: schematic of the catalyst cycle [17]

table 8: List of fluidization regimes in different sections of the FCC pilot plant

section	fluidization regime	function	medium
bottom	fluidized bed	gas barrier, even catalyst circulation	nitrogen
syphon	fluidized bed	gas barrier, stripper, catalyst circulation	nitrogen
regenerator	fluidized bed	catalyst regeneration, heat/enthalpy supply	air
cooler	moving bed	temperature control	air
riser (reactor)	pneumatic transport	high heat and mass transfer between gas and solids	nitrogen, feed

4.1 Plant Modifications

As mentioned before in chapter 3.7 different modifications of the feeding system were used/tested in this thesis. Depending on the miscibility of the different feeds one pump (Variation A; feed is miscible) or two pumps (feed is not miscible) were used. Two different versions of the feeding system with two pumps came into use: Variation B and Variation C.

Pumping not miscible feeds separately (if they do not form an emulsion) guarantees a consistent admixture ratio, whereas with a shared reservoir it would not be possible due to inhomogeneous distribution that is present even with vigorous stirring.

For Variation B (P&ID figure 26) the pipes of the two feeds were merged before the tubular oven (pre-heater). If possible, this is the preferred modification since both feeds are preheated before going into the Riser, promoting fast evaporation. The P&ID figure 26 also represents Variation A if one of the pumps is closed off.

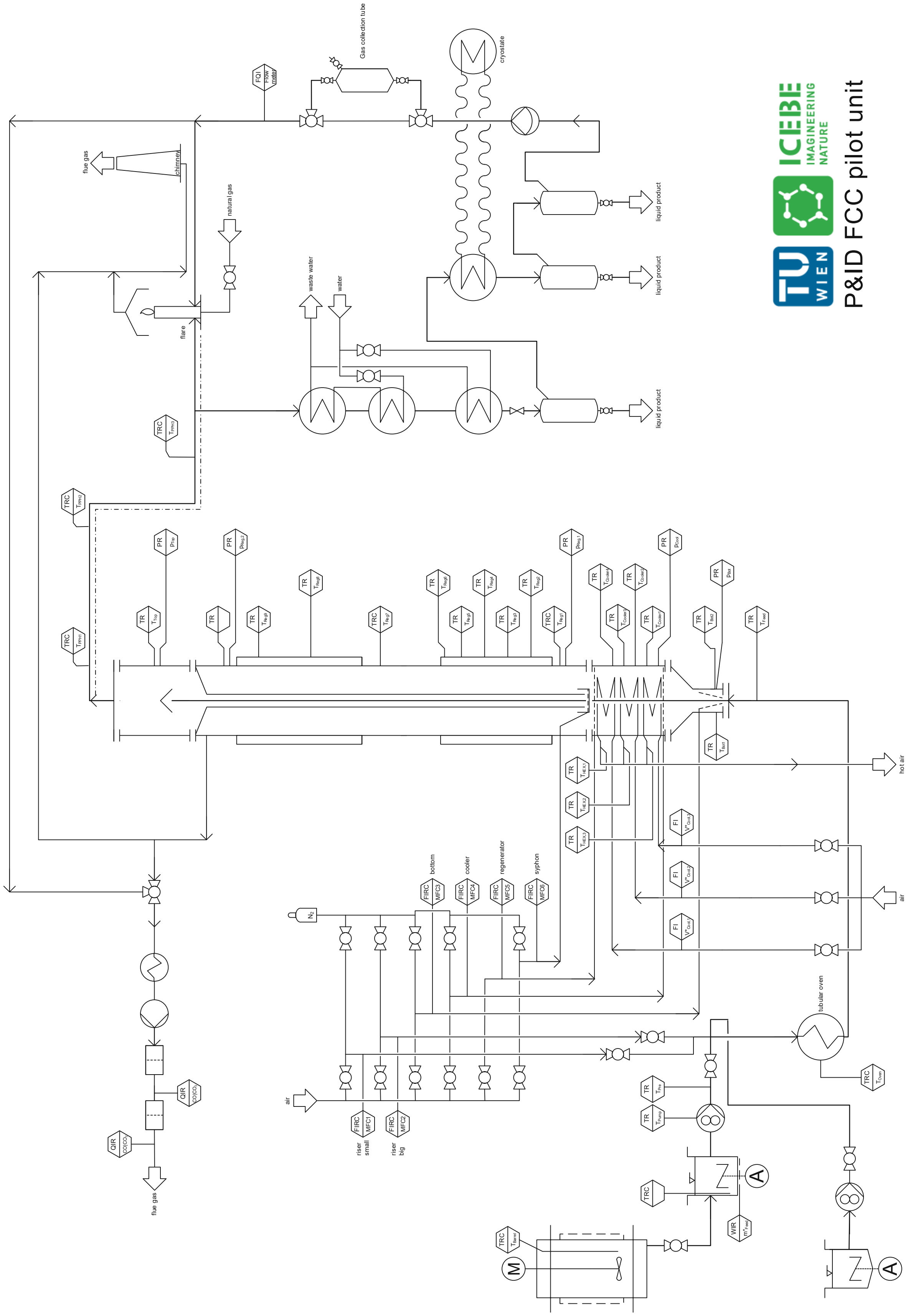


figure 26: P&ID of FCC pilot unit Variation B with the pipes of the two pumps merging before the tubular oven adapted from [136] by [17] reprinted with permission; closing of one of the pumps results in Variation A

For Variation C (P&ID figure 28) the pipes of the two feeds were merged after the tubular oven before the riser. Here two different variations of feed inlet pipes were tested.

Inlet pipe α is the standard and one simple pipe that leads into the Riser (Variation C1). Inlet pipe β consists of two concentric pipes (Variation C2). In each of them one of the feeds is transported. The feed transported in the inner pipe is not preheated. The feed inlet pipe variation β should enable the use of two different feed inlets without the need of intensive modifications of the FCC pilot plant. This gives the possibility to feed a component that is still at room temperature while feeding a preheated feed. Modification γ uses nitrogen for further insulation of the inlet with not preheated feed. Such feeding systems can be necessary if a feed is temperature sensitive and starts to polymerize at higher temperatures. Schematics of the inlet pipe modifications are shown in figure 27.

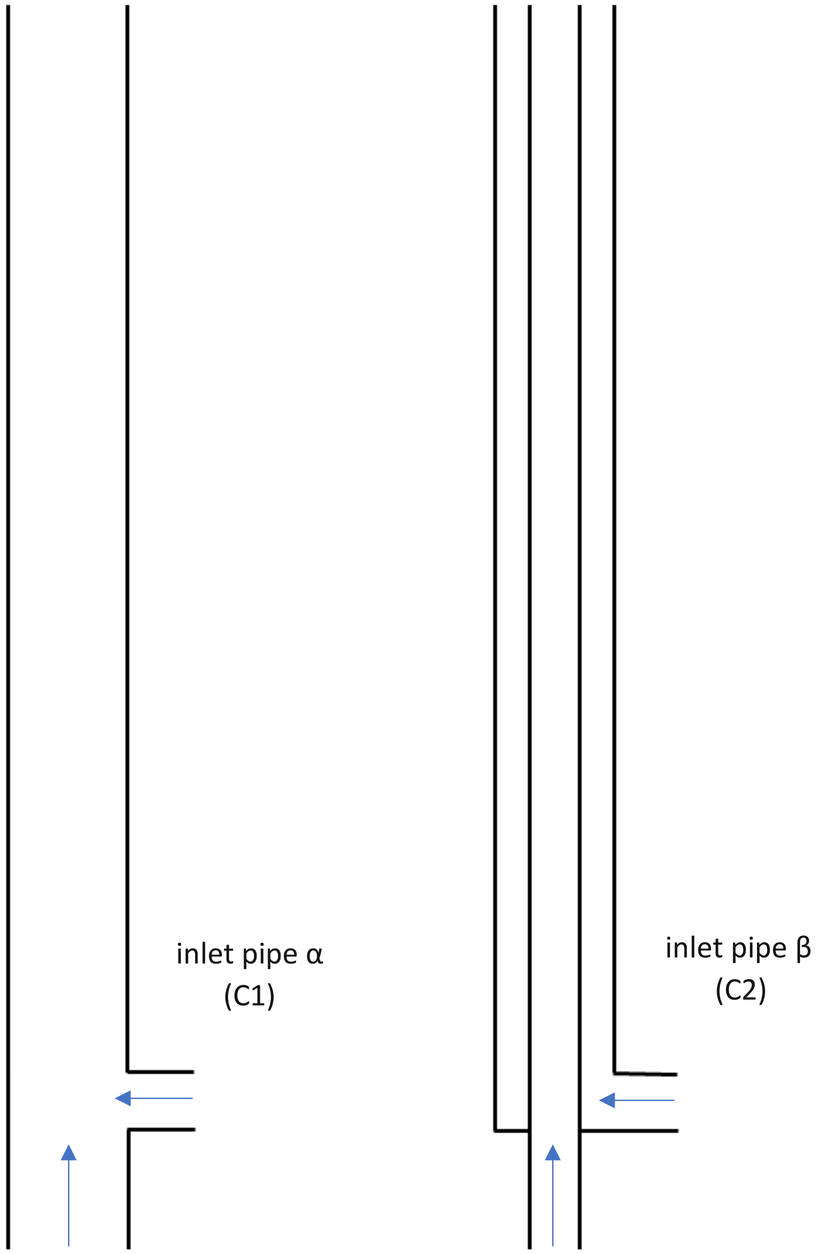


figure 27: schematic of inlet pipe α and inlet pipe β

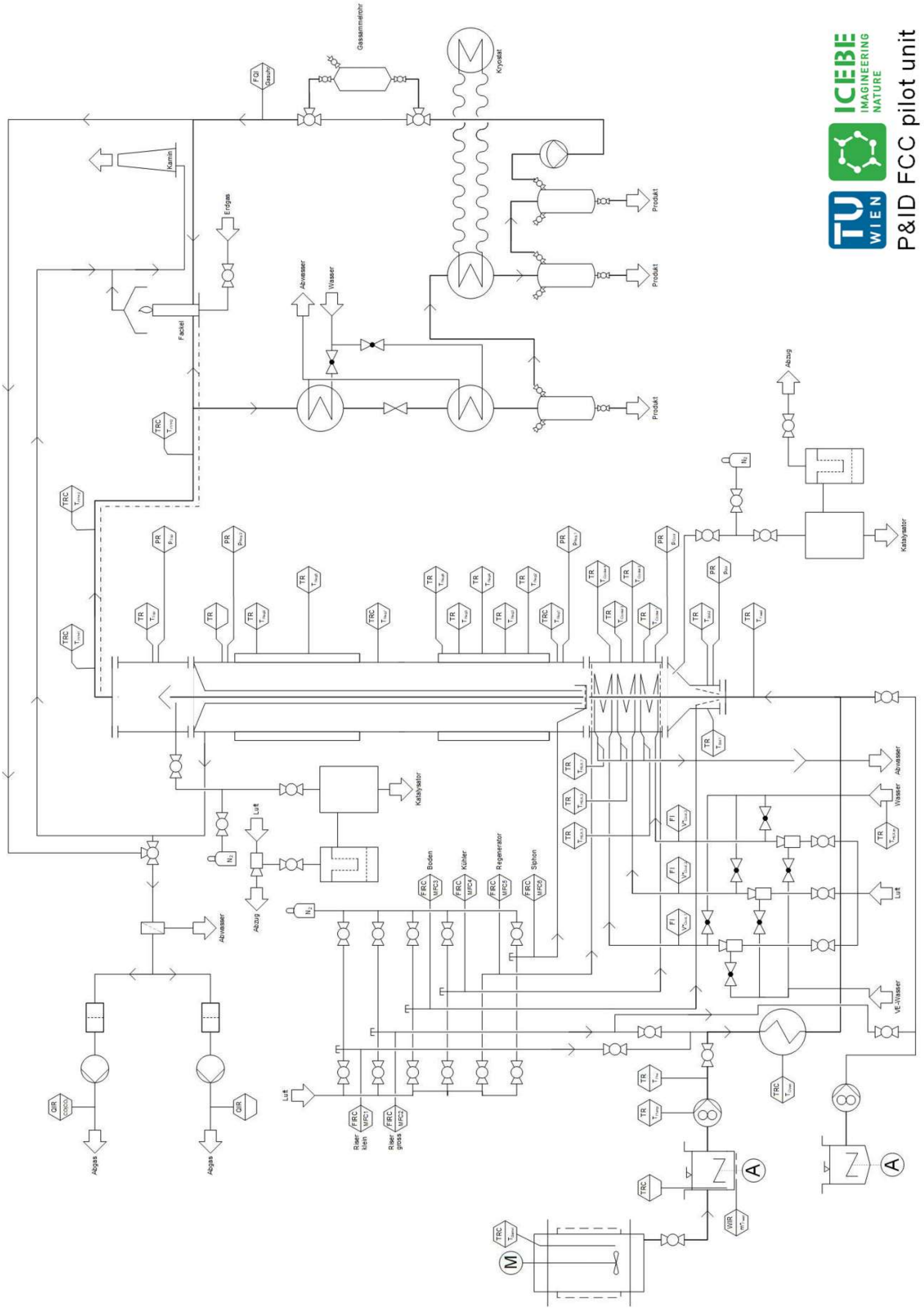


figure 28: P&ID of FCC pilot unit Variation C with the pipes of the two pumps merging after the tubular oven

4.2 Parameter Studies

This subchapter is a summary of studies done to gauge the influence of different operating conditions and process parameters that can be varied at the pilot plant on the product spectrum. The parameter study done in this thesis is presented in this chapter for a better overview.

4.2.1 Pressure

Due to the way in which catalytic cracking units work the pressure is given by its construction and thus is not a changeable operating condition [117].

4.2.2 Catalyst and Catalyst Aging

As mentioned in chapter 2.7.5 there are many ways to customize catalysts for certain applications e.g. production of specific products or optimization for a type of feed. Büchele et. al. [137] compared three different catalysts using the FCC pilot plant at TU Wien being able to validate the claims of the catalyst manufacturer for the increase of the promoted products.

In industrial applications roughly 45-450 g of fresh catalyst per barrel feed (159 L) is added to make up for loss of catalyst activity and the reduction of catalyst due to the discharge of finer particles with the flue gas [107]. The aging phenomenon mainly results from the contact with steam at high temperatures, the deposition of heavy metals and the destabilization caused by sodium [117]. This would mean a need for new catalyst roughly every twenty experiments. But the fact that the contact of catalyst with steam is strongly reduced in the FCC pilot plant compared to industrial plants, since the fluidization medium is nitrogen, further reduces the need for catalyst renewal.

4.2.3 Catalyst to Oil Ratio

Higher Catalyst to Oil (C/O) ratios results in an increased formation of coke and gaseous products. Lower C/O ratios are more favorable for gasoline and LCO production [77].

The control of the catalyst to oil ratio of the pilot plant can only be influenced to a limited extent. An important parameter for the variation of the catalyst to oil ratio is the catalyst circulation rate. Bielansky [135] and Berchtold [138] showed that the fluidization rate of bottom and cooler, the height difference between the catalyst level in the regenerator and the feed inlet tube have a significant influence on the circulation rate. The fluidization can be easily controlled using installed MFC’s. The penetration depth of the feed inlet can also be changed by using a shorter or longer pipe. Furthermore, a cone to influence the width of the catalyst inlet into the riser was designed by Bielansky [135] which was further developed by Berchtold [138].

4.2.4 Riser Temperature

An increase in temperature leads to a decrease in average molecular mass of the formed products, resulting in an increase of gaseous products and a decrease in gasoline and LCO production. Higher temperatures also show an increase in conversion to ethane, propene and butadiene in comparison to their alkane counterpart [117], formation of aromatic hydrocarbons is also favored [117]. The cracking behavior of paraffinic feedstocks is less dependent on the temperature than that of aromatic feedstock [77]. Examples for studies with different Riser temperatures done on the pilot plant are from Büchele et. al. [20], [137] and Berchtold [138]. In figure 29 and figure 30 the results of the hydrocarbon gas and the gasoline lumps from three different temperature studies (A, B and C) are depicted. As expected for all the studies (different catalyst and VGO with a feed rate of 2.45 kg/h) the hydrocarbon yield increased with increasing temperatures whereas the gasoline yield decreased.

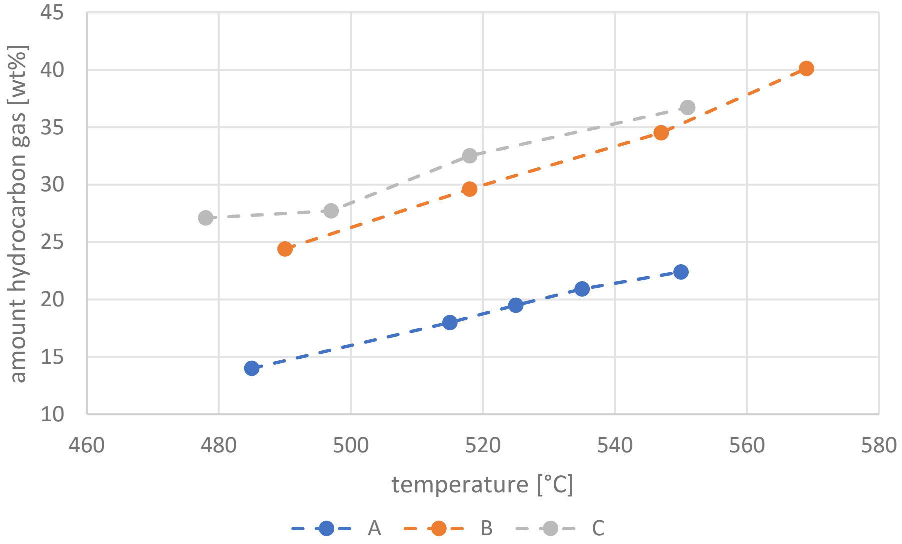


figure 29: Results for the hydrocarbon gas lump yield from three temperature studies (A,B,C); data from [138]

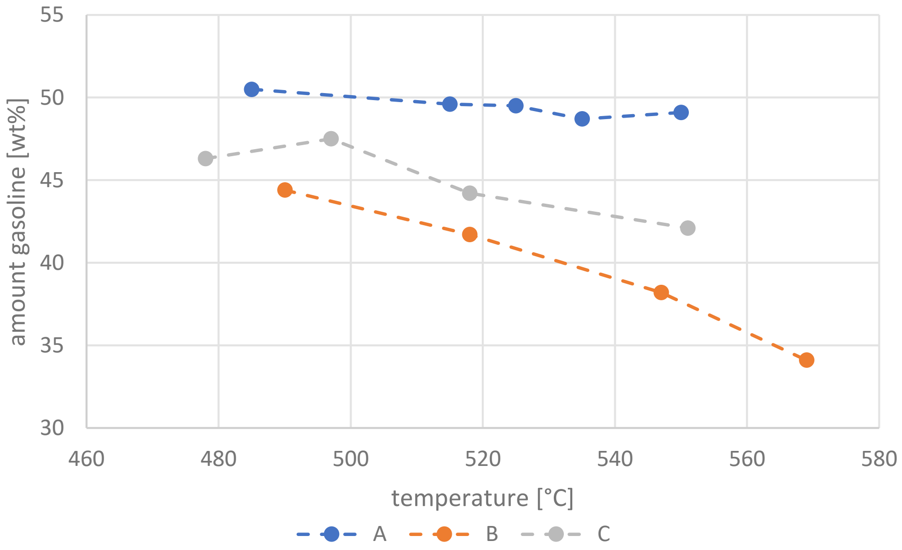


figure 30: Results for the gasoline lump yield from three temperature studies (A,B,C) [138]

4.2.5 Contact Time

The contact time of catalyst and feed is shorter in the FCC pilot plant compared to an industrial plant due to the smaller construction size. This can be somewhat counter acted with higher catalyst circulation rates resulting in higher catalyst to oil ratios similar to the concept of SCT (short contact time) catalytic cracking [79].

4.2.6 Riser auxiliary Fluidization

Following there will be two studies presented a smaller one done for determination of relevancy and one done in more detail. Büchele [17] investigated the influence of the riser auxiliary fluidization on the product spectrum since increasing the riser fluidization is a good tool when dealing with feeds with high CCR values. The information of the experiments' conditions are given in table 9, the results for the lumps, hydrocarbon gas and gasoline as well as the total fuel yield are depicted in figure 31.

table 9: Experiment conditions for the riser fluidization study done by Büchele [17] conducted at a riser temperature of 550 °C and a federate of 2 kg/h

feedstock	**riser auxiliary fluidization [NL/min]**	**C/O-ratio [-]**
VGO_5	0.1	20.5
VGO_5	1	32.3
VGO_5	2.5	45.3
VGO_5	5	57.7

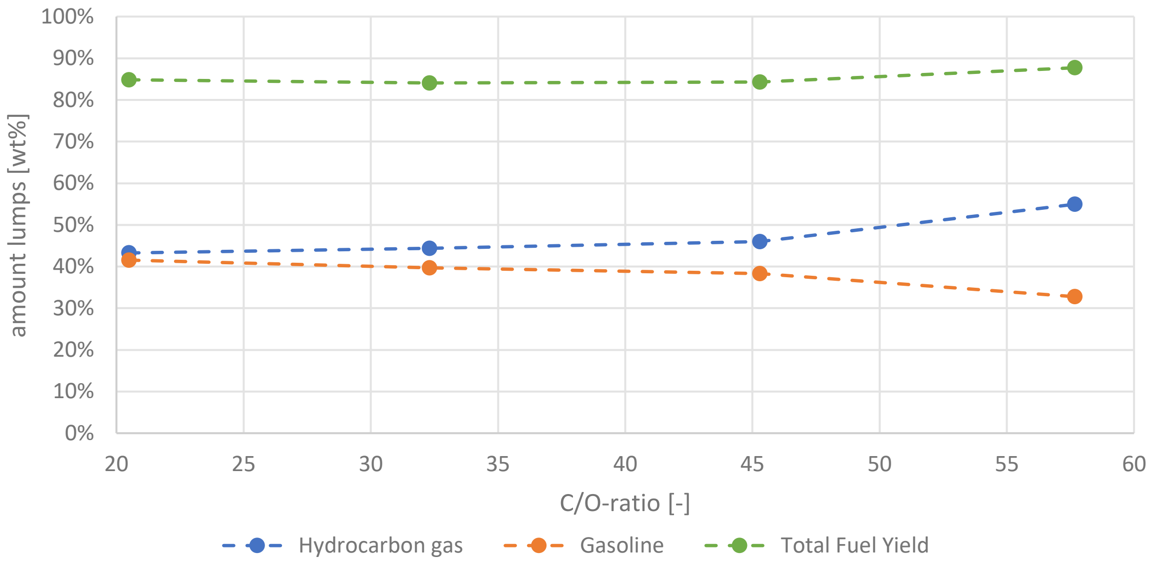


figure 31: Results of the riser fluidization study done by Büchele [17]

The information of the experiments conditions of the study regarding the riser auxiliary fluidization are given in table 10, the results for the lumps hydrocarbon gas and gasoline as well as the total fuel yield in relation to the riser auxiliary fluidization respectively the C/O are depicted in figure 32 and figure 34. In figure 33 the C/O in relation to the riser auxiliary fluidization is depicted. It can be seen that the increase of the C/O ratio from a fluidization of 0.1 NL/min to 5 NL/min is of a similar extent. But the C/O ratio does not increase in a linear fashion.

table 10: Conditions of the riser fluidization sturdy carried out in the course of this thesis done at a riser temperature of 550 °C and a federate of 2 kg/h

feedstock	**riser fluidization [NL/min]**	**C/O-ratio [-]**
VGO_4	0.1	25.0
VGO_4	0.5	27.7
VGO_4	1	35.5
VGO_4	1.5	41.8
VGO_4	2	34.5
VGO_4	2.5	40.3
VGO_4	3	36.7
VGO_4	3.5	46.7
VGO_4	4	44.5
VGO_4	4.5	45.7
VGO_4	5	62.3

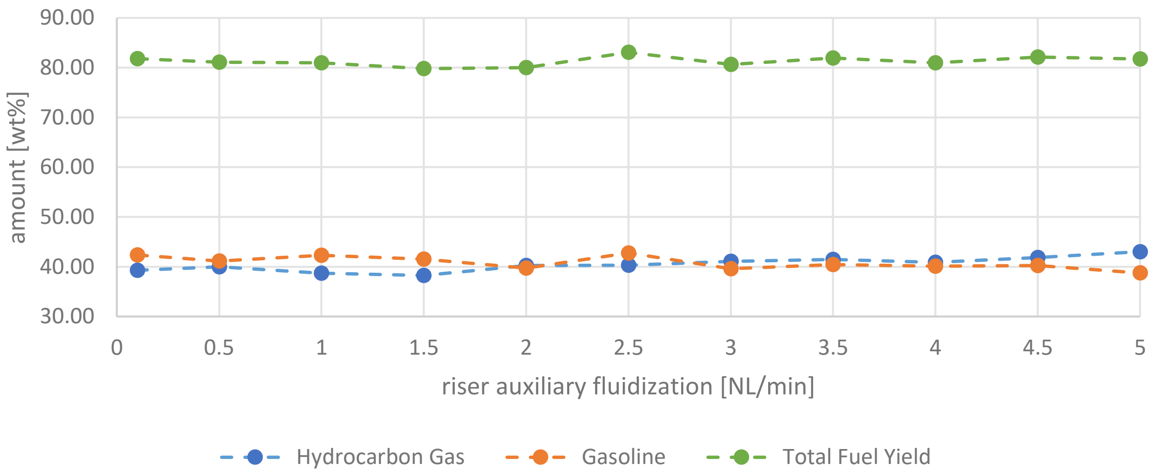


figure 32: Results of the riser fluidization study in relation to the riser auxiliary fluidization

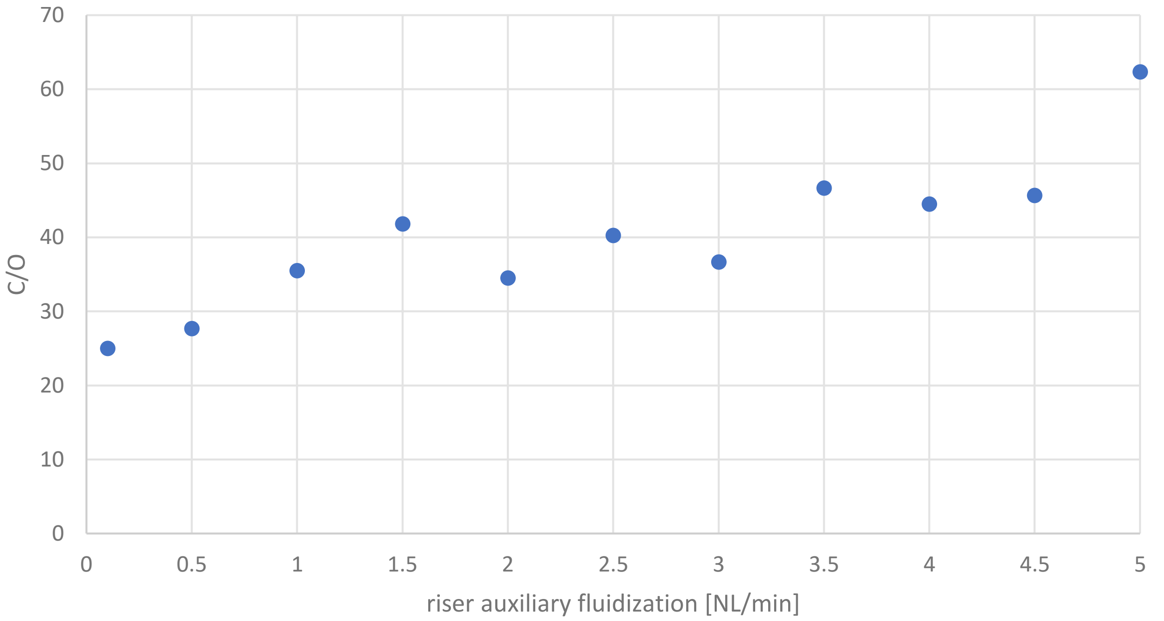


figure 33: C/O ratio in the relation to the riser auxiliary fluidization

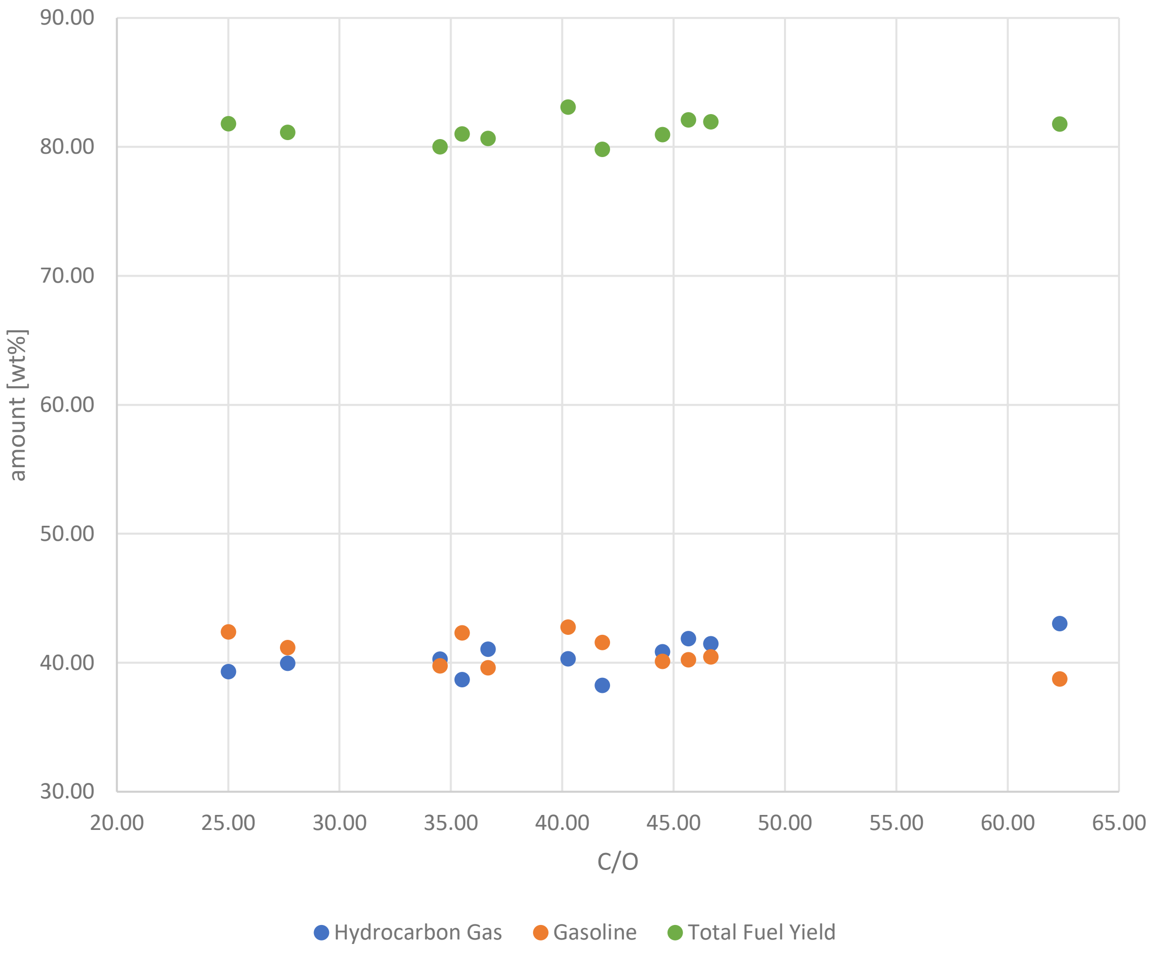


figure 34: Results of the riser auxiliary fluidization study in relation to the C/O ratio

The study from Büchele as well as the one done in this thesis show that the C/O increases with higher riser auxiliary fluidization. Likewise the amount of hydrocarbon gas produced increases whereas the produced amount of gasoline decreases.

4.2.7 Feed Rate

Berchtold [138] investigated the influence of the variation of the feed rate on the product spectrum. The results are shown in figure 35. It can be seen that higher feed rates lead to higher C/O ratios, although measures were set to keep the C/O ratio constant. The increase of the feed rate results in an increase of the velocity in the riser which means a higher amount of catalyst is drawn into the riser. This phenomenon does not seem to be linear. The produced amount of LCO + residue lump stays the same. Gasoline slightly increases and hydrocarbon gas decreases.

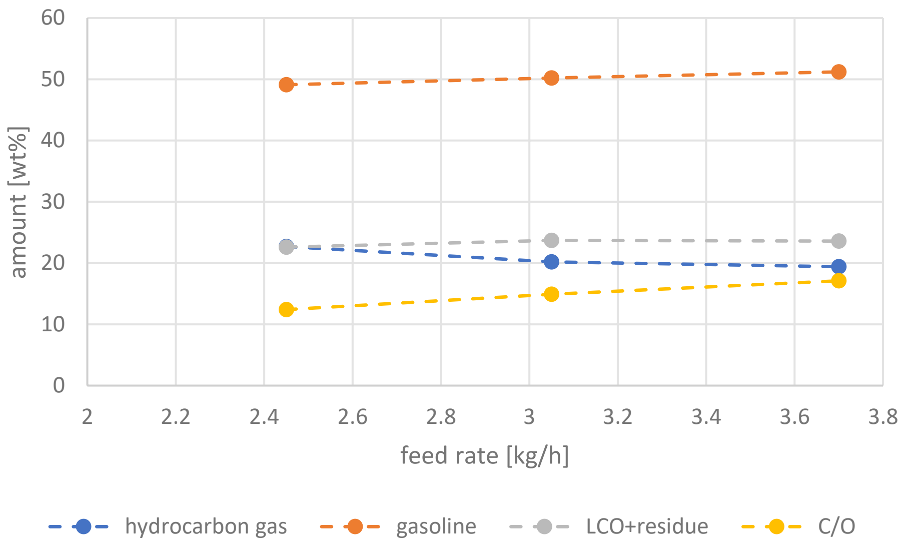


figure 35: Results of a study done at the pilot plant to evaluate the influence of the feed rate; data from [138]

4.3 Pilot Plant Operation

In advance to an experiment the feed has to be filled into heated reservoirs, the function of the pumps is checked and the product gas pipes to the flare and the online analyzer are cleaned. For each new series of experiments, or after a long stand still of the plant, the online analyzer is recalibrated.

At first the plant is heated to operating temperature. Since the Regenerator and the Freeboard have the highest operating temperature their heating is turned on first. More heating elements and electrical devices are turned on later to ensure use of electricity only when necessary. When the plant is heated to operating temperature the different cooling systems are turned on and last safety check-ups are done (e.g. function of the hot vent and gas detector).

The next step is changing the fluidization from Riser, Siphon, Cooler and Bottom from air to nitrogen. After the oxygen content in the regenerator is stabilized, the sample collection unit is flushed with nitrogen. The oxygen content is also observed to rule out possible leaks or obstructions. At this point the feeding of the plant can be started. In order to have stable operation conditions, especially catalyst circulation (hence enough heat in the Riser to evaporate the feed) the feed rate is slowly increased and the Riser fluidization decreased. When the pilot plant is in a steady state within the desired operation conditions (feed rate, riser temperature) the first sample can be taken. If the feed is problematic (e.g. because of high CCR value or ash content) or if there is not much feed available, the first part of feed start can be done with VGO or another suitable feed. Shortly before reaching stationary operation it can be switched to the correct feed and the last adjustments are made.

During the sampling the pilot plant is kept in stationary operation. The detailed sequence of events during sample collection is described in chapter 4.4. Especially important here is the correct measurement of the carbon oxide concentration of the flue gas. It will later serve as the basis for the calculation of produced coke. After the sample is drawn the carbon oxide concentration of the product gas as well as the catalyst circulation rate are determined. When the operating conditions are stable again the next sample can be collected.

After all samples are collected or in the case of loss of steady state due to blockages plant shutdown can be initiated. First, the feed supply is stopped and the riser fluidization is turned up to standby conditions. To ensure the longevity of the pumps they are cleaned with an appropriate liquid (depending on the feed) which can stay in them for storage. The flare extinguishing is the sign, that the Riser is free of feed and sample collection unit can be flushed with nitrogen. Afterwards all the nitrogen fluidization can be changed to air and the various cooling systems can be turned off. The pilot plant is regenerated at elevated temperatures afterwards to guarantee the burn-off of all possible coke blockages and build ups.

The collected gas samples must be measured on the same day due to leakage of the gas collection tubes. The collected liquids are prepared and measured on the day after the experiment.

The different stages of an experiment can be summarized as followed:

- Preparation of plant and feed (4 h)
- Heating the plant to operating temperatures (4 h)
- Start-up of measuring devices and pilot plant until it reaches stationary operation (3 h)
- Plant operation at stationary point and sampling (4 h)
- Shutdown of pilot plant (cleaning and regeneration) (3 h)
- Measuring of the gaseous products (can be started after the first is obtained) (6 h)
- Preparation and measuring of the liquid products (12 h)

4.4 Sample Collection

The product of the FCC pilot plant is burned in a torch. During sample collection the valve to the sample collection unit is opened and a membrane pump turned on. This allows to direct a portion of the product gas into the sample collection without destabilizing the torch as it guarantees a flue gas that can be released into the environment. A schematic of the sample collection unit is depicted in figure 36. During sample collection the flue gas from the Regenerator is measured by the online analyzer to determine the concentration of carbon oxides and oxygen. The product gas passes through three cooling sections of which the first two are cooled via water and the third cooled via ethanol with -20 °C. Afterwards it is directed through a frit to capture droplets. The three liquid fractions from water cooling, ethanol cooling and droplet collection are combined and represent the liquid product. The gaseous fraction passes another gas washing bottle containing glass wool and a filter to guarantee it is droplet free before it enters the pump. Afterwards it is directed into the gas collection tube from where it flows into the gas meter and then further into the torch for combustion. After the sample collection the gas collection tube is sealed and removed. The liquid fractions are combined and weighted and the volume of treated gaseous product read from the gas meter. After the samples are collected the sample collection unit is turned on again and a portion of the gaseous product (cleaned from gas which could condense at room temperature) is sent to the online analyzer for the carbon oxides content measurement. The last step of sample collection is the measurement of the catalyst circulation rate. This step destabilizes the steady state of the pilot plant. So, there is a waiting period until the next sample can be collected.

The gaseous sample can be measured as is, but the liquid fraction has to be separated if there are two phases (water and organic) and the organic phase has to be filtrated before the GC measurement.

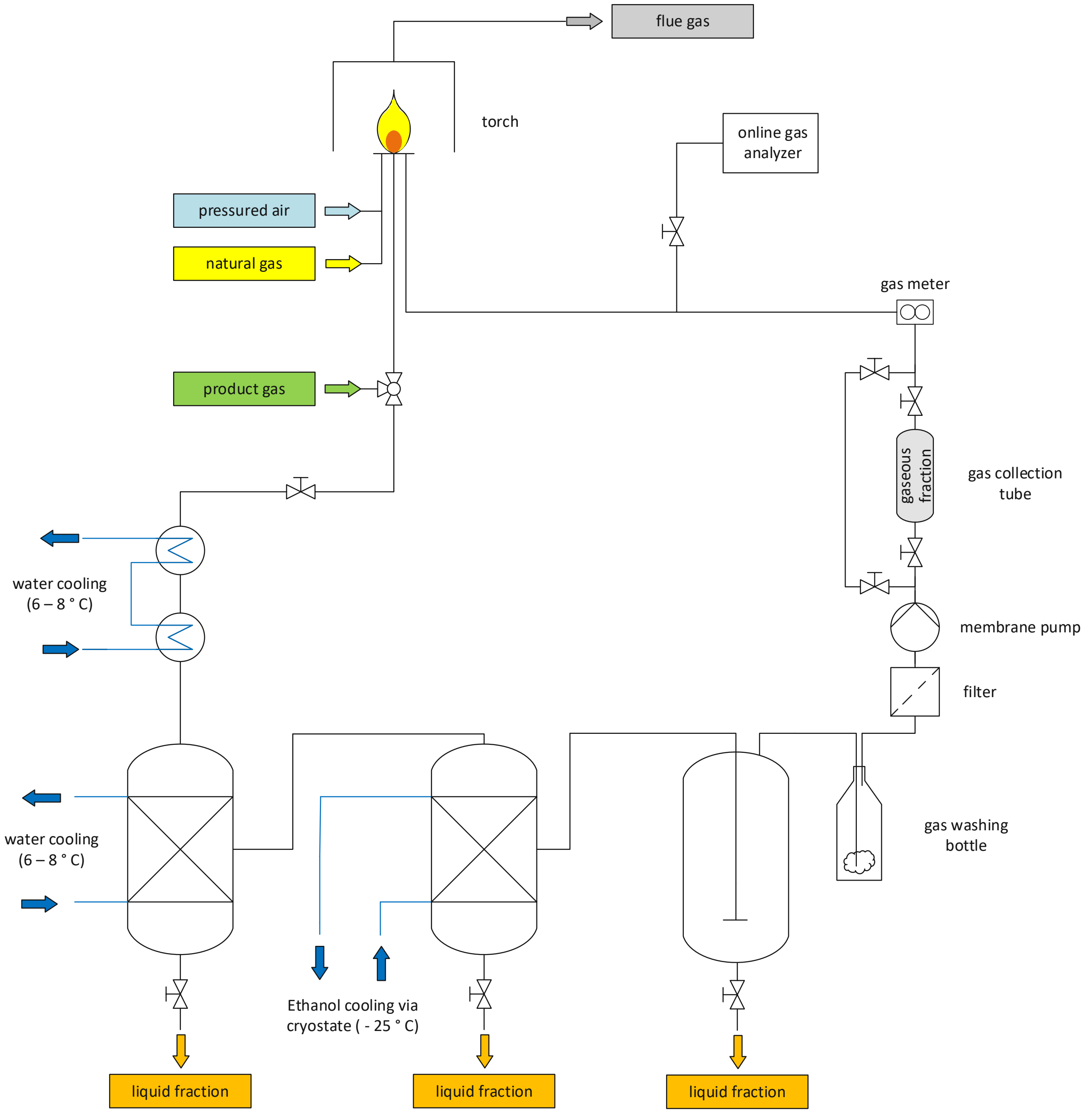


figure 36: Product sample collection unit from the FCC pilot plant adapted from Bielansky [135] by Büchele [17]

4.5 Analysis Methods

The different analysis methods used to characterize the feed enable predictions for the behavior of the feed and possible sources of problems during the experiment. One of the biggest obstacles to overcome in conducting experiments with alternative feeds is the feeding into the pilot plant. With the knowledge won by the characterization of the feed preventive adjustments can be made and some trial and error for the optimization of the feeding of problematic feed can be avoided. Measurements during the experiment enable plant operation and give the first results. The analysis of the products is important to quantify and qualify them enabling the assessment of the influence of the changed parameter (e.g. catalyst, feed, temperature) on the products.

4.5.1 Analysis of the Feed

Conradson Carbon Residue

The Conradson Carbon Residue value (CCR) is the percentage of residue produced if volatile substances are evaporated and the residue is thermally decomposed in the absence of oxygen. The CCR value provides an indication for the tendency of coke formation. The CCR test is defined in the standard ASTM D189 [139]. Although the coke formation in an FCC plant does not follow the same reaction path the tendencies can be translated. On one hand feeds with a high coke formation often lead to smaller possible throughputs in pilot plants due to excessive heat production or too much usage of oxygen for the combustion. On the other hand, feeds that produce a lot of coke can be added when too little coke is produced to keep the temperature up in an FCC plant. Furthermore, one of the main problems encountered during experiments with the FCC pilot plant are blockages especially in the feeding system. The decomposition reactions in the system equate the reactions during the CCR test, due to the absence of catalyst in the feeding system. One of the measures used to counter act high CCR values is the utilization of higher riser fluidization values.

Ash Content

The ash content is the percentage of residue produced if the substance is burned and the residue burned out for an extended period of time. The measurements were conducted based on the standard DIN EN ISO 6245 [140]. The value does not correspond one to one with the content of inorganics in the feed since some of it will evaporate and due to the combustion the oxygen content will increase. It also does not equate to the amount of inorganic solids formed in the FCC plant since the conditions are different. Nonetheless the ash content gives a good grasp on the amount of ash formed since the differences are not significant in the scheme of plant operation. Although there is a difference in behavior depending on the composition of inorganic species, the main problems for the operation of the pilot plant is buildup in the feeding system due to solidification when part of the feed is evaporated in the tubular oven or at the feed inlet due to the evaporation of the rest of the liquid feed. These blockages make the maintenance of stable operation condition for longer periods of time unlikely. Due to this fact feeds/admixtures with ash contents > 1 % express a high likely hood to lead to premature terminations of experiments. If possible experiments are done to find a way to reduce the ash content of the potential feed. Furthermore, high ash contents are problematic in the utilization of the feeds in the industry. They increase the emissions of particulate matter, promote the wear on the plant and they accumulate on the surface of the catalyst, reducing its efficiency.

Miscibility

The miscibility of the feed is of high importance for co-feeding to guarantee homogeneous feed composition. If a homogeneous mixture is not possible the feeding system has to be adapted accordingly. Different possible adaptions are presented in chapter 4.1. During this work many different challenges due to the behavior of non-miscible feeds were encountered.

4.5.2 Analysis during the Experiment

The operation parameters of the FCC pilot plant such as temperature and pressure in the different plant sections as well as feed rate are continuously monitored so they can be adjusted if necessary.

The measurements taking place during the plant operation that are important for the results of the experiment are:

- Recording of oxygen and carbon oxides contents in the flue gas during sample collection
- Measurement of hydrocarbons and nitrogen in the gaseous product treated in the sample collection
- Online measurement of carbon oxides content of the gas sample
- Determination of the catalyst circulation rate

Carbon oxides content

CO and CO_2 concentrations of the gaseous fractions are measured online via a Rosemount NGA2000 MLT3 gas analyzer. The analyzer utilizes an NDIR method. The Non-dispersive infrared measurement (NDIR) is a spectrometric method where the absorption of a, for the measured molecule, specific wavelength is detected and the concentration calculated with the help of a calibration curve.

Oxygen content

The concentration of oxygen in the gases is measured as well via a Rosemount NGA 2000 MLT3 gas analyzer. This time utilizing a paramagnetic measurement method. This method uses a heated flow cell with a magnetic field and a measuring resistor. The gas flow cools down the measuring resistor. If oxygen is present its paramagnetic properties accelerates it within the magnetic field creating a stronger flow cooling down the measuring resistor even further. This acceleration of the stream is dependent on the amount of oxygen present.

Gas volume

The used gas meter is a diaphragm gas meter which counts as a positive displacement meter. Oscillating diaphragm form chambers which alternated between being filled and expelling. This allows for a nearly continuous flow. The cycles of the diaphragm are counted to determine the flow rate.

Circulation rate

The fluidization of the syphon is turned off, which stops the circulation of the catalyst. Instead of being transported into the regenerator the catalyst remains in the syphon. The consequence is a sinking catalyst level in the regenerator which comes hand in hand with a pressure drop. This pressure drop corresponds with the amount of catalyst transported into the riser. The derivation of this method based on fluidized bed technology is mentioned by Weinert [136] in more detail. The final calculation of the catalyst mass flow rate can be described as followed:

$$\dot{m}_{catalyst} \approx \frac{A_{Regenerator}}{g} \cdot \frac{\Delta(\Delta p_{Regenerator})}{\Delta t_U} \tag{29}$$

Utilizing the catalyst mass flow and the feed rate the catalyst to oil (C/O) ratio can be calculated (equation (30)).

$$\frac{C}{O}\, ratio = \frac{\dot{m}_{catalyst}}{\dot{m}_{feed}} \tag{30}$$

4.5.3 Analysis of the Products

In figure 37 the analytical pathway of the product after leaving the Riser is summarized. The online analysis of the gaseous fraction was already mentioned in the chapter above.

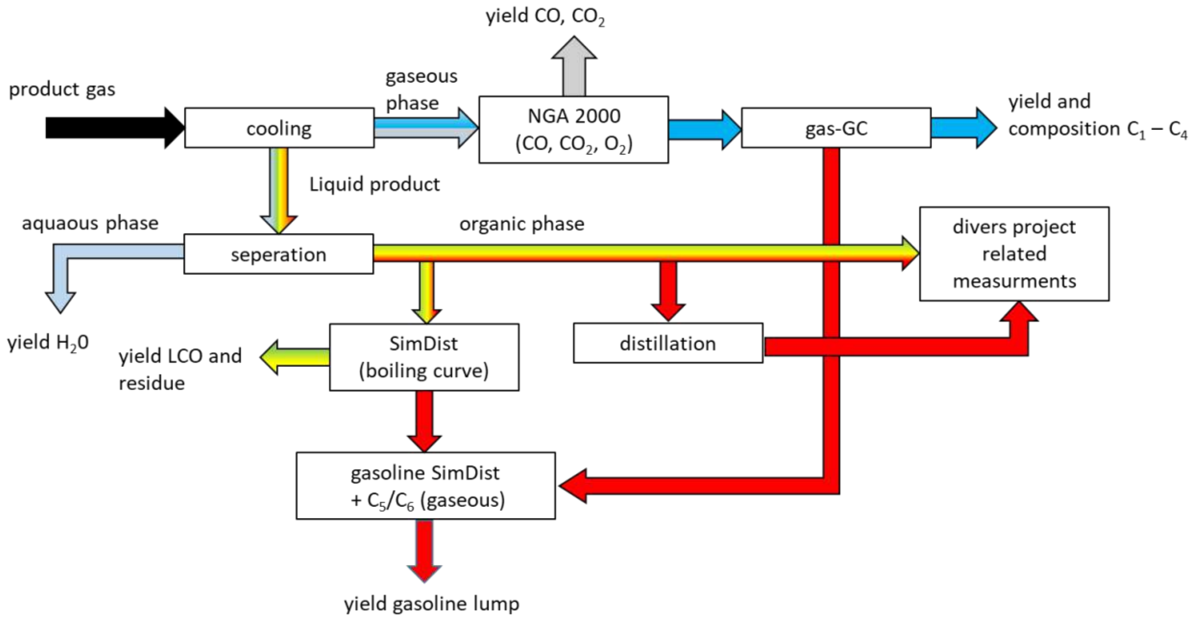


figure 37: Analytical path of the gaseous and liquid products

4.5.3.1 Liquid Fraction

The liquid fraction is collected from the cooling system before the measurement of the concentrations of carbon oxides. In the presence of water in the product an additional step must be taken, due to the fact that some of the water in the product stream freezes on the cooling coils in the ethanol cooler. To calculate a representative value for the water fraction all the liquids condensed in the sample collection unit are collected (from sample collection itself and from the CO_x measurement). For water free products only the liquids from the sample collection itself is collected. On the day after the experiment the melted liquid products are added to the additional vessel. In order to calculate the real water content the sum of the different organic phases and water phases are used. It is important to recalculate the amount of the original samples in order to fix the falsified water content.

The liquid fraction is weighted and if necessary, separated in a separating funnel. The aqueous phase is weighted as well and the weight of the organic phase is calculated from these two values. The organic phase is filtrated. With the filtrated sample the distillation curve is determined via simulated distillation. For some cases non-filtrated samples or distilled gasoline samples were sent to an external laboratory for measurements. Additional analysis procedures were not disclosed for confidentiality purposes of the laboratory. The details of the gas chromatograph that was used for the determination of the simulated distillation can be taken from table 11.

table 11: Configurations of the gas chromatograph used for the simulated distillation measurement

type	**Shimadzu GC-17A**
injector	split 30:1 1.5 µl @ 350 °C
carrier gas	hydrogen 1.68 ml/min constant flow
temperature program	35 °C to 350 °C; dwell-time 22 min
column	Zebron ZB-1
dimension	30 m length x 0.32 mm inner diameter x 0.25 µm film thickness
detector	flame ionization detector (FID) @ 350 °C

4.5.3.2 Gaseous Fraction

In Addition to the online measurement mentioned above further gas chromatography is conducted to determine the content of N_2 and the different hydrocarbons C_1-C_6. The details of the gas Chromatograph used for the measurement of the gaseous product can be taken from table 12.

table 12: Configurations of the gas chromatograph used for the nitrogen and hydrocarbon gas determination

type	**Shimadzu GC-17A**
injector	splitless 50 µl @ 200 °C
carrier gas	helium 1.46 ml/min constant flow
temperature program	50 °C to 200 °C; dwell time 30 min
Number of sections	2 (I & II)
columns	I: Varian CP-Al_2O_3/Na_2SO_4
	II: CP CarboPLOT P7
dimensions	I: 50 m length x 0.25 mm inner diameter x 4 µm film thickness
	II: 25 m length x 0.53 mm inner diameter x 25 µm film thickness
detectors	I: flame ionization detector (FID) @ 200 °C
	II: thermal conductivity detector (TCD) @ 125 °C

4.5.4 Evaluation of the Results

For purposes of proper interpretation the products of the FCC experiments were summarized into lumps. Lump models are usually used for processes with a multitude of different products which can hamper the characterization of each individual substance or make the evaluation unnecessarily complicated. In this work a model with 7 lumps (figure 38) was chosen. As indicated in the figure only hydrocarbon gas and gasoline are considered as products of the experiments. Carbon oxides, light cycle oil, residue, water and coke fall under by-products in this evaluation.

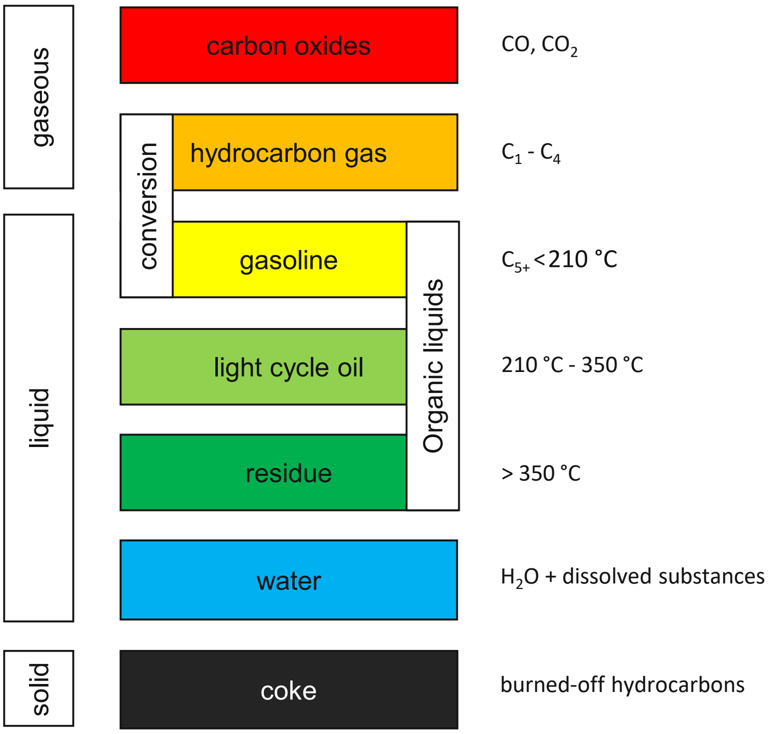


figure 38: Lump model used for evaluation of the products

5 Experimental

In table 10 of chapter 4.2.6 the conditions of the experiments for the riser fluidization study are listed. In table 13 the conditions of the different co- feeding experiments conducted in this thesis are summarized. All experiments were done at a riser temperature of 550 °C, a riser auxiliary fluidization of 0.1 NL/min and a feed rate of 2 kg/h. Exceptions are the experiments marked with * which had a feed rate of 2.5 kg/h. For every experimental series a “BaseCase” with pure VGO was conducted, providing a baseline the different admixtures can be compared to.

table 13: List of experiments conducted during the course of this thesis; ✓ stands for a successful experiment ✗ for an unsuccessful one

Name	VGO	Co-feed	Admixture co-feed [%]	Modification	
VGO_4_1*	VGO_4	-	-	A	✓
LST10*	VGO_4	LST	10	A	✓
VGO_3_1	VGO_3	-	-	A	✓
HSyn5	VGO_3	HSyn	5	A	✓
HSyn10	VGO_3	HSyn	10	A	✓
HSyn20	VGO_3	HSyn	20	A	✓
VGO_3_2	VGO_3	-	-	A	✓
DiRe5	VGO_3	DiRe	5	A	✓
DiRe10	VGO_3	DiRe	10	A	✓
DiRe20	VGO_3	DiRe	20	A	✗
VGO_1	VGO_1	-	-	A	✓
PO5	VGO_1	PO	5	B	✓
PO5	VGO_1	PO	5	C1;C2	✗
VGO2_1	VGO_2	-	-	A	✓
SPOcw5	VGO_2	SPOcw	5	B	✓
SPOcw10	VGO_2	SPOcw	10	B	✗
SDPOcw5	VGO_2	SDPOcw	5	A	✓
SDPOcw5	VGO_2	SDPOcw	5	B	✗
SDPOcw10	VGO_2	SDPOcw	10	A;B	✗
Mix10	VGO_2	SPOcw/SDPOcw	3/7	A	✓
VGO_2_2	VGO_2	-	-	A	✓
VGO_4_2	VGO_4	-	-	A	✓

6 Results and Discussion

The detailed data for the experiments can be found in the appendix.

6.1 Results of Parameter Studies

6.1.1 Influence of the Riser Fluidization

The results of this study can be found in chapter 4.2.6. They were brought forward for the completeness of that chapter. It is shown that the C/O increases with higher riser fluidization. Likewise the amount of hydrocarbon gas produced increases whereas the produced amount of gasoline decreases.

6.1.2 Water Recovery Rate

In experiments with different bio-based feeds it became apparent, that the collection of liquid samples distorts the amount of water found. This happens because not all of the water is condensed in the water cooler. The vaporous water that reaches the ethanol cooler partially freezes on the cooler surface. This circumstance was brought to attention by strongly varying water contents in samples obtained in the same experiment. The amount of water increased from sample to sample. Probably due to the fact that the ice layer got thicker and thus the temperature of the surface decreased, allowing more water to condense and not freeze in connection. Thus, a new strategy for sample collection with a water phase was developed.

With 3.85 % water admixed to VGO via the modification B a water content of 3.35 % feed-based was determined. Which means a water recovery rate of 87 % can be achieved with the new method. It must be noted that this recovery rate was done for only one admixture and slightly different to a usual experiment, due to the fact that one long sample collection was done (1 h) in contrast to the three collections (each 15 min) done during a typical experiment. For future studies a more thorough investigation of the recovery rate of water dependent on the absolute water content in samples is advised to gain a more accurate understanding of this behavior.

6.2 Lipstick Mass

The experiments were done with plant modification A.

In figure 39 it can be seen that with the addition of 10 % LST the lump hydrocarbon gas increases from 40.74 % to 43.99 %. While the lumps gasoline (-1.28 %), LCO (-0.87 %), residue (-0.66 %) and coke (-0.55 %) decrease.

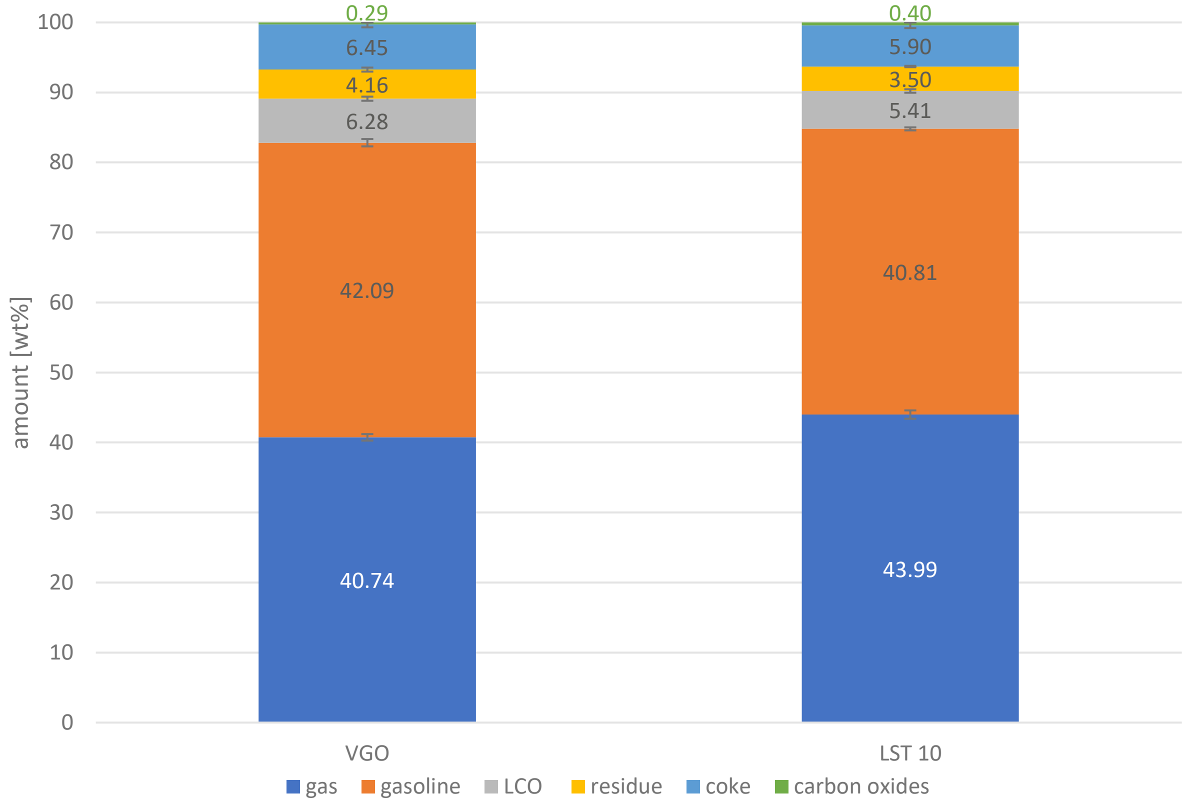


figure 39: Results from the experiment series with treated lipstick mass (LST)

In the hydrocarbon gas lump there is a slight increase in the concentration of methane from 2.45 % to 2.81 % and butanes from 21.90 % to 22.36 % as well as a more significant increase of the butanes concentration from 19.97 % to 23.73 %. The concentrations of ethylene (-1.17 %), propane (-0.61 %) and propylene (-1.73 %) decrease due to the admixture of 10 wt% LST, while the concentration of ethane stays the same.

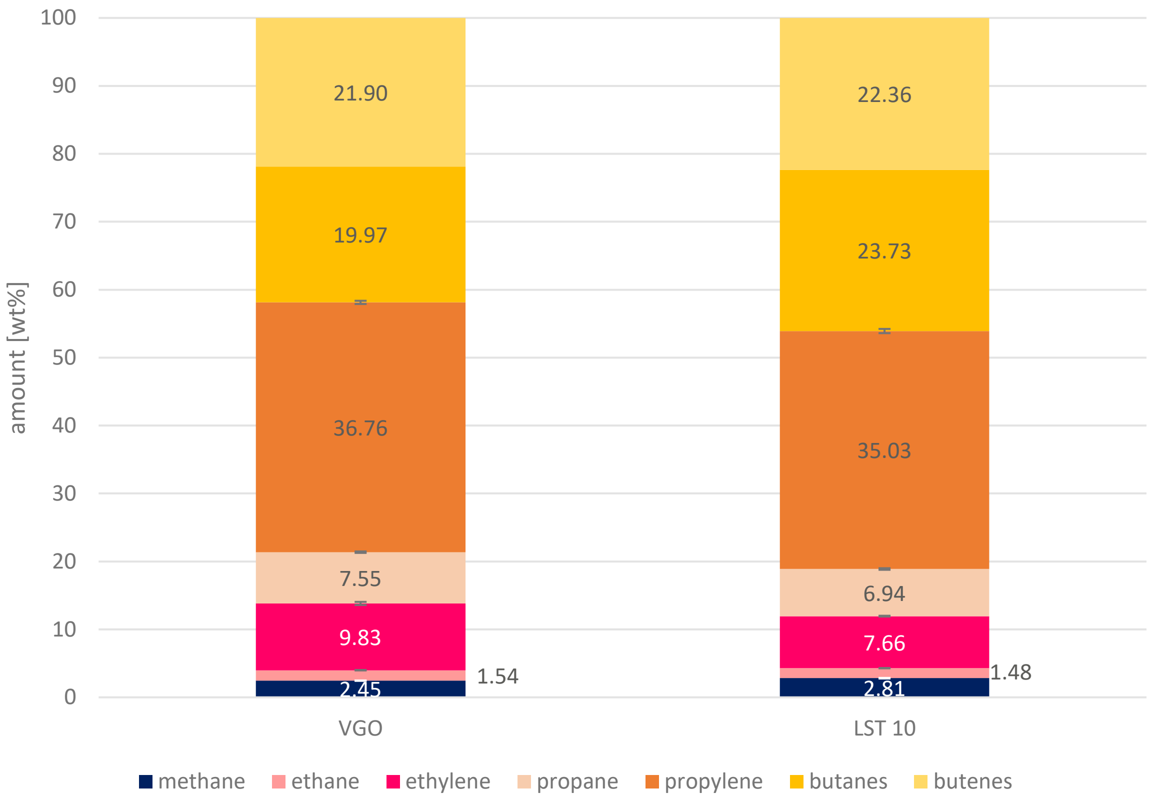


figure 40: Composition of the gaseous product of the experiment series with treated lipstick mass

Since this experimental series was a feasibility study, the liquid product was not analyzed in more detail.

Lipstick mass which is free from any solid is a suitable co-feed for the FCC process. It did not cause problems within the feeding system or the FCC pilot plant. The results are similar to other studies using wax as a co-feed for the FCC process [141], [142]. Waxes favor the hydrocarbon gas production, owing to the fact that they consist mostly of long chain n-paraffins which gain an easy access to the active sites in the catalyst [141]. This makes it a suitable co-feed for refineries which optimize hydrocarbon gas production. But if it is to be used in commercial applications a feasible industry scale way of separating the solids has to be found.

6.3 Pyrolysis Oils from Plastic Waste

All experiments were done with plant modification A.

6.3.1 Heavy SynCrude

Heavy SynCrude has a similar product spectrum as VGO. In figure 41 it can be seen that there is barely any difference in the lump distribution between the admixtures. Heavy SynCrude produces slightly more hydrocarbon gas and less carbon oxides than VGO. The lumps gasoline, LCO, residue and coke show no significant trend, which leads to the assumption that all lumps contribute to the slight increase of the hydrocarbon gas lump.

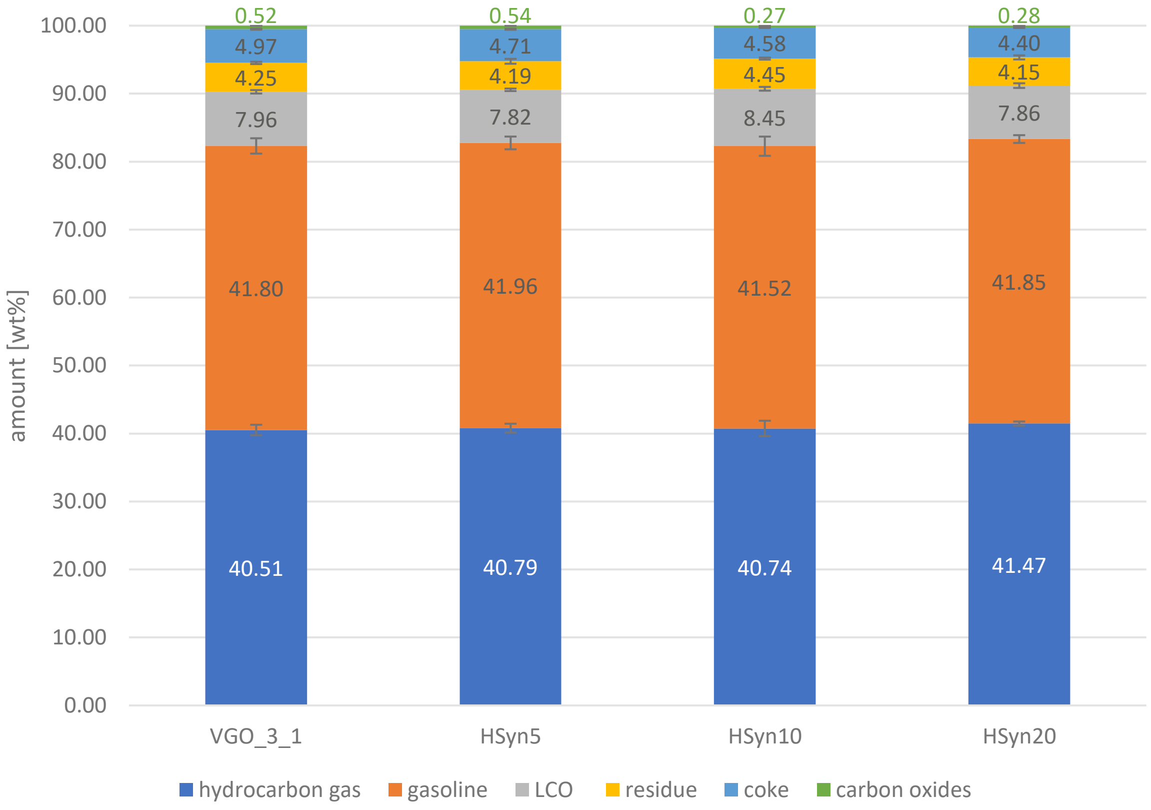


figure 41: Results from the experiment series with Heavy SynCrude

In figure 42 the composition of the lump hydrocarbon gas is depicted. No significant trends for the influence of Heavy SynCrude on the amounts of produced gases can be observed.

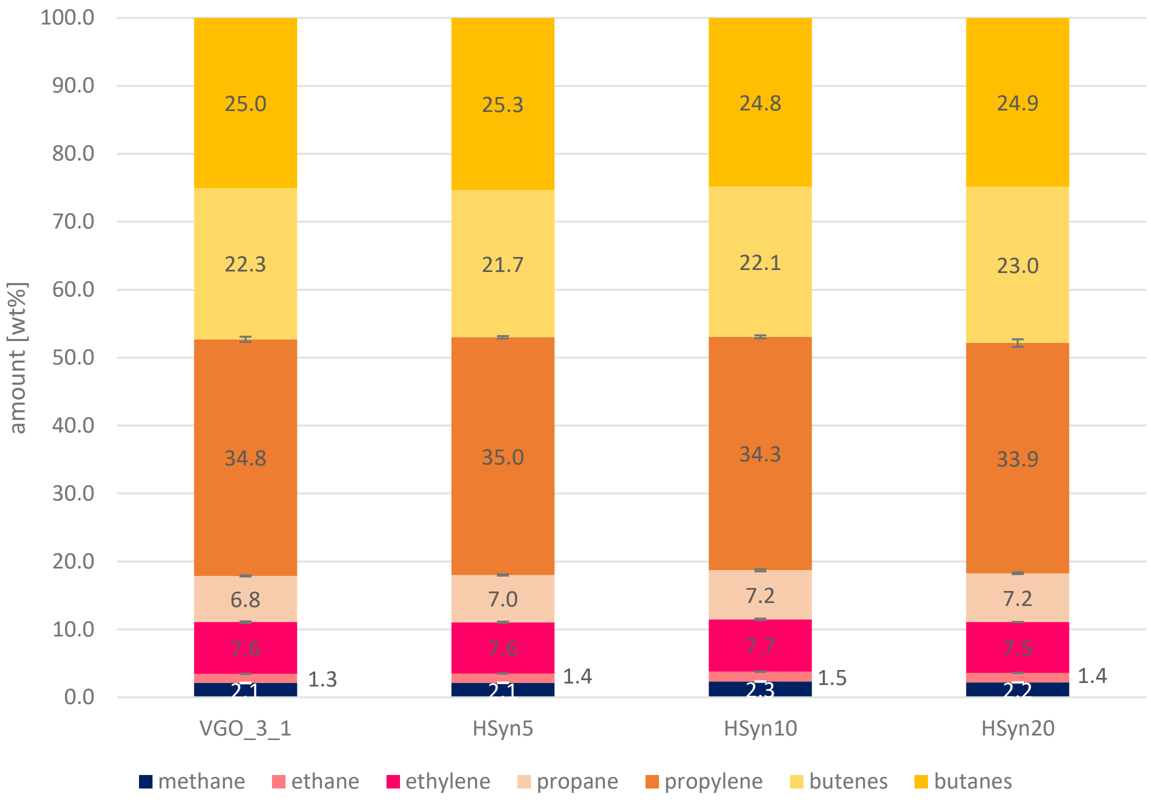


figure 42: Composition of the gaseous product of the experiment series with Heavy SynCrude

In table 14 the analysis data of the liquid organic phase is shown. It becomes apparent that a higher admixture of Heavy SynCrude reduces the amount of sulfur from 434 mg/kg to 382 mg/kg (20 wt% Heavy SynCrude) and Halogens (as Cl) from 3.11 mg/kg to 2.55 mg/kg (20 wt% Heavy SynCrude) in the liquid product. Whereas the amount of nitrogen increases from 140 mg/kg to 151 mg/kg (20 wt% Heavy SynCrude). The total content of aromatics shows no clear trend depending on the admixture of Heavy SynCrude. All inorganic elements analyzed in the samples were under the detection limit with the exception of Na (0.007 mg/kg) and Ni (0.026 mg/kg) in the case of the VGO sample.

table 14: Measured parameters of the liquid organic phase from the experiment series with Heavy SynCrude

		VGO_3_1 organic phase	**HSyn5** organic phase	**HSyn10** organic phase	**HSyn20** organic phase
sulfur	**mg/kg**	434	408	404	382
nitrogen	**mg/kg**	140	147	139	151
initial boiling point	**°C**	0	-2	1	-3
final boiling point	**°C**	466	466	465	465
free water	**mL/L**	0	0	0	0
total aromatics	**wt%**	81.4	77.2	77.7	79.4
sum halogens (Cl,Br) as Cl	**mg/kg**	3.11	3.62	2.71	2.55
Mn	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Pb	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Fe	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Al	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Ca	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Cr	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Mo	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Na	**mg/kg**	0.007	-	<0.1	-
Ni	**mg/kg**	0.026	<0.1	<0.1	<0.1
V	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Zn	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Hg	**mg/kg**	<0.005	<0.005	<0.005	<0.005
Ag	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Cd	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Cu	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Mg	**mg/kg**	<0.01	<0.1	<0.1	<0.1
Sn	**mg/kg**	<0.01	<0.1	<0.1	<0.1
As	**µg/kg**	<0.005	<0.005	<0.005	<0.005

In figure 43 the boiling curves of the organic phases are shown, which are nearly identical.

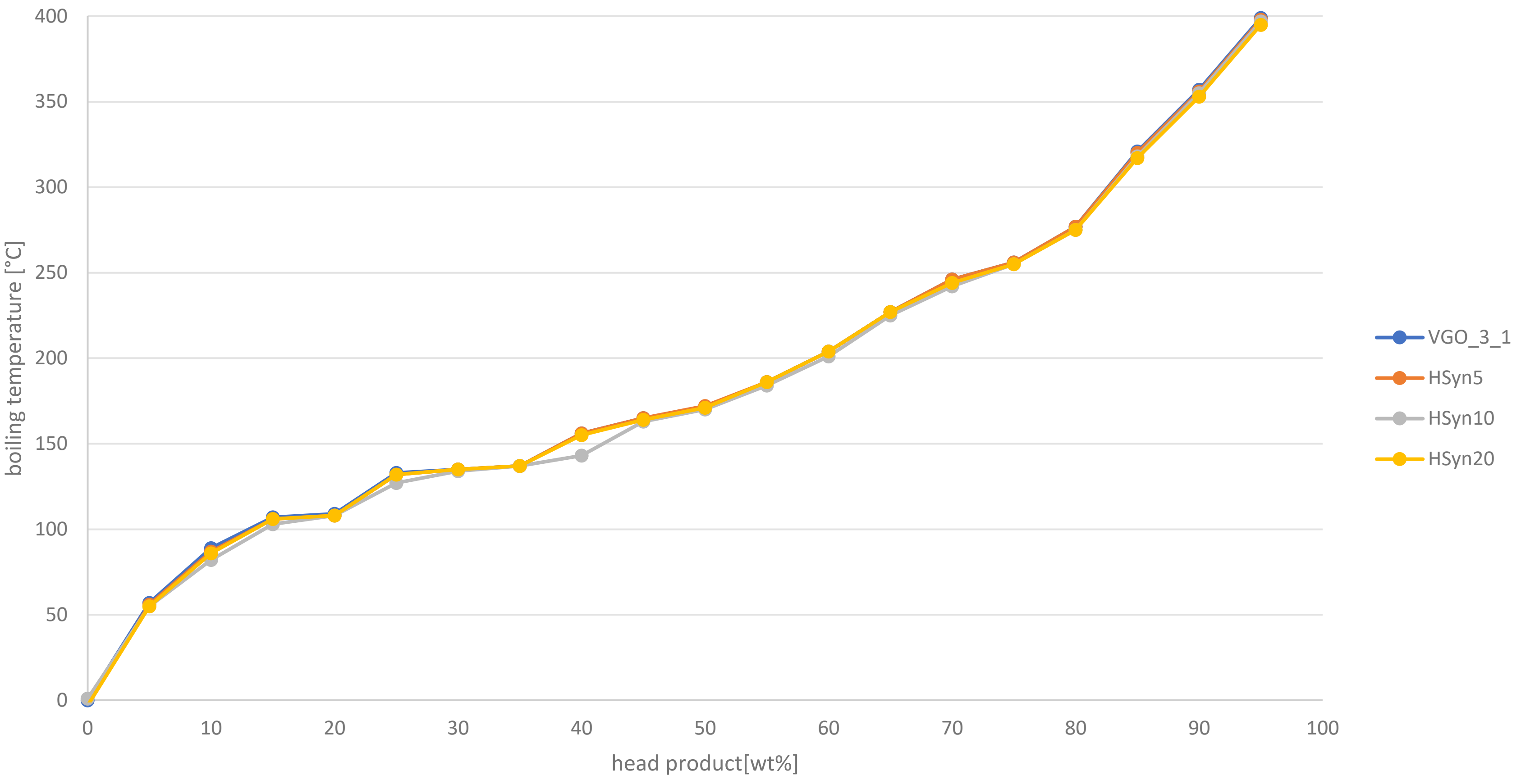


figure 43: Boiling curves of the organic phases produced in the experimental series with Heavy SynCrude

Heavy SynCrude has a slightly lower boiling curve (figure 20) and a similar product spectrum as VGO. Also, the quality of the different products (gaseous and liquid) stay roughly the same for the analyzed parameters. Its low ash content and the small CCR value make it a suitable feed for the FCC process. It can be assumed that even higher admixtures of Heavy SynCrude can be utilized without problems. Nonetheless confirmation via experiments is still recommended before higher admixtures are implemented at an industrial plant.

6.3.2 Distillation Residue

Higher admixtures of Distillation Residue caused problems in the experiments due to the increasing ash content of the feed, impeding an experiment with an admixture of 20 % Distillation Residue. The lumps hydrocarbon gas and coke show an increasing trend. The increase in coke production is not surprising due to the high CCR value of Distillation Residue. Gasoline and LCO show a decreasing trend. The lumps residue and carbon oxides stayed the same.

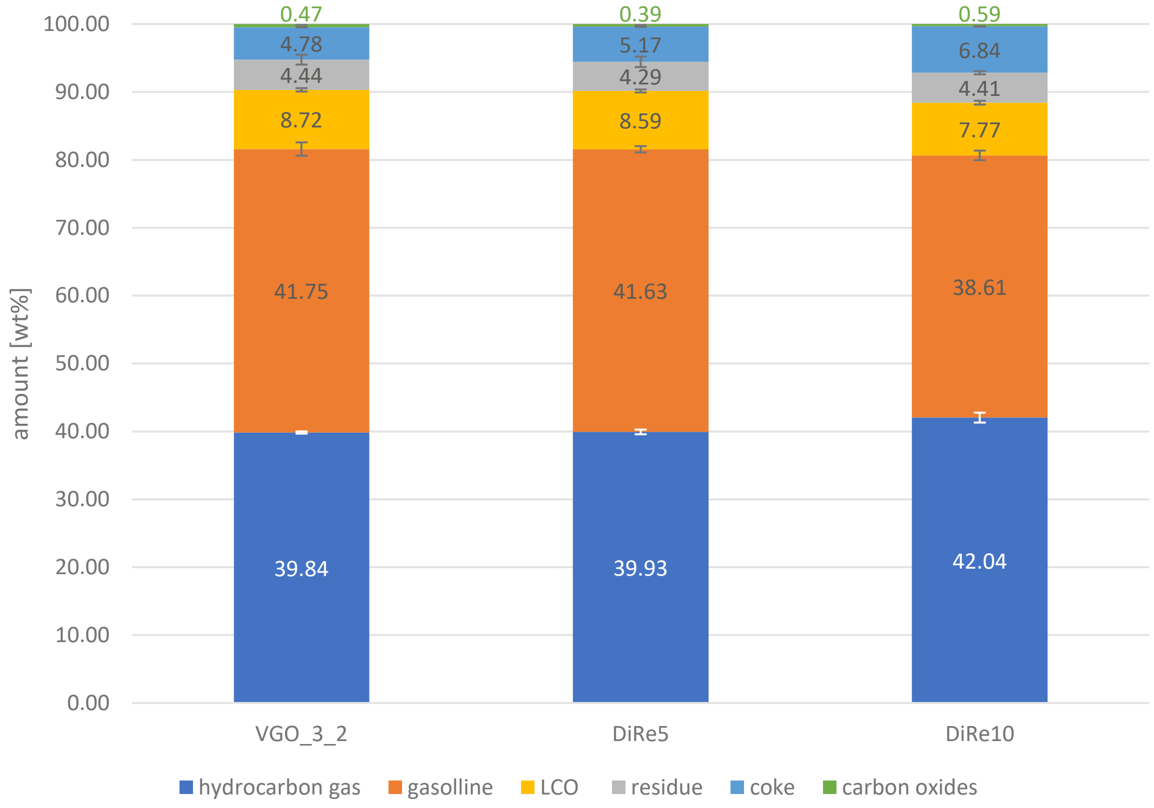


figure 44: Results from the experiment series with Distillation Residue

In figure 45 the composition of the hydrocarbon gas lump is depicted. There is a strong increase of butenes and a less intensive increase in propylene with increasing admixture of Distillation Residue. The amounts of the gases methane, ethane, ethylene, propane and butanes produced decreases with increasing Distillation Residue admixture. Since butenes and propylene are highly sought after products this means a higher gas quality and a slightly higher amount of gas produced.

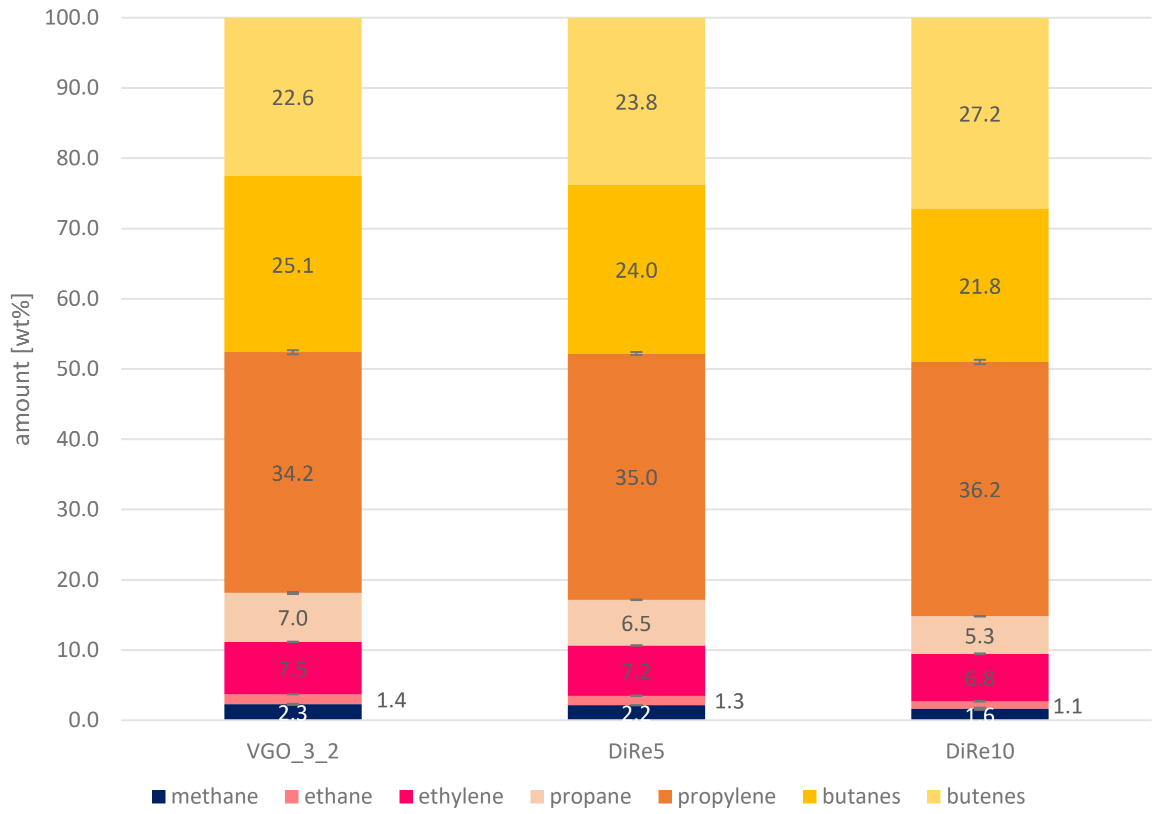


figure 45: Composition of the gaseous product of the experiment series with Distillation Residue

In table 15 the analysis data of the liquid organic phase is shown. It becomes apparent that a higher admixture of Distillation Residue increases the amount of nitrogen from 158 mg/kg to 207 mg/kg (10 wt% Distillation Residue). The content of sulfur, total aromatics and halogens (as Cl) shows no clear trend depending on the admixture of Distillation Residue. Most of the inorganic elements analyzed were below the detection limit in the samples. The exceptions are Pb (1.1 mg/kg), K (1.7 mg/kg), Na (10.4 mg/kg), Si (90.9 mg/kg) and Zn (1.4 mg/kg) in the organic phase when 10 wt% Distillation Residue is co-fed. For the organic phase of the experiment with an admixture of 5 wt% Distillation Residue the exceptions are Na (4.6 mg/kg) and Si (15.4 mg/kg). The liquid organic product of pure VGO has a detectable value for Na (6.3 mg/kg) and Si (57.4 mg/kg) and in addition Zn with a concentration with 0.9 mg/kg.

table 15: Measured parameters of the organic phase from the experiment series with Distillation Residue

		VGO_3_2 organic phase	**DiRe5** organic phase	**DiRe10** organic phase
sulfur	**mg/kg**	384	362	392
nitrogen	**mg/kg**	158	179	207
Initial boiling point	**°C**	<36.1	<36.1	<36.1
Final boiling point	**°C**	512.6	510.5	504.2
free water	**mL/L**	0	0	0
total Aromatics	**wt%**	72.6	70.2	74
Sum halogens (Cl,Br) as Cl	**mg/kg**	4.1	2.6	2.6
Mn	**mg/kg**	<0.5	<0.5	<0.5
Pb	**mg/kg**	<0.5	<0.5	1.1
Fe	**mg/kg**	<0.5	<0.5	<0.5
Al	**mg/kg**	<0.5	<0.5	<0.5
Ca	**mg/kg**	<0.5	<0.5	<0.5
Cr	**mg/kg**	<0.5	<0.5	<0.5
K	**mg/kg**	<0.5	<0.5	1.7
Mo	**mg/kg**	<0.5	<0.5	<0.5
Na	**mg/kg**	6.3	4.6	10.4
Ni	**mg/kg**	<0.5	<0.5	<0.5
Si	**mg/kg**	57.4	15.4	90.9
V	**mg/kg**	<0.5	<0.5	<0.5
Zn	**mg/kg**	0.9	<0.5	1.4
Hg	**mg/kg**	<0.005	<0.005	<0.005
Ag	**mg/kg**	<0.5	<0.5	<0.5
Cd	**mg/kg**	<0.5	<0.5	<0.5
Cu	**mg/kg**	<0.5	<0.5	<0.5
Mg	**mg/kg**	<0.5	<0.5	<0.5
Sn	**mg/kg**	<0.5	<0.5	<0.5
As	**µg/kg**	<0.005	<0.005	<0.005

In figure 46 the boiling curves of the organic phases are shown, which are nearly identical with slight differences in the lower temperature range.

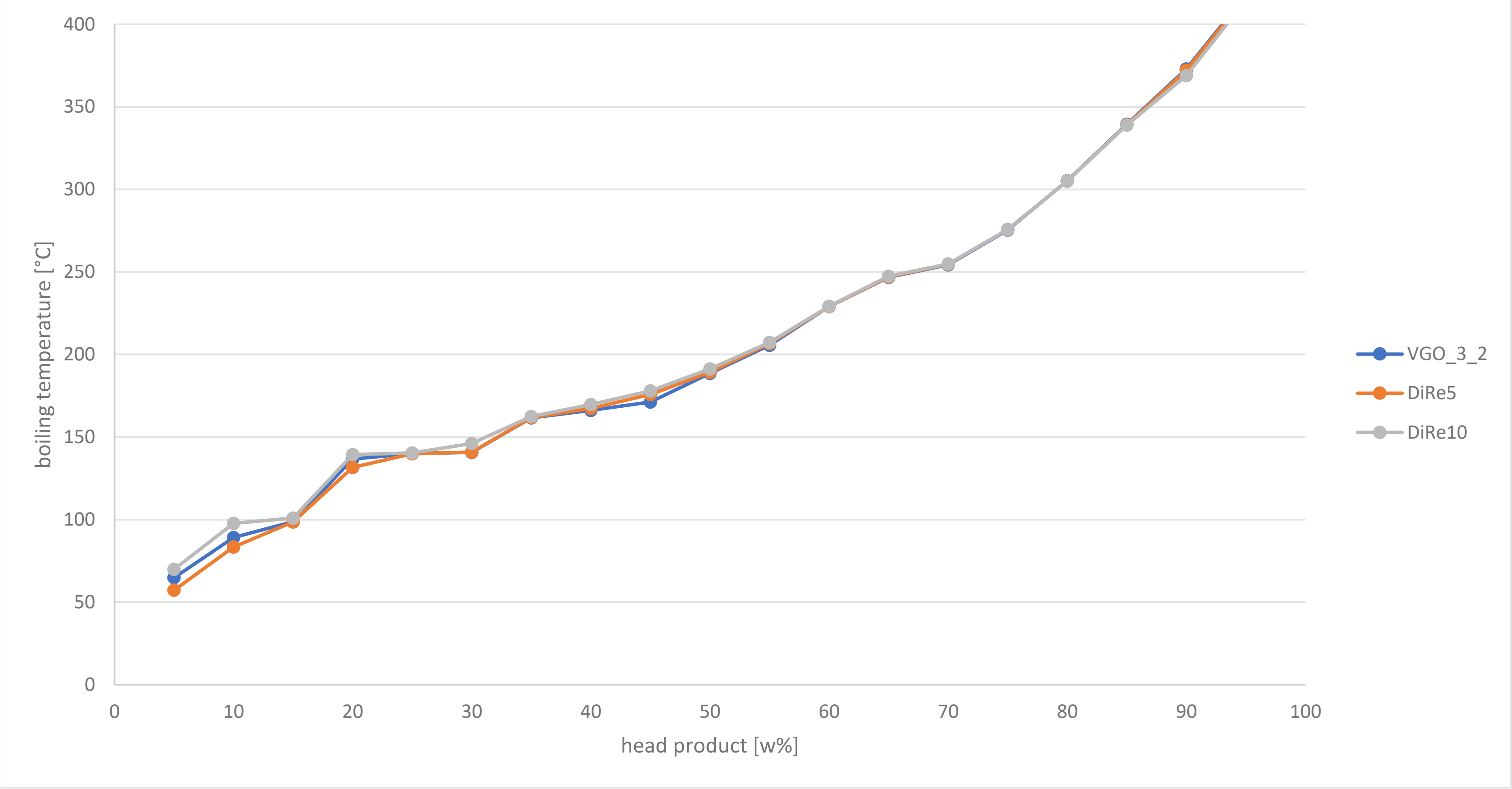


figure 46: Boiling curves of the organic phases produced in the experimental series with Distillation Residue

The utilization of Distillation Residue as co-feed resulted in cloggage of the feed inlet system which was anticipated, due to the high ash content and Conradson Carbon value of Distillation Residue, with the first being most problematic for the utilization in FCC units, lowering the usability of Distillation Residue. If the ash content of Distillation Residue can be decreased it would be an interesting co-feed for the FCC process due to its tendency to form more propylene and butenes while the amounts of gas produced are similar to VGO. Also the quality of the liquid product stays roughly the same for the analyzed parameters.

6.4 Pyrolysis Oils from Clean and Contaminated Wood

6.4.1 Pyrolysis Oil from Clean Wood

Experiments with an admixture of 5 % PO were tested with the modifications B, C1 and C2. Only with modification B sample collection was achieved. For the modifications C1 and C2 the feed inlet system clogged as soon as PO was introduced. It can be seen in figure 47 that the addition of PO to VGO increases the hydrocarbon gas (44.97 % to 47.37 %) and coke production and decreases the gasoline, LCO and residue amount produced. It is also noticeable that PO contains water and oxygen containing components since there is a water lump and the carbon oxide lump increases compared to pure VGO. The amount of water found corresponds to the amount introduced due to the admixed PO which contains about 20 % water (table 5) (1 % of 5 % equals 20 % of 100 %). This leads to the conclusion that the oxygenated compounds in the PO react to CO_x, stay in the liquid phase or are bound in the formed coke.

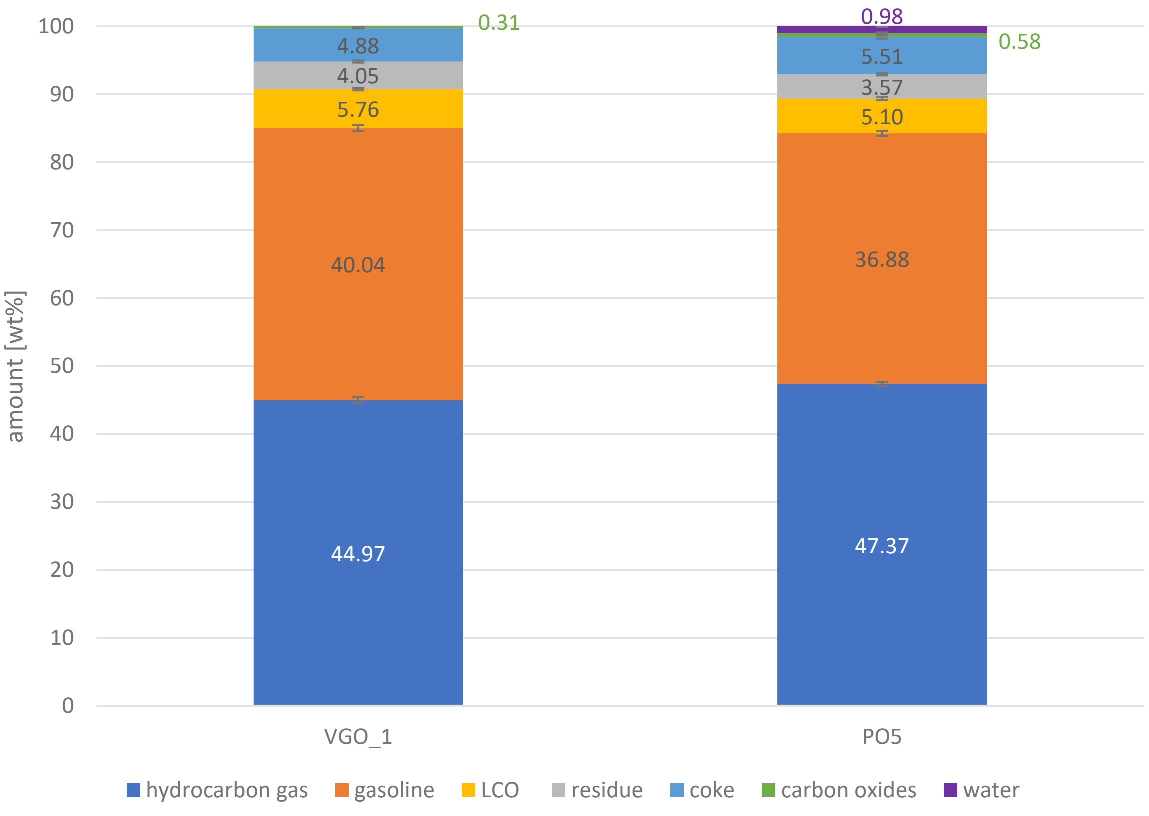


figure 47: Results from the experiment series with pyrolysis oil from clean wood

Further analysis of the gas lump reveals that the admixture of PO results in an increase of propylene (32.5 % to 34.9 %) and butenes (21.3 %to 23.5 %) in the produced gas phase. In connection to this increase in alkenes the content of propane (8 %-7 %) and butanes (26.3 % to 22.4 %) decreases. The content of C1 and C2 gases is consistent.

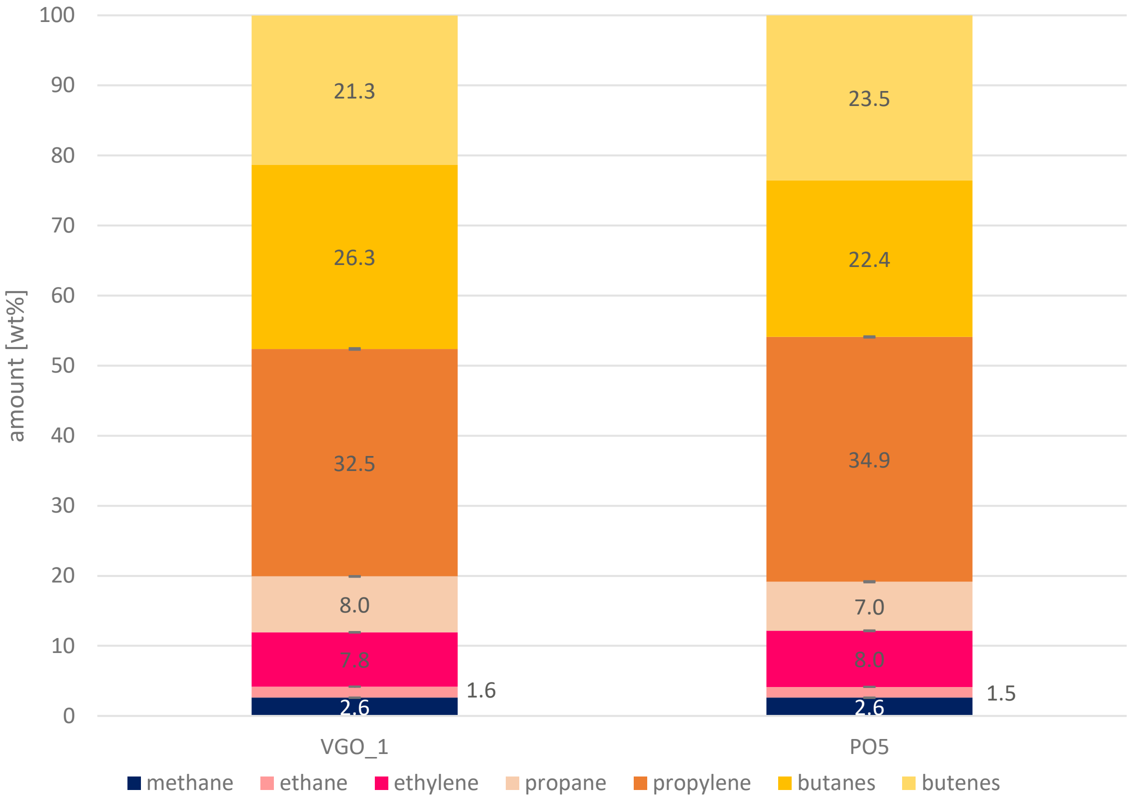


figure 48: Composition of the gaseous product of the experiment series with pyrolysis oil from clean wood

The utilization of PO as co-feed resulted in cloggage of the feed inlet system, which was anticipated because of its high Conradson Carbon value. It is still an interesting co-feed for the FCC process, due to its tendency to form more propylene and butenes by even higher amounts of gas produced in comparison to VGO. Cloggage of the pilot plant due to coke formation in the feeding system does not automatically disqualify it as a co-feed in larger FCC plants. An elaboration on the difference of operational instabilities in small-scale units in comparison to commercial FCC units and their circumvention was done by Pinho et al. [143].

6.4.2 Comparison of Pyrolysis Oils from Clean Pine Wood with Different Treatment Grades

The results for the admixture of 5 wt% pyrolysis oil from clean pine wood with different treatment grades done within the project Waste2Road are summarized in figure 49. The pyrolysis oil from clean wood was treated the same way as the pyrolysis oil from contaminated wood resulting in stabilized pyrolysis oil from clean wood (SPO) and stabilized deoxygenated pyrolysis oil from clean wood (SDPO). With further treatment the production of the lumps gas, carbon oxides and water reduces and the amount of produced residue and coke stays the same. Stronger treated pyrolysis oil results in higher amounts of gasoline. The product spectrum of VGO lies somewhere between SPO5 and SDPO5. A more in depth comparison was published in the paper “wood derived fast pyrolysis bio-liquids as co-feed in a fluid catalytic cracking pilot plant: effect of hydrotreatment on process performance and gasoline quality” [18]

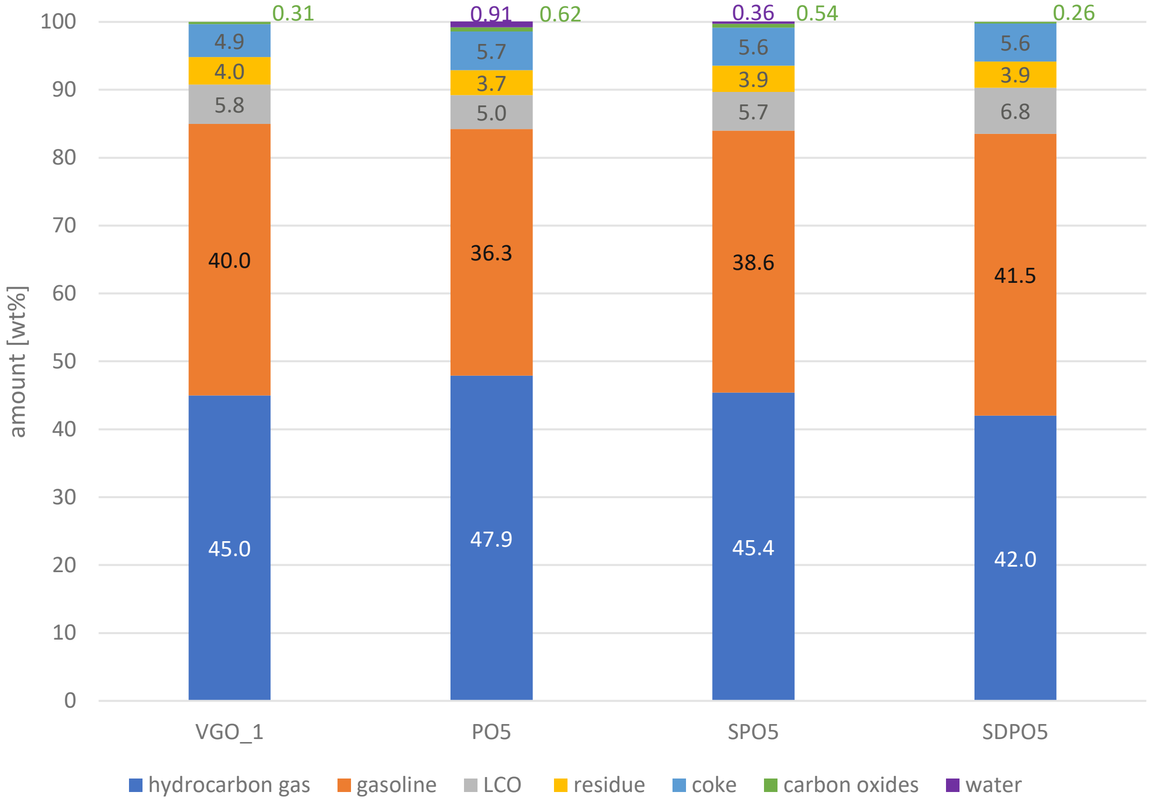


figure 49: Comparison of 5 wt% pyrolysis oil from clean pine wood with different treatment grades

6.4.3 Pyrolysis Oils from Contaminated Wood

figure 50 and figure 51 are a summary of all experiments done with the different types of pyrolysis oils from contaminated wood and the corresponding “BaseCase”. Each co-feed will be discussed in more detail below. Although the hydrocarbon gas and gasoline yields are higher for SDPOcw5 the amount of coke produced also increases compared to SPOcw5. Compared to VGO the addition of the pyrolysis oils from contaminated wood result in an increase in gasoline yield and a decrease in hydrocarbon gas yield, as well as the formation of water.

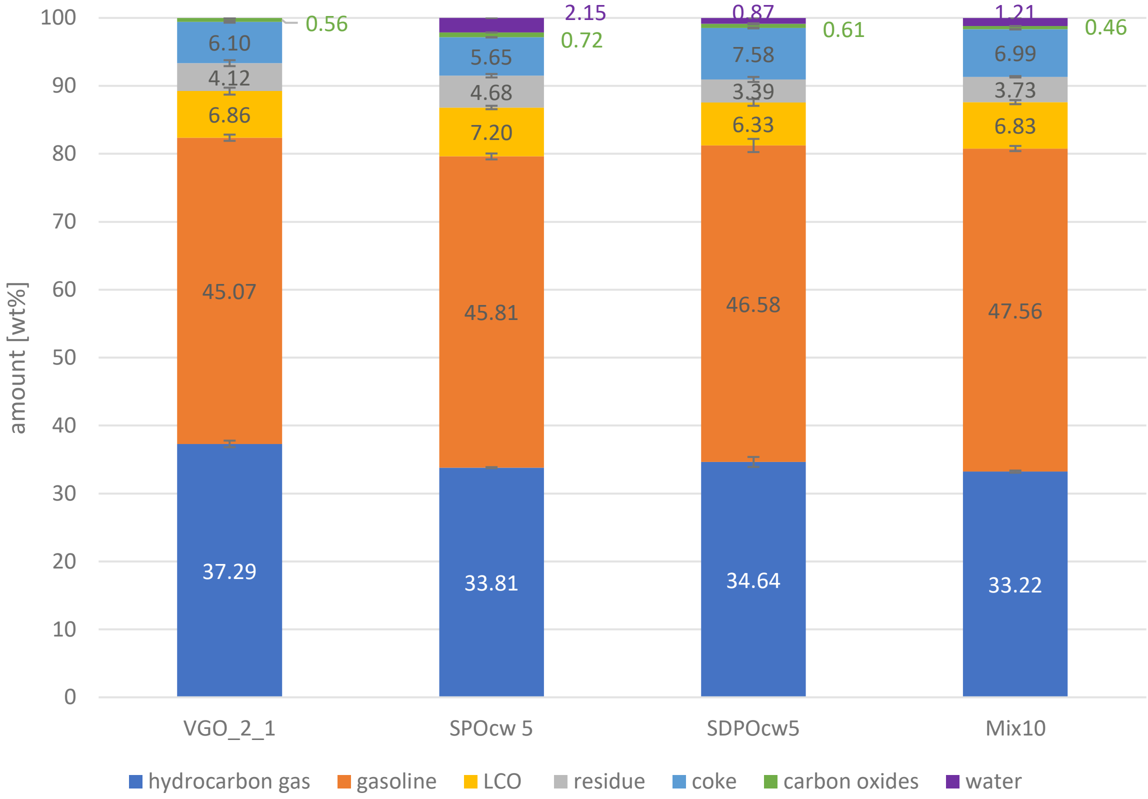


figure 50: Results from the experiment series with differently treated pyrolysis oils from contaminated wood

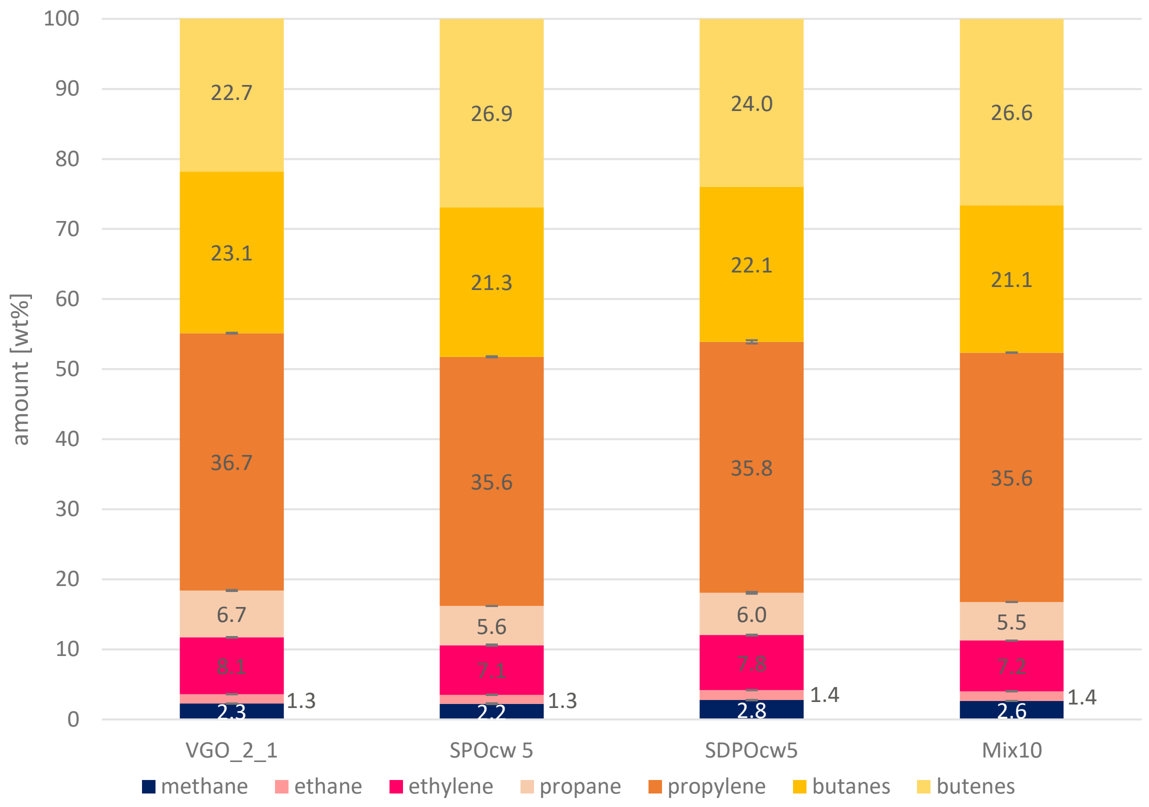


figure 51: Composition of the gaseous product of the experiment series with differently treated pyrolysis oils from contaminated wood

6.4.3.1 Stabilized Pyrolysis Oil from Contaminated Wood

The experiments were done using modification B. The experiment with an admixture of 5 % SPOcw had troubles with clogging of the feed inlet system. The amplification of the clogging issue due to a higher admixture hindered the experiment with 10 % SPOcw.

The results are depicted in figure 50 and figure 51. Compared to pure VGO the admixture of 5 wt% SPOcw decreases the production of hydrocarbon gas (-3.84 %) and coke (-0.45 %) as well as increasing the production of gasoline (+0.74 %), LCO (+0.34 %) and residue (+0.56 %). Furthermore, adding 5 % of SPOcw to the feed results in a water lump of 2.15 %. The water content of SPOcw would have implied a water lump of 0.65 %. It can be concluded that the remaining 1.50 % of water stems from oxygenated compounds in the SPOcw.

The content of methane and ethane in the gaseous product stayed the same, while ethylene, propane, propylene and butanes decrease. The content of butenes increases from 22.7 % to 26.9 %.

It can be concluded that SPOcw is a possible co-feed for the FCC process due to the fact, that the clogging issues were triggered by the coke formation in the feeding system and not by ash formation. If butenes and gasoline are especially desired products the addition of SPOcw is desirable. It increases the gasoline production and even though it reduces the hydrocarbon gas production, the content of butenes in the gas increases resulting in a feed-based conversion into butenes of 9.09 % for the admixture with 5 % and 8.46 % for pure VGO.

6.4.3.2 Stabilized and Deoxygenated Pyrolysis Oil from Contaminated Wood

Experiments with admixtures of 5 % and 10 % SDPOcw were done with the modifications A and B. The solids formed when SDPOcw was mixed with VGO and led to severe clogging problems in the feeding system by sticking to the pipes.

It may be hypothesised that the experiment with 5 % and modification A only worked due to the fact that a major part of the solids stayed in the feed reservoir sticking to the container surfaces. The results of this experiment are also depicted in figure 50 and figure 51. The addition of 5 % SDPOcw resulted in a decrease of the lumps hydrocarbon gas (-2.65 %), LCO (-0.5 %) and residue (-0.73 %) while the lumps gasoline (+1.51 %) and coke (+1.48 %) increased. Furthermore, it led to a water lump of 0.87 %, which is higher than the amount introduced into the system (0.27 %) due to the water content of SDPOcw. This can be attributed to its still relatively high oxygen content even after deoxygenation, leading to reactions producing water.

The content of ethane in the gaseous product stayed the same compared to VGO. Methane showed a slight increase (+0.5%) and butanes increase by 1.3 %. Ethylene (-0.3 %), propane (-0.7 %), propylene (-0.9 %) and butanes (1.0 %) all decreased when SDPOcw is co-fed.

The severe clogging problems caused by the solid formation upon mixture could be circumvented in industrial plants by feeding the SDPOcw through a second feed inlet at some distance to the VGO inlet into the plant. But this solution would reduce the economic feasibility due to the new facilities needed as well as their up-keep cost.

6.4.3.3 Combination of Stabilized Pyrolysis Oil and Stabilized and Deoxygenated Pyrolysis Oil from Contaminated Wood

As shown in chapter 3.7 the addition of SPOcw to SDPOcw reduced the formation of solids when mixed with VGO. Because SPOcw resulted in cloggage problems due to the high Conradson Carbon value the smallest amount that resulted into a reduction of the solids was chosen (30 % SPOcw and 70 % SDPOcw). 10 wt% of this mixture was admixed to VGO. The experiment was done with modification B of the FCC pilot plant.

The results of this experiment are depicted also in figure 50 and figure 51. The admixture of 10 % of the 7/3 mixture of SDPOcw/SPOcw resulted in a decrease of the lumps hydrocarbon gas (-4.07 %) and residue (-0.49 %). In contrast the lumps gasoline (+2.49 %) and coke (+0.89 %) increased. The LCO lump stayed the same. The addition of the bio-feed resulted in a water lump of 1.21 %.

The content of ethane in the gaseous product stays the same compared to VGO. Methane shows a slight increase (+0.4%) and butanes increase by 3.0 %. Ethylene (-0.8 %), propane (-1.1 %), propylene (-0.7 %) and butanes (-1.8 %) all decrease when the mixture is co-fed.

The feeding system still clogged during the experiment, because of coke formation, but this combination allowed for a replacement of 10 % VGO with biogenic feed. Showing an inventive way of combining different alternative feeds to offset their negative traits.

6.4.4 Pyrolysis Oil from Sunflower Husks

Due to the high amount of solids formed by mixing the pyrolysis oil with VGO. No tests were done with this pyrolysis oil, due to the failed attempts with the similar treated pyrolysis oil from contaminated wood. No solution was found to prevent solids formation.

6.4.5 Comparison of Gasoline Samples from Different Pyrolysis Oils from Biomass

One goal of the project Waste2Road is the increase of the technology readiness level to produce gasoline from the waste of renewable resources. For a comparison of all the different feeds utilized during the course of the project not only the results of gasoline samples produced in the course of this thesis, but also those produced from admixtures of 5 wt% SPO and 5 wt% SDPO of clean wood are listed in table 16, table 17 and table 18.

When comparing the results it has to be kept in mind, that Mix10 is the only experiment with an admixture of 10 wt%. All the other samples where produced using admixtures of 5 wt%.

In table 16 the measured parameters with legal requirements in ASTM D4814-16e or DIN EN 228:2017-08 are listed. figure 52 is a depiction of the results for sulfur, benzene, aromat and olefin content and their respective limitations mentioned in DIN EN 228:2017-08.

The density of the gasoline samples varies between 790.4 and 807.7 kg/m³. The sulfur content of the gasoline samples produced in the course of this thesis are around two third (which equals 10 mg/kg), higher than the one done beforehand with pyrolysis oils from pine wood. The main reason for this difference is the VGO batch used. As it can be seen the VGO used for the experiments with pine wood pyrolysis oils results in a gasoline sample with a sulfur content of 14.2 mg/kg and the VGO used for the experiments with pyrolysis oils from contaminated wood results in a gasoline sample with 25.4 mg/kg. Similar to the pine wood, the sulfur content in the gasoline lump increases with the treatment grade of the pyrolysis oil from contaminated wood. The sulfur content in all gasoline samples is below the maximum value of 0.0080 wt% set by the American Society for Testing and Materials, but above the European maximum of 10 mg/kg. Similar to the sulfur content there is a big difference between the total olefin contents of both VGO samples, with one being 9.4 and the other 15.0 wt%.

The concentration of benzene and total aromatics is above the maximum value of ~1.2 wt% (40.8-41.9 wt% respectively). Although the benzene concentrations for all samples vary between 1.8 and 2.0 wt%, the difference between the total aromatic concentrations of the two experimental series with pine wood pyrolysis oils and contaminated wood pyrolysis oils is more prominent, due to the different VGO batches used. Whereas the higher treatment grade seems to increase the total aromatics in the gasoline of pine wood oils, it leads to a decrease of total aromatics in the gasoline from contaminated wood oils. It is interesting to note that the concentration of total aromatics of the mix10 gasoline decreases compared to VGO by 1.3 wt% which leads to the conclusion that the mixture of SPOcw and SDPOcw does not only have a positive synergetic effect on the processability of the bio-oils but also on some of the reactions taking place.

The final boiling point is too high for all the samples but this can be adjusted easily by optimizing the distillation process.

For all the samples the concentrations of Mn, Fe, methanol, ethanol and total oxygen are below the detection limit of 1.0 and 0.1 respectively of the used analysis method.

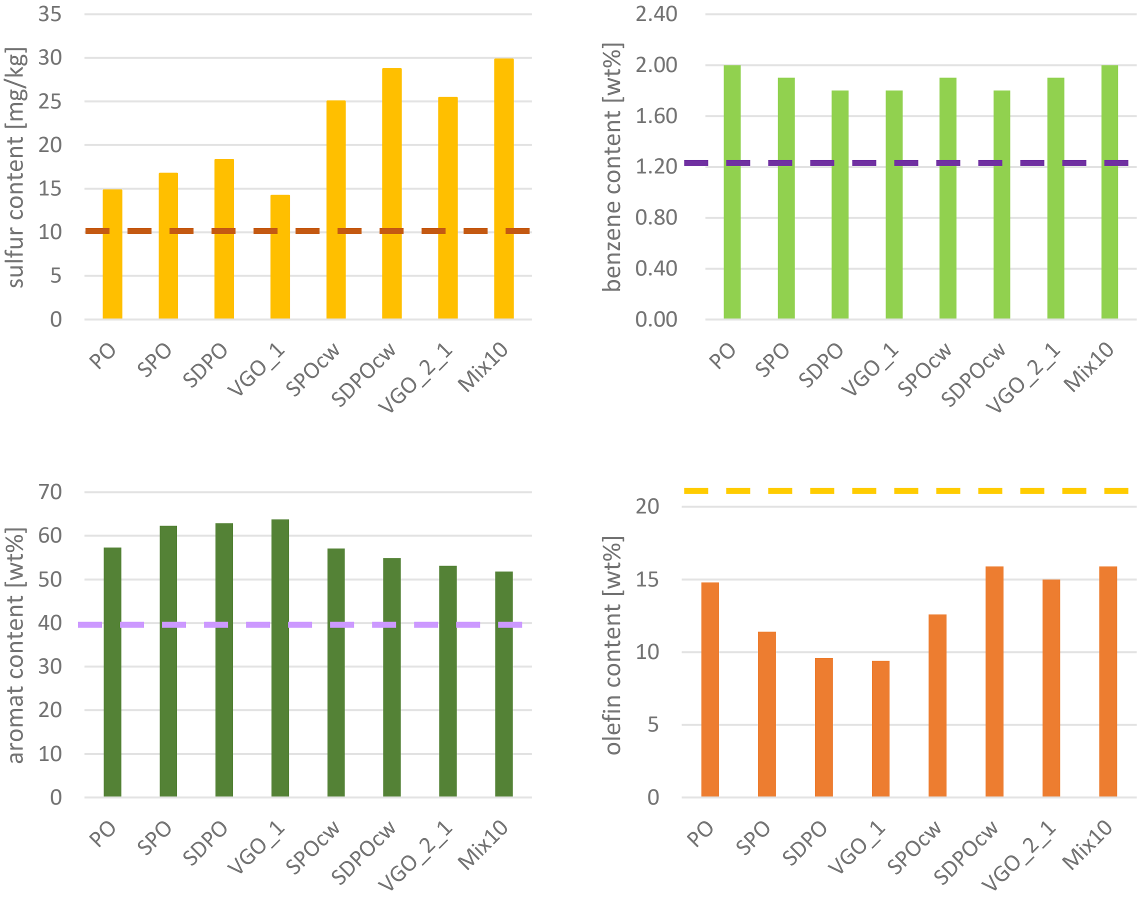


figure 52:Comparison of the sulfur, benzene, aromat and olefin content of the different gasoline samples with the respective legal maximum limits mentioned in DIN EN 228:2017-08

In table 17 the measured parameters which must be measured according to ASTM D4814-16e or DIN EN 228:2017-08 but have no indication of maximum or minimum values, are listed.

As can be seen in table 16 the admixture of PO reduces the formation of aromatics, although the benzene concentration increases slightly (0.2 wt%). The concentrations of toluene, C8-, C9- and C10 aromatic compounds decrease. The biggest difference is in the concentration of C9 aromatics with -2.6 wt% closely followed by C8 aromatics with a decrease of -2.5 wt%. Whereas the addition of pine wood pyrolysis oils results in a decrease of aromatic content, the addition of contaminated wood pyrolysis oils results in an increase. The increase is indirectly proportional to the treatment grade of the pyrolysis oil.

The addition of SPO and SDPO from pine wood has no influence on the sum of naphthenes. Whereas PO from pine wood and SPOcw and SDPOcw increase it. The sum of olefinic naphthenes decreases with the treatment grade of the bio-oil from pine wood in contrast to the increase with the treatment grade for pyrolysis oils from contaminated wood. This trend can also be seen for the concentration of the sum of i-olefines and n-olefines. For the i-olefine sum once again the difference of the products from different VGO batches gets obvious with 5.1 wt% for VGO and 0.63 wt% for VGO2. The sum of i-paraffins and n-paraffins in the gasoline samples of the experimental series with pine wood bio-oils stays roughly the same. The differences in the gasoline samples of the experimental series with contaminated wood bio-oil are more pronounced with up to 3.58 wt%.

It can be assumed that the differences in the concentration of propane, butanes and pentanes in the gasoline samples is more strongly related to the age of the samples at the time of analysis than to the actual production, due to their low boiling points.

The concentration of polynaphthenes is the same for all samples with 0.1 wt%. The concentration of Fe, TAME, ETBE, MTBE and t-Butanol are lower than the detection limit of the analysis method used. The gasoline samples did not contain free water.

For all the inorganic elements mentioned in table 18 the concentrations in the different samples are below the detection limits of the analysis methods used. The carbon and hydrogen content of the gasoline samples within the different experimental series stays roughly the same in all cases. The addition of bio-oils leads to an increase in the concentrations of nitrogen and dissolved water in all cases. With the difference being more significant for the samples produced with bio-oils from contaminated wood.

*table 16: Measured parameters of the gasoline samples with legal requirements in ASTM D4814-16e or DIN EN 228:2017-08; ✓ means the parameter has to be measured but there is no value limitation; the values marked with * were first published by Büchele et al. [20] the ones marked with $^{+}$ were first published by Lutz et al. [18]*

		ASTM D4814-16e [144]		DIN EN 228:2017-08 [145]		PO gasoline	SPO gasoline	SDPO gasoline	VGO_1 gasoline	SPOcw gasoline	SDPOcw gasoline	VGO_2_1 gasoline	Mix10 gasoline
		Min	Max	Min	Max								
density (15 °C)	**kg/m³**	-	-	720	775	796.1^{+}	804.7*	804.2*	807.7*	801.8	802.2	790.4	791.4
sulfur	**mg/kg**	-	0.0080 wt% 80 mg/kg	-	10	14.8^{+}	16.7*	18.3*	14.2*	25.0	28.7	25.4	29.8
Mn	**mg/kg**	-	0.25 mg/L ~0.33 mg/kg	-	2.0 mg/L ~2.7 mg/kg	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Pb	**mg/kg**	-	0.013 g/L ~17 mg/kg	-	5.0 mg/L ~6,9 mg/kg	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Methanol	**wt%**	-	✓	-	3.0 v% ~3.2 wt%	<0.1^{+}	<0.1^{+}	<0.1^{+}	<0.1^{+}	<0.1	<0.1	<0.1	<0.1
Ethanol	**wt%**	-	✓	-	5.0 v% ~5.3 wt%	<0.1^{+}	<0.1^{+}	<0.1^{+}	<0.1^{+}	<0.1	<0.1	<0.1	<0.1
Benzene	**wt%**	-	-	-	1 v% ~1.2 wt%	2.0^{+}	1.9^{+}	1.8^{+}	1.8^{+}	1.9	1.8	1.9	2.0
total aromatics	**wt%**	-	-	-	35.0 v% 40.8-41.9 wt%	57.3^{+}	62.3*	62.9*	63.8*	57.1	54.9	53.1	51.8
total olefins	**wt%**	-	-	-	18 v% 21-22 wt%	14.8^{+}	11.4^{+}	9.6^{+}	9.4^{+}	12.6	15.9	15.0	15.9
Total oxygen	**wt%**		✓		2.7	<0.1^{+}	<0.1^{+}	<0.1^{+}	<0.1^{+}	<0.1	<0.1	<0.1	<0.1
Final boiling point	**°C**		225		210	253.2^{+}	251.7^{+}	255.7^{+}	253.3^{+}	255.0	248.8	253.0	243.7
Reid Vapor Pressure	**kPa**		AA 54 E 103		A 45 F/F1 100	30^{+}	35^{+}	33^{+}	36^{+}	8.6	38.9	48.4	44.7

*table 17: Measured parameters of the gasoline samples that have to be measured according to ASTM D4814-16e or DIN EN 228:2017-08 but have no indication of maximum or minimum values; ✓ means the parameter has to be measured according to this standard; the values marked with * were first published by Büchele et al. [20] the ones marked with $^+$ were first published by Lutz et al. [18]*

		ASTM D4814-16e [144]	DIN EN 228:2017-08 [145]	PO gasoline	SPO gasoline	SDPO gasoline	VGO_1 gasoline	SPOcw gasoline	SDPOcw gasoline	VGO_2_1 gasoline	Mix10 gasoline
Propane	**v%**		✓	0^+	0^+	0^+	0^+	0.09	0.1	0.07	0.06
i-Butane	**v%**		✓	0.5^+	0.4^+	0.6^+	0.4^+	0.66	0.64	0.88	0.74
i-Pentane	**v%**		✓	3.9^+	4.1^+	4.7^+	3.7^+	3.93	3.26	5.41	4.96
n-Butane	**v%**		✓	1.6^+	1.5^+	1.8^+	1.3^+	1.77	1.84	2.46	2.18
n-Pentane	**v%**		✓	5.7^+	4.8^+	4.4^+	3.8^+	5.46	5.81	7.04	7.23
Toluene	**wt%**		✓	10.9^+	11^+	11^+	11.4^+	10.31	9.96	9.64	9.65
C8 aromatic content	**wt%**		✓	19.4^+	21^+	21.1^+	21.9^+	18.7	17.8	17.0	16.6
C9 aromatic content	**wt%**		✓	17.3^+	19.4^+	19.5^+	19.9^+	17.7	16.9	15.9	15.8
C10 aromatic content	**wt%**		✓	5.4^+	6.2^+	6.4^+	6.0^+	6.1	6.3	6.2	5.8
Polynaphthenes	**wt%**		✓	0.1^+	0.1^+	0.1^+	0.1^+	0.1	0.1	0.1	0.1
Sum Naphthenes	**wt%**		✓	8.3^+	7.3*	7.4*	7.5*	8.76	9.11	7.83	8.98
Sum olef. Naphthenes	**wt%**		✓	4.5^+	3.2^+	2.4^+	2.7^+	8.38	11.11	9.62	10.46
Sum i Olefins	**wt%**		✓	7.8^+	6.2^+	5.4^+	5.1^+	0.5	0.62	0.63	0.58
Sum n Olefins	**wt%**		✓	2.5^+	2^+	1.8^+	1.6^+	3.74	4.22	4.80	4.75
Sum i Paraffins	**wt%**		✓	17^+	16.6^+	17.6^+	16.9^+	18.83	17.6	21.18	20.58
Sum n Paraffins	**wt%**		✓	2.6^+	2.4^+	2.5^+	2.4^+	2.7	2.47	2.87	2.77
Fe	**mg/kg**		✓	$<1.00^+$	$<1.00^+$	$<1.00^+$	$<1.00^+$	<1.00	<1.00	<1.00	<1.00

		ASTM D4814-16e [144]	DIN EN 228:2017-08 [145]	PO gasoline	SPO gasoline	SDPO gasoline	VGO_1 gasoline	SPOcw gasoline	SDPOcw gasoline	VGO_2_1 gasoline	Mix10 gasoline
MTBE	**wt%**	✓	✓	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1	<0.1	<0.1	<0.1
ETBE	**wt%**	✓	✓	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1	<0.1	<0.1	<0.1
TAME	**wt%**	✓	✓	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1	<0.1	<0.1	<0.1
t- Butanol	**wt%**	✓	✓	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1$^+$	<0.1	<0.1	<0.1	<0.1
free water	**ml/L**	✓		0$^+$	0$^+$	0$^+$	0$^+$	0	0	0	0

*table 18: Measured parameters of the gasoline samples that are not mentiond in ASTM D4814-16e or DIN EN 228:2017-08; the values marked with * were first published by Büchele et al. [20] the ones marked with $^+$ were first published by Lutz et al. [18]*

		PO gasoline	SPO gasoline	SDPO gasoline	VGO_1 gasoline	SPOcw gasoline	SDPOcw gasoline	VGO_2_1 gasoline	Mix10 gasoline
Initial boiling point	**°C**	-5.2$^+$	-5.9$^+$	-5.4$^+$	-8.6$^+$	-11.8	-11.0	-13.9	-11.8
Dissolved water	**mg/kg**	125*	184*	125*	101*	119	127	76	157
nitrogen	**mg/kg**	6.4$^+$	11.1*	7.5*	2.3*	23.03	19.4	7.26	53.67
hydrogen	**wt%**	12$^+$	11.8$^+$	11.9$^+$	11.8$^+$	11.64	11.6	11.8	11.82
carbon	**wt%**	87$^+$	87.2$^+$	87.1$^+$	87.3$^+$	88.36	88.39	88.2	88.16
Al	**mg/kg**	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00	<1.00	<1.00	<1.00
Ca	**mg/kg**	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00	<1.00	<1.00	<1.00
Cr	**mg/kg**	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00	<1.00	<1.00	<1.00
K	**mg/kg**	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00$^+$	<1.00	<1.00	<1.00	<1.00

		PO gasoline	SPO gasoline	SDPO gasoline	VGO_1 gasoline	SPOcw gasoline	SDPOcw gasoline	VGO_2_1 gasoline	Mix10 gasoline
Mo	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Na	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Ni	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Si	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
V	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Zn	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Hg	**mg/kg**	<0.003^{+}	<0.003^{+}	<0.003^{+}	<0.003^{+}	<1.00	<1.00	<1.00	<1.00
Ag	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Cd	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Cu	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Mg	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
Sn	**mg/kg**	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00^{+}	<1.00	<1.00	<1.00	<1.00
As	**µg/kg**	<10.0^{+}	<10.0^{+}	<10.0^{+}	<10.0^{+}	<1.00	<1.00	<1.00	<1.00
Sum halogens (Cl,Br) as Cl	**mg/kg**	<1^{+}	<1^{+}	<1^{+}	<1^{+}	<1	<1	<1	<1

It can be summarized that for some parameters there are big differences in the trends produced by bio oils from pine wood compared to bio-oils from contaminated wood. Whereas the samples from PO fit to the trends shown by the bio-oil from the same batch with higher treatment grades. The difference in trends for the different series cannot be explained solely by the results of the gasoline products and would need a more in depth analysis of the bio-oils themselves.

6.5 Comparison of Different VGO Batches

In figure 53 the results of different reference experiments with pure VGO are depicted. The plant modification used for the experiments was A. The only difference between those experiments is the VGO batch used.

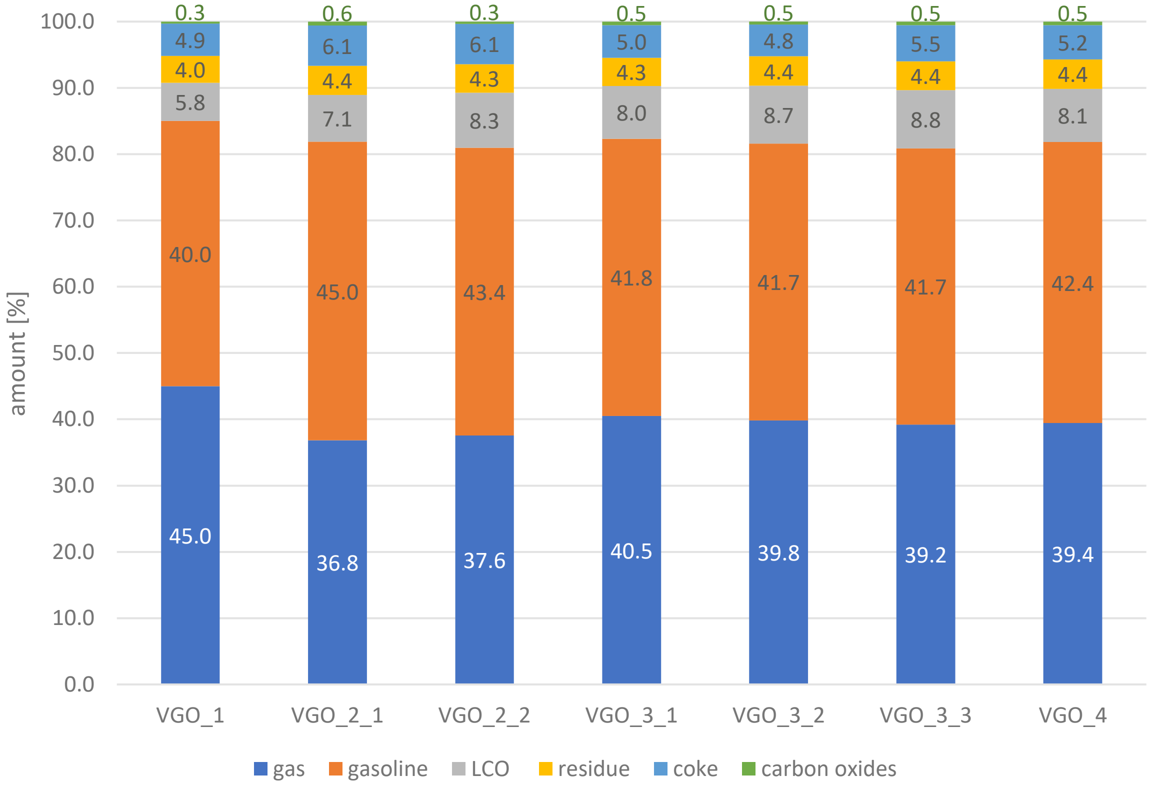


figure 53: Comparison of results from different BaseCase experiments with the same plant conditions

VGO_3_1, VGO_3_2 and VGO_3_3 used the same batch of VGO. The average and deviation of the different lumps of VGO_3 are listed in table 19. In table 20 the maximal and minimal value and the deviation for each lump of all the results are listed. For the deviation the average values for VGO_3 were used instead of the results from each measurement.

table 19: Average and deviation of three different experiments with the same feed

VGO_3	**gas [wt%]**	**gasoline [wt%]**	**LCO [wt%]**	**residue [wt%]**	**coke [wt%]**	**carbon oxides [wt%]**
Average	39.9	41.7	8.5	4.4	5.1	0.5
Deviation	0.5	0.06	0.4	0.08	0.3	0.02

table 20: Comparison of the maximal and minimal values measured for the lumps

	gas [wt%]	**gasoline [wt%]**	**LCO [wt%]**	**residue [wt%]**	**coke [wt%]**	**carbon oxides [wt%]**
max	45.0	45.0	8.8	4.4	6.1	0.6
min	36.8	40.0	5.8	4.0	4.8	0.3
Deviation	2.4	1.5	1.0	0.1	0.5	0.1

It can be seen that the deviations for the lumps of experiments with the same feed are 0.5 or below. A possible reason for the high deviation of the gas lump could be the instability of the sample. It also becomes apparent that there can be vast differences in the products of different VGO batches used.

7 Conclusions and Outlook

As part of this thesis different studies to further characterize the influences of adjustable parameters of the FCC pilot plant unit at TU Wien were done. Although the study on the influence of the riser fluidization showed an overall increasing trend of the C/O ratio the increase was not steadily. It also showed, that the change in C/O ratio is not the only influence on the cracking process, since the product spectrum still varies for different riser fluidization which had a similar C/O ratio. The water recovery rate was found to be 87 % for an admixture of 3.85 wt% water to VGO. Although there is already an extensive list of different studies further supplementing it is recommended for example with studies to the possible influence of the preheat temperature of the feed, a water recovery rate study with a range of different water contents, the influence of the feed rate without action to reduce the C/O ratio and studies regarding the ageing of the liquid and gaseous samples.

Multiple alternative feeds were successfully tested for their compatibility as co-feeds for the FCC process. Only SDPOsun was eliminated as potential co-feed in the FCC pilot plant after feed characterization due to the amounts of solids formed when combined with VGO. This does not mean it can fully be eliminated as co-feed for the FCC process, but that the issue of solid formation has to be solved before further tests are possible.

It was possible to show that the utilization of two fractions of pyrolysis oil from mixed plastic waste (Heavy SynCrude and Distillation Residue) in the FCC process is possible. The experiments with admixtures of 5 wt%, 10 wt% and 20 wt% of Heavy SynCurde resulted in a product spectrum with no significant difference to pure VGO. Although the high ash content of Distillation Residue reduces its quality as co-feed strongly, endeavors to reduce the ash content are planned by the producers. It is possible that pyrolysis of plastics and the subsequent valorization increases the monetary value of mixed plastic waste animating people to adhere to the correct way of disposal. This positive influence could lead to a reduction of mismanaged plastic wastes, which the OECD estimated to be 79.3 Mt in 2019 [5].

A similar problem to Distillation Residue is shown by lipstick mass. For it to be processable in the pilot plant a reduction of the ash content was necessary. It was done via sedimentation of the dispersed solids. However, this lab-scale process is not feasible for industrial use. Thus a utilization of lipstick mass would presuppose the development of a large-scale removal of the dispersed solids in the lipstick mass. Without the solid contents lipstick mass shows a great potential as co-feed, with a high tendency to form hydrocarbon gas.

The experiments done in the course of the project Waste2Road prove that bio-liquids from contaminated wood can be used as co-feed in the FCC process although further optimization of the feeding process is recommended. There is a clear difference concerning the trend between 5 wt% admixtures of SPO and SDPO from clean pine wood compared to the trend between 5 wt% admixtures of SPOcw and SDPOcw. A short summary of these trends is shown in table 21. This shows that the use of contaminated wood compared to clean wood has an influence on the product even after hydrotreatment, possible due the increased deactivation of the catalyst during treatment.

table 21: Trend comparison from SDPO to SPO between clean wood and contaminated wood

	SDPO5 compared to SPO5	**SDPOcw5 compared to SPOcw5**
hydrocarbon gas	↓	↑
gasoline	↑	↑
LCO	↑	↓
residue	≈	↓
coke	≈	↑
carbon oxides	↓	↓
water	↓	↓

More focus on the combination of alternative feeds is needed. Firstly, positive synergetic effects can take place (e.g. chapter 6.4.5 and Xue et.al. [106]). Secondly, even the substitution of only 10 wt% fossil oil processed in the FCC process can hardly be achieved with one alternative feed due to the sheer amount needed. With a processing capacity of 500-700 Mt per year [77], [107] depending on the source consulted, an amount of 50-70 Mt of alternative feed would be needed. Presumed this amount is provided by fast pyrolysis of biomass with a conversion rate of solid to liquid from 60 wt% the fast pyrolysis processing capacity of the world would need to be 83-117 Mt per year. For example the fast pyrolysis plant Empyro produces 43800 t bio-liquid annually [146], which means in order to meet the need of fast pyrolysis oils for the FCC process worldwide at least 1895 Empyro plants would be needed.

As described in chapter 6.5 and chapter 6.4.5 the VGO batches used have a big impact on the products and thus on how alternative feeds compare to them. An experimental series is always only a brief snapshot, but is enough to roughly categorize alternative feeds in different types of quality. This means alternative feeds with small difference to the VGO “BaseCase” can be assumed to be the same feed quality. For a detailed categorization experiments with different batches of VGO and the alternative feed would have to be done, since both of them vary in their quality.

*table 22: Summary of the influence of the examined alternative co-feeds on the products gas, gasoline, ethylene, propylene and butenes; results for Co-feeds marked with * were done by Büchele et al. [20]*

Co-Feed	gas yield	gasoline yield	ethylene yield	propylene yield	butenes yield
Lipstick mass	↑	↓	↓	↑	↑
Heavy SynCrude	≈	≈	≈	≈	≈
Distillation Residue	↑	↓	≈	↑	↑
Pyrolysis oil from clean wood	↑	↓	↑	↑	↑
Stabilized pyrolysis oil from clean wood*	≈	↓	≈	↑	≈
Stabilized deoxygenated pyrolysis oil from clean wood*	↓	↑	≈	≈	↓
Stabilized pyrolysis oil from contaminated wood	↓	↑	↓	↓	≈
Stabilized deoxygenated pyrolysis oil from contaminated wood	↓	↑	↓	↓	↑
Stabilized deoxygenated pyrolysis oil from sun flowers	×	×	×	×	×

8 Abbreviations and Formula Symbols

BTL	Biomass to liquid
C/O ratio	catalyst to oil ratio
CCR	Conradson Carbon Residue
CNG	compressed natural gas
CO2 eq	CO2 equivalent
Corine	Coordination of Information on the Environment
CTL	coal to liquid
CTL CCS	coal to liquid-carbon capture and storage
cw	contaminated wood
DG	Directorate-General
DG ENV	Directorate-General Environment
DiRe	Distillation Residue
E-cat	equilibrium catalyst
Eionet	European environment information and observation network
EU	European Union
FCC	fluid catalytic cracking
GHG	greenhouse gas
GTL	gas to liquid
GWP	global warming potential
Hsyn	Heavy SynCrude
LCO	light cycle oil
Lge	liter of gasoline equivalent
LPG	liquefied petroleum gas
LS	Lipstick mass
LST	Lipstick mass treated
MLO	Mauna Loa Observatory
NDIR	nondispersive infrared sensor
NMVOC	non-methane volatile organic compounds
NZE	net zero emission
PAH	polycyclic aromatic hydrocarbon
PM	particulate matter
PM10	particulate matter with a diameter of 10 µm or less
PM2.5	particulate matter with a diameter of 2.5 µm or less
PO	pyrolysis oil
SDPO	stabilized deoxygenated pyrolysis oil
SDPOcw	stabilized deoxygenated pyrolysis oil from contaminated wood
SDPOsun	stabilized deoxygenated pyrolysis oil from sunflower husk
SMM	Sustainable materials management
SOA	secondary organic aerosols
SPO	stabilized pyrolysis oil
SPOcw	stabilized pyrolysis oil from contaminated wood

TAPs	toxic air pollutants
TTW	Tank to Wheel
UCS	Unit cell size
UN	United Nations
UNECE	United Nations Economic Commission of Europe
USY	ultrastable zeolite Y
VGO	vacuum gas oil
VOC	volatile organic compounds
WTT	Well to Tank
WTW	Well to Wheel
ZSM-5	zeolite socony mobil-5

$\dot{m}_{catalyst}$	mass flow catalyst [kg/h]]
$A_{Regenerator}$	Regenerator area [m2]
$\Delta p_{Regenerator}$	pressure loss within Regenerator [mbar]
Δt_U	measuring interval [h]
g	acceleration due to gravity [m/s^2]
$\dot{m}_{feed}$	mass flow feed [kg/h]

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11 References

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12 Appendix

	T_{Riser} [°C]	Feedrate [kg/h]	**Product**							
			Gas	Gasoline	LCO	residue	Coke	Carbon oxides	water	Conversion
VGO_1	550	2	45.0	40.0	5.8	4.0	4.9	0.3	0	85.0
VGO_2_1	550	2	39.2	41.7	8.8	4.4	5.5	0.5	0	80.9
VGO_2_2	550	2	41.8	40.8	7.6	4.0	5.2	0.5	0	82.6
VGO_3_1	550	2	40.5	41.8	8.0	4.3	5.0	0.5	0	82.3
VGO_3_2	550	2	39.4	42.4	8.1	4.4	5.2	0.5	0	81.8
VGO_3_3	550	2	36.8	45.0	7.1	4.4	6.1	0.6	0	81.9
VGO_4	550	2	37.6	43.4	8.3	4.3	6.1	0.3	0	81.0

	Gaslump-feed based					**Gaslump-gas based**			
	Ethen	Propen	Butens	other Gases	Sum	Ethen	Propen	Butens	other Gases
VGO_1	3.49	14.61	9.57	17.30	0.45	7.77	32.49	21.28	38.47
VGO_2_1	3.08	13.45	9.23	13.45	0.39	7.86	34.30	23.55	34.30
VGO_2_2	3.18	14.61	10.17	13.863	0.42	7.59	34.94	24.32	33.15
VGO_3_1	3.08	14.10	9.03	14.29	0.41	7.61	34.82	22.29	35.29
VGO_3_2	3.19	13.29	8.19	14.76	0.39	8.08	33.70	20.78	37.44
VGO_3_3	3.00	13.57	8.36	12.36	0.37	8.05	36.39	22.42	33.14
VGO_4	3.00	13.74	8.18	12.63	0.38	7.98	36.59	21.78	33.65

	Gase feed bezogen												
	CO	CO_2	Methane	Ethane	Ethene	Propane	Propene	Isobutane	1-Butene	Isobutene	n-Butane	Trans-2-Butene	cis-2-Butene
VGO_1	0.05	0.26	1.17	0.71	3.49	3.59	14.61	10.04	1.71	3.66	1.79	2.44	1.77
VGO_2_1	0.07	0.45	0.76	0.47	3.08	2.61	13.45	8.19	1.62	3.52	1.43	2.38	1.72
VGO_2_2	0.08	0.45	0.79	0.49	3.18	2.67	14.61	8.45	1.81	3.87	1.46	2.60	1.89
VGO_3_1	0.14	0.38	0.86	0.54	3.08	2.76	14.10	8.69	1.66	3.38	1.45	2.31	1.68
VGO_3_2	0.13	0.40	1.05	0.64	3.19	3.00	13.29	8.60	1.58	3.08	1.48	2.03	1.50
VGO_3_3	0.14	0.42	0.84	0.50	3.00	2.48	13.57	7.33	1.54	3.20	1.21	2.10	1.51
VGO_4	0.08	0.25	0.85	0.50	3.00	2.49	13.74	7.61	1.52	3.14	1.19	2.05	1.47

	T_{Riser} [°C]	**Feedrate [kg/h]**	**Product**						
			Gas	Gasoline	LCO	residue	coke	carbon oxides	Konversion
VGO_3_1	550 °C	2	40.51	41.80	7.96	4.25	4.97	0.52	82.3
HSyn5	550 °C	2	40.79	41.96	7.82	4.19	4.71	0.54	82.8
HSyn10	550 °C	2	40.74	41.52	8.45	4.45	4.58	0.27	82.2
HSyn20	550 °C	2	41.47	41.85	7.86	4.15	4.40	0.28	83.3

	Gaslump-feed based					**Gaslump-gas based**			
	Ethen	Propen	Butens	other Gases	Sum	Ethen	Propen	Butens	other Gases
VGO_3_1	3.08	14.10	9.03	14.81	41.03	7.51	34.38	22.00	36.11
HSyn5	3.08	14.27	8.84	15.17	41.36	7.45	34.50	21.38	36.68
HSyn10	3.14	14.00	9.03	14.86	41.02	7.65	34.12	22.00	36.23
HSyn20	3.10	14.05	9.53	15.06	41.74	7.43	33.65	22.84	36.08

b

	CO	CO_2	Methane	Ethane	Ethene	Propane	Propene	Isobutane	1-Butene	Isobutene	n-Butane	Trans-2-Butene	cis-2-Butene
VGO_3_1	0.14	0.38	0.86	0.54	3.08	2.76	14.10	8.69	1.66	3.38	1.45	2.31	1.68
HSyn5	0.14	0.40	0.87	0.56	3.08	2.84	14.27	8.89	1.64	3.30	1.45	2.27	1.64
HSyn10	0.07	0.21	0.95	0.59	3.14	2.95	14.00	8.61	1.65	3.38	1.50	2.31	1.68
HSyn20	0.13	0.15	0.91	0.58	3.10	2.98	14.05	8.77	1.72	3.61	1.54	2.44	1.77

	T_{Riser} [°C]	Feedrate [kg/h]	Anteile - Produkt						
			Gas	Gasoline	LCO	residue	Coke	Carbon oxides	water
VGO_3_2	550	2	39.84	41.75	8.72	4.44	4.78	0.47	81.60
DiRe5	550	2	39.93	41.63	8.59	4.29	5.17	0.39	81.55
DiRe10	550	2	42.04	38.61	7.77	4.41	6.84	0.59	80.42

	Gaslump-feed based					Gaslump-gas based			
	Ethene	Propene	Butens	other Gases	Sum	Ethene	Propene	Butens	other Gases
VGO_3_2	2.98	13.64	8.99	14.71	40.32	7.40	33.84	22.29	36.48
DiRe5	2.86	13.99	9.50	14.39	40.74	7.02	34.35	23.33	35.31
DiRe10	2.88	15.41	11.57	13.31	43.16	6.66	35.70	26.81	30.83

	CO	CO_2	Methane	Ethane	Ethene	Propane	Propene	Isobutane	1-Butene	Isobutene	n-Butane	Trans-2-Butene	cis-2-Butene
VGO_3_2	0.08	0.40	0.91	0.57	2.98	2.77	13.64	8.55	1.63	3.36	1.44	2.31	1.69
DiRe5	0.07	0.32	0.86	0.53	2.86	2.60	13.99	8.20	1.73	3.55	1.40	2.45	1.78
DiRe10	0.08	0.51	0.70	0.46	2.88	2.28	15.41	7.96	1.98	4.08	1.33	3.44	2.07