

Study and evaluation on the topic

**Direct liquefaction of biomass –
Reaction mechanisms and product distributions
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through

Prof. Dr. Frank Behrendt

with the participation of

**York Neubauer, Dipl.-Ing., Karen Schulz-Tönnies, Dr. Birgit
Wilmes, Dipl.-Ing. and Nico Zobel, Dipl.-Ing.**

Technical University of Berlin

Institute for Energy Technology

**Field of expertise: Energy process engineering and
Conversion technologies for renewable energies**

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SUMMARY

The limited reserves of fossil primary energy sources – and thus of the liquid secondary energy carriers produced from them, especially for mobile applications – is a crucial driving force behind the search for possible alternatives. Two fundamental strategies for at least partial substitution are conceivable. Firstly, there is the possibility of using plant parts (e.g., rapeseed for the production of biodiesel or grain for bioethanol); secondly, there is the option, likely more sensible in the long term, of using whole plants.

A distinction must be made between the two-stage process of gasification to synthesis gas (CO/H₂) followed by Fischer-Tropsch or methanol synthesis to obtain liquid hydrocarbons, and the so-called direct liquefaction of biomass, which, at least in principle, is intended to lead to such fuels in a single-step process without the intermediate step of synthesis gas. The evaluation of this latter process is the subject of this study.

Based on a compilation of historical works on the direct liquefaction of coal and biomass, this study briefly describes theoretically conceivable reaction pathways. A substantial portion is devoted to an overview of the experimental investigations described in the literature on numerous aspects of the direct liquefaction of biomass.

This is followed by an overview of the direct liquefaction processes currently known in Germany. Although flash pyrolysis is not strictly one of the direct liquefaction processes covered in this study, the associated processes are also presented. Based on this information, a recommendation for action is formulated. An extensive bibliography is included with the study.

Direct liquefaction of biomass to produce liquid hydrocarbons is methodologically based on a nearly century-old and well-established process for liquefying coal under elevated pressure in a hydrogen atmosphere. The indispensable role of hydrogen becomes clear when considering the chemical aspects of converting biomass into liquid hydrocarbons.

Dried wood can be described by the chemical formula CH_{1.4}O_{0.7}, liquid fuel by CH₂. can be described so that the chemical basis and at the same time the technical challenge of the process is explained by the summary reaction equation.



The presence of hydrogen thus formally serves, on the one hand, to adjust the C/H ratio of the wood to that of the liquid hydrocarbon, and on the other hand, to remove the oxygen as water. The actual chemical process is of considerable complexity, which cannot even be remotely represented by such general formulas.

Even during the first oil crisis in the mid-1970s, various approaches to the direct liquefaction of biomass were examined in extensive comparative studies, but ultimately not pursued further. This was not only due to the excessively high process costs compared to the oil price at the time, but was ultimately attributed to unresolved process engineering problems. A key point of criticism was the lack of a scientific understanding of the underlying process, which ultimately led to the failure of the large demonstration plants built early on.

In the meantime, numerous international studies have been conducted that help to explain at least some aspects of the reaction process and its dependence on operating parameters.

Some of the approaches currently being pursued for the direct liquefaction of biomass in Germany are directly based on work done on coal liquefaction and also use similar reaction conditions. Other process providers believe that, through a suitable choice of reaction conditions and/or special catalysts, the process can also be carried out at normal pressure without hydrogen.

The majority of current process developments in Germany for the direct liquefaction of biomass are following in the footsteps of their failed predecessors.

Some of the assumptions made about the reaction process are quite adventurous and do not withstand rigorous chemical scrutiny. The summary reaction equation given above is sometimes adopted uncritically as the basis for process development. A further shortcoming of current processes in Germany is the lack of a systematic scientific investigation of the postulated process steps and a realistic product analysis to ensure full compliance with the relevant fuel standards.

Another group of process providers focuses on the thermal conversion of waste plastics into liquid hydrocarbons. These approaches are not particularly innovative, but offer a comparatively high probability of implementation. Based on past experience with such approaches, the process and product costs require careful consideration.

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1 WORKING FUNDAMENTALS

This study on the direct liquefaction of biomass is based on publicly available information.

No confidential company documents were available or included in this document. Furthermore, no orally disclosed information designated as confidential or unsuitable for further dissemination was used.

The use of terms for processes and materials does not indicate whether these are protected terms in any way. This should not be interpreted as meaning that such protection rights do not exist or need not be observed.

On March 9, 2006, the German Renewable Energy Federation (FEE) hosted a private workshop in Berlin on the topic of "Direct Liquefaction of Carbon Compounds." Researchers of the present study participated in this workshop. All presenters were informed and agreed that information from their presentations could be incorporated into the study currently underway.

2 INTRODUCTION AND OBJECTIVES

The production of technically usable, i.e., standard-compliant, fuels can be achieved via various pathways:

- Complete decomposition of the molecule into its elements or smaller molecules by means of pyrolysis or gasification, followed by total synthesis of new compounds. This approach is used, for example, in Fischer-Tropsch synthesis.
- Partial decomposition through pyrolysis with the rejection of all unsuitable components reaction products
- Direct liquefaction under reducing conditions (i.e., hydrogenation). This approach involves based on Bergius's work on the liquefaction of coal.

The challenge that any direct liquefaction process must face can be described by the following overall reaction equation:



This blanket description of the transformation of dry wood into liquid hydrocarbons is a process that nature did not follow. According to current knowledge, large quantities of marine microorganisms, primarily algae (and not wood or plants), were the starting material for the formation of petroleum. These lived predominantly as free-floating plankton in seawater; after they died, they sank to the bottom and decomposed, provided sufficient oxygen was present.

If oxygen was absent, however, the organic matter was preserved and, together with the finest rock fragments, formed a putrid sludge. From this, under the influence of various factors,

Factors (especially pressure) influence the so-called source rock. Over a period of 100 to 400 million years, petroleum and natural gas formed within it. Higher temperatures (ideally 65°C to 120°C), found as natural heat in deeper layers of the earth [Aral], were a prerequisite.

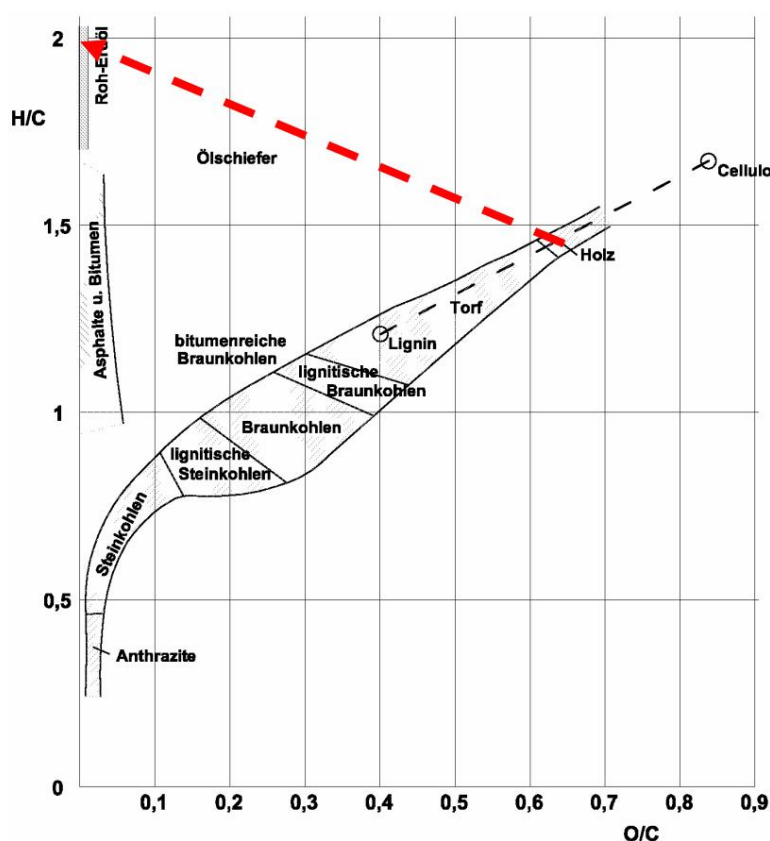


Figure 2-1: Carbonization diagram

Starting with wood and other plant material, however, a formation pathway was traced that is described by the so-called coalification diagram (Figure 2-1). The natural development pathway of wood leads via peat, various forms of lignite, finally to bituminous coal, and in the limiting case to graphite.

The process used in the direct liquefaction of biomass (as well as coal) and formally described by the equation above is shown in Figure 2-1 by the dashed red line.

The complex composition of plant biomass and the necessary conversion steps to the comparatively simple liquid hydrocarbons make the chances of success for simple "one-pot" reactions appear extremely low. This is clearly demonstrated in this study by means of a comprehensive literature review.

3 BASICS

3.1 HISTORICAL COAL LIQUEFICATION PROCESSES

"How wonderful it would be if liquid fuels could be produced economically from solid fuels through a suitable reduction process! It seems to me that this is a fundamental problem in the heating fuel industry, and all the tools of modern science should be mobilized and all possibilities explored to solve it."

Emil Fischer (1852-1919) at the opening of the Kaiser Wilhelm Institute for Coal Research in Mülheim/Ruhr on July 29, 1912 [Osteroth85].

The first described experiments on liquefaction were carried out by Berthelot in France around 1865. He reacted saturated hydroiodic acid with organic substances and also coal at temperatures of 280°C for 24 hours. Wood was thus almost completely converted into liquid hydrocarbons. The required hydrogen was supplied by the acid. Berthelot stated a hydrogen requirement of slightly more than eight mass parts based on the mass of the wood. He investigated the composition of the wood used as well as the reaction products and established mass balances [Berthelot 01].

The Bergius-Pier process for catalytic pressure liquefaction (also known as the IG Farben process) is closely related to other high-pressure processes that had been developed and implemented on an industrial scale in the preceding years. One such process is the ammonia synthesis developed by Haber and Bosch, in which nitrogen is reacted with hydrogen to produce ammonia at pressures around 200 bar and temperatures around 500°C using mixed iron catalysts. Approximately ten years later, Pier successfully carried out the methanol synthesis, in which carbon monoxide is hydrogenated with hydrogen using chromium oxide/zinc oxide catalysts at 300 bar and 350–400°C. Until then, methanol had been obtained from the resulting "wood spirit" during the carbonization of wood.

Building on the experience gained in high-pressure chemistry, the hydrogenation of tars, shale oils, and coal was also implemented on an industrial scale a few years later. The following table provides a chronological overview of these developments.

1869	Berthelot discovers that coal can be converted into oil through chemical reduction. can be
1908-1913	Development of ammonia synthesis to technical maturity by Carl Bosch (Haber-Bosch process, BASF)
1910-1914	Bergius' work on coal liquefaction in Hanover, patented in 1913
1912	Establishment of the Kaiser Wilhelm Institute for Coal Research in Mülheim/Ruhr
1921	Discovery of the fluidized bed principle by Fritz Winkler (BASF)
1923	Methanol synthesis by Mathias Pier (BASF)
1925	Discovery of the principle of aliphatic hydrocarbon formation by Hydrogenation of carbon monoxide on suitable catalysts by Franz Fischer and Hans Tropsch; takeover of EVAG AG (holder of Bergius' patents) by BASF
1924/1927	First pilot plant for coal hydrogenation in Oppau (near Ludwigshafen) / Commissioning of the first large-scale plant using the IG process (also known as the Bergius-Pier process) in Leuna
1931	Nobel Prize in Chemistry awarded to Friedrich Bergius and Carl Bosch for their work in the field of high-pressure chemistry

1935	Pott-Broche process (liquefaction in hydrogen-donating solvent)
1943/44	Twelve plants for the liquefaction of lignite, hard coal and tar with an annual capacity of approximately 4 million tons of liquid fuels are in operation. Nine Fischer-Tropsch synthesis plants with an annual production of 570,000 tons of gasoline in Germany
1945	Facilities destroyed or taken out of service (subsequently prohibited by the Allies until about 1950)
since 1955	Sasol operates Fischer-Tropsch systems in South Africa

The last coal hydrogenation plants were partially restarted between 1949 and 1951 after the Allied ban was lifted. Some plants continued to be used for the hydrogenation of heavy oils for a time. With the surge in petroleum production, particularly from 1950 onward, coal hydrogenation was no longer economically viable. Only in South Africa was coal hydrogenation established and later expanded, primarily for political reasons.

3.1.1 BERGIUS AND PIER

After receiving his doctorate in 1909, Friedrich Bergius (1884-1965) worked for Fritz Haber (1868-1934) in Berlin. It was here that he received the crucial impetus for his work on high-pressure reactions. He conducted his first development work between 1910 and 1914 in his private laboratory in Hanover, and later continued this work at Th. Goldschmidt AG Essen in their Mannheim plant. In 1931, Bergius, together with Carl Bosch (1874-1940), received the Nobel Prize in Chemistry. In his Nobel Prize lecture, he also discussed, among other things, investigations into coalification, in which wood was converted into a coal-like substance in water under the influence of pressure and temperature [Bergius32]. Following his work on coal conversion, he turned to wood pulping processes that could be used to obtain starch from lignocellulose for animal feed production (Willstätter-Bergius process) [Bergius28, Martin49].

Bergius had outlined the basic principle of high-pressure hydrogenation and taken initial steps toward its technical implementation. Only a large corporation could raise the financial resources for large-scale industrialization. In 1925, the Bergius patents were acquired by BASF (part of the IG Farben group) under the leadership of Carl Bosch. At that time, the company already possessed extensive experience in catalytic high-pressure processes for the synthesis of ammonia and methanol.

The further development and technical implementation of the hydrogenation process was carried out under the direction of Mathias Pier (1882-1965). In contrast to Bergius, who aimed to achieve hydrogenation of coal through thermal means, Pier employed catalysts to control the reaction process. Following the successful hydrogenation of lignite carbonization tars to liquid products in 1925, the actual work on coal hydrogenation began. Pier recognized that it was impractical to hydrogenate coal to gasoline in a single step. A two-stage process was implemented, consisting of a bottom phase with a finely dispersed catalyst and a gas phase with a catalyst fixed within the reaction chamber [Osteroth89]. Solutions were developed for the addition, distribution, concentration adjustment, and renewal of the catalysts in the bottom phase. In the gas phase, the development progressed from versatile and robust catalysts to more specific and sensitive ones [Höring66]. The catalyst systems were designed to produce high-quality fuels and petroleum products from the various raw materials with high yields. As fuel demands increased, new operating methods and catalysts for aromatization, dehydrogenation, and isomerization were systematically developed [Höring66]. Extensive details regarding the apparatus design and process variants of the Bergius-Pier process can be found in [Krönig50].

"Coal hydrogenation is as much more complicated than methanol synthesis as a modern airplane. opposite a glider." Mathias Pier [Höring66]

Current development efforts should consider and build upon the findings of earlier work. The insight already gained with coal, which in the case of bituminous coal has a relatively straightforward composition compared to wood (see Figure 3-1), and clearly documented by Piers' statement above, that one-step reactions do not lead to a defined and readily usable product, should not be disregarded in the context of the direct liquefaction of wood.

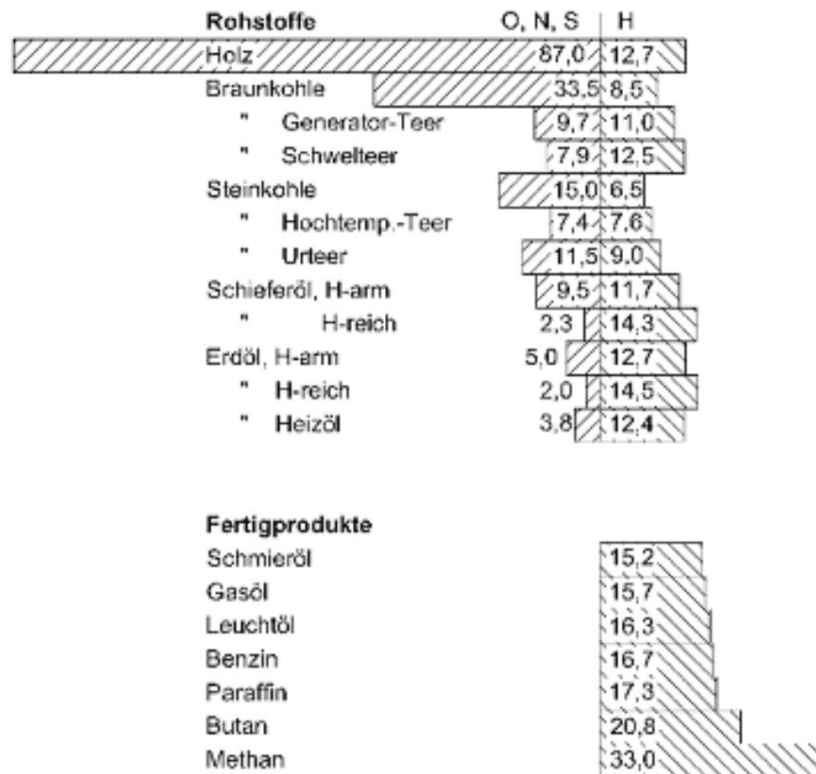


Figure 3-1: Elemental analyses of raw materials and hydrogenation products based on 100 parts Carbon, according to [Pier39]; supplemented by wood

To roughly estimate the hydrogen requirement for hydrogenation, Pier presented the scheme shown in Figure 3-1 [Pier39]. This scheme depicts the mass fractions of hydrogen, oxygen, sulfur, and nitrogen per 100 parts of carbon. It clearly shows that petroleum products, carbonization products, and tars are already close to the target products in terms of their composition. Methane formation in the process should be suppressed as much as possible. The original diagram was supplemented with wood. This version particularly highlights the unfavorable oxygen-to-hydrogen ratio in wood for the production of liquid hydrocarbons.

3.1.2 Liquefaction During Oil Crises

The oil crises of the 1970s temporarily led to greater interest in technologies that could substitute oil with other energy carriers. Research into solutions for using coal to produce fuels and also SNG (substitute natural gas) was conducted, particularly in countries like the USA, Great Britain, Germany, and Japan. The goals of further developing liquefaction processes were to reduce system pressure and minimize hydrogen consumption.

In the USA, the Department of Energy (DoE) launched a research program that led to the construction of several large coal liquefaction plants. Processes were also tested in Great Britain and Japan. In Germany, a coal-oil conversion plant (coal-oil process, new IG Farben process) with a capacity of 200 t/d was commissioned in Bottrop in 1981 (Figure 3-2). Initially, coal was hydrogenated in this plant, which was jointly operated by Ruhrkohle AG and VEBA AG. From 1993 until the plant's closure in 1999, plastic waste from the dual system (DSD) was converted into oils. For this purpose, the plant's capacity was doubled in 1995 from 40,000 to 80,000 t/a [Müll00]. Since the plant could not be operated economically at that time, it was decommissioned and offered for sale in individual parts on the online auction platform eBay in February 2000. This unsuccessful attempt, costing 250 million DM, is considered the most expensive abandoned project to date [Müll00]. The facility was subsequently demolished.

The last German plant of this type on a pilot plant scale (DMT - Deutsche Montan Technologie GmbH) was sold to China in 2004. With a throughput of 0.2 t/d, it was able to convert almost 60% of coal into gasoline and diesel [EEK04].



Figure 3-2: Coal olea plant Bottrop (Source: www.gvst.de/dokumente/fakten/Argumente18_kohleoel.pdf)

The Chinese energy company Shenhua, with the assistance of German experts (DMT), is planning to build a coal liquefaction plant in Majata, Mongolia. The plant is expected to produce approximately 5 million tons of gasoline, kerosene, diesel, and other fuels annually from around 9.7 million tons of coal. Given the favorable conditions and a crude oil price of approximately US\$20 per barrel, the plant would be economically viable. While still in the contract award phase, it is slated to begin operations in 2007 and is expected to spur further plant construction. The Chinese government considers this world's first industrial-scale plant for direct coal hydrogenation, with an investment volume of approximately €2.45 billion, to be significant within the framework of the domestic energy infrastructure.

A report by the UK Department for Trade and Technology provides an overview of the major coal liquefaction processes studied during this period (approximately 1980 to 1999). It distinguishes between single-stage and multi-stage processes. As these are sometimes also mentioned in connection with biomass, they are listed here in Table 3-1 [dti99].

Most of the one-step processes were not pursued further, with the exception of the coal-oil process and the NEEDOL process, which reached technical maturity and were prepared for market launch by the manufacturers. Of the two-step processes, only CTSL, LSE, and BCL were further developed in the late 1980s (see Table 3-1).

A very detailed overview of the development of liquefaction processes to date can be found in [Kaneko01]. Further information on the processes is listed in [Schmieder00, dti99, DoE01a, DoE01b].

The conclusion of a DoE final report on liquefaction activities is interesting. Under the heading "Lessons Learned," it states that, in retrospect, technological development in the field of direct coal liquefaction during the 1970s and early 1980s was not adequately pursued by either government-sponsored or industrial research programs.

Larger demonstration plants were planned before the underlying technology was understood. Furthermore, there was a miscalculation of the impact of high crude oil prices on the further development of exploration and production technologies.

Another reason for the lack of maturity in the demonstration programs was the absence of suitable ongoing long-term research programs at the onset of the first oil crisis. The hasty launch of large and complex research programs, especially under the pressure of a crisis, is ineffective and costly. It follows that a continuous allocation of R&D funding over a longer period is suitable for reducing overall costs, coordinating individual processes to be developed, and achieving a better overall solution [according to DoE01b].

Table 3-1: Developments in direct coal liquefaction processes from about 1980 [dti99]

Single-stage processes	Multi-stage processes
• Coal oil (Ruhrkohle, West Germany) • - NEDOL (NEDO, Japan) • H- - Coal (HRI, USA) • Exxon - Donor Solvent (EDS) (Exxon, USA) • SRC-I and - II (Gulf Oil, USA) • Imhausen high- - pressure (West Germany) • Conoco zinc chloride (Conoco, USA)	• Catalytic Two-Stage Liquefaction (CTSL) (USDOE and HRI, now HTI, USA) • - Liquid Solvent Extraction (LSE) (British - Coal Corporation, UK) • Brown Coal Liquefaction (BCL) (NEDO, - Japan) • Consol Synthetic Fuel (CSF) (Consolidation - Coal Co, USA) • Lummus ITSL (Lummus Crest, USA) • - Chevron Coal Liquefaction (CCLP) (Chevron, USA) • Kerr-McGee ITSL (Kerr-McGee, USA) • - Mitsubishi Solvolysis (Mitsubishi Heavy - Industries, Japan) • Pyrosol (Saarbergwerke, BR Germany) • - Amoco CC-TSL (Amoco, USA) • - Supercritical Gas Extraction (SGE) (British - Coal Corporation, UK).

3.2 BIOMASS

3.2.1 BUILDING OF BIOMASS

Plant biomass consists essentially of the three biopolymers cellulose, hemicellulose (also known as polyose), and lignin. In temperate woods, these components typically make up 97–99% of the wood substance. Of this, cellulose accounts for 30–35%, hemicellulose for 15–35%, and lignin for 20–35%. Extractives (1–3%) and inorganic components (ash) (0.1–0.5%) are present in significantly smaller proportions. Generally, the lignin content is higher in coniferous woods than in deciduous woods, while the hemicellulose content is somewhat higher in deciduous woods [Fengel84]. The varying concentrations of the main components of biomass are described in

Table 3-2 is shown. In addition to woody plants, annual plants are listed, which also include "straw-like" plants (e.g. grasses).

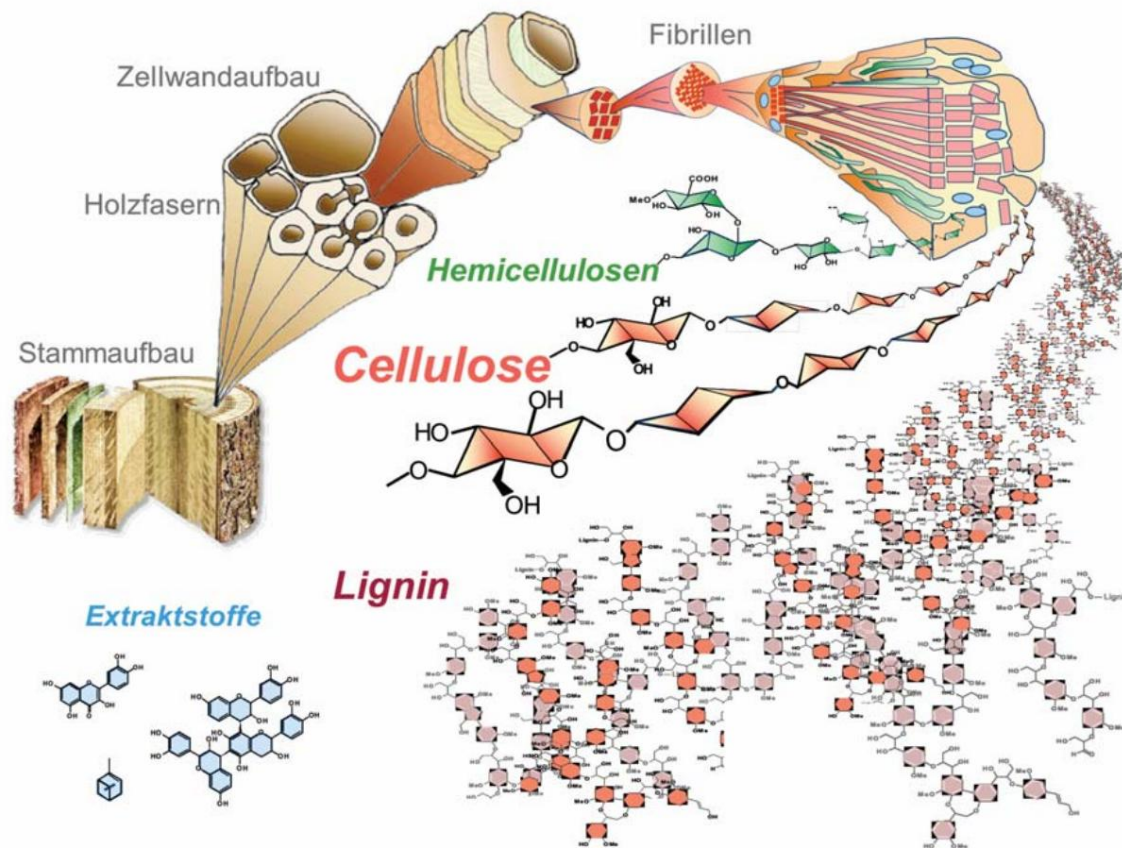


Figure 3-3: Structure of wood [Meier06a]

Table 3-2: Proportions of cellulose, hemicellulose, lignin and extractives or ash in various biomasses (percentage by mass) [Kaltschmitt01]

	Cellulose	Hemicellulose	lignin	Extracts/Ash
Deciduous	40-42	30-35	20-22	2-3
Coniferous wood	40-43	21-23	27-28	3-5
Annual plants	38-42	25-30	15-21	5-10

For thermochemical conversion processes, in which biomass is broken down into individual molecules or even into its elemental components, not only the basic molecular structure but also the overall structure of the plant is important. This has implications for upstream process steps such as comminution and feeding, as well as for the possibilities of chemical or thermal digestion.

The parts of plants that can be used for energy (shoots, branches, twigs, peels, and, in a broader sense, straw, etc.) are composed of fibers, which in turn consist of plant tissue cells. Figure 3-3 schematically shows the structure of wood, from the trunk through the fibers to the cell walls with their fibrils and ultimately the macromolecules they contain. In addition, some extractives are shown that are responsible, for example, for the typical color and smell of wood.

3.2.2 MOLECULAR STRUCTURE OF THE CELL WALL

The main components of biomass are contained within the cells of the cell walls. These are composed of different layers. The cell wall layers differ in the proportion of chemical components, but especially in the orientation of the cellulose.

Figure 3-4 schematically shows the structure of softwood tracheids (parts of the vascular tissue). A very thin middle lamella, which is usually not recognizable as an individual layer, acts as an adhesive layer between the cells. It is therefore grouped together with the two adjacent primary walls of neighboring cells as the middle layer (M). The primary wall (P) consists mainly of polyoses (hemicelluloses) and lignin. Embedded within it are thin, irregularly crosswise layers of cellulose fibrils. The primary wall is followed by the secondary wall 1 (S1) with flat, spirally arranged, parallel cellulose fibrils. Within S1, there are several layers with counter-rotating fibrils. If the individual layers are very thin, as in beechwood fibers, the counter-rotating fibrils are visible as a crossed system. The thickest wall layer is the secondary wall 2 (S2). In this wall, the cellulose fibrils run at a very acute angle to the fiber axis, often almost parallel to it. In parenchyma cells (tissue ground cells), a further secondary wall layer (S3) is formed. The angle of inclination of the fibrils in this layer lies between that in S1 and S2. Multilayered secondary walls are found in the fibers of monocotyledons (monocotyledonous plants; e.g., bamboo). The secondary layers primarily serve to stabilize and strengthen the cell wall. The steeply inclined fibrils of S2 are responsible for tensile strength. The flat, spirally inclined fibrils of S1, in conjunction with the lignin, prevent the inner wall layers from breaking out under compressive stress. The tertiary wall forms the boundary towards the lumen. In this wall, the cellulose fibrils are not strictly parallel and are arranged in a flat, spiral pattern. In various wood species, a wart-bearing layer is deposited on the lumen side (towards the vascular canal) of the tertiary wall.

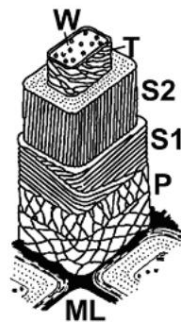


Figure 3-4: Cell wall structure of softwood tracheids (P - primary wall, S1 - secondary wall, S2 - Secondary wall, T - Tertiary wall, W - Wart layer on the lumen side, ML - Middle lamella [Fengel84])

The described structure of the cell wall is subject to changes during growth.

In particular, the incorporation of lignin (lignification) significantly alters the structure and composition, and thus the properties, of the cell wall. Deciduous and coniferous wood consist of almost 50% cellulose, which is primarily located in the S2 layer. Polyoses make up approximately one-fifth of the total amount, and lignin about one-quarter. During lignification, the ground substance is by no means removed from the cell wall, but merely expanded and compressed. Nevertheless, those wall layers that were originally characterized by a high ground substance content (cement layer, primary wall, S1 layer) exhibit the highest lignin content after lignification is complete; it can reach 90% in the middle layer. The lignification process also begins here, only later affecting the younger wall layers. Fundamentally, however, lignin can only be incorporated into already existing wall layers (typical incrustation). The properties of lignin, especially its ability to form rigid, isotropic-amorphous masses, are rooted in its molecular structure. The large macromolecules are highly branched and can grow through the wall scaffold in all directions during their formation [Sitte65].

3.2.3 CHEMICAL COMPOSITION

3.2.3.1 CELLULOSE

Cellulose is a fundamental component of plant matter, and its production exceeds that of all other natural substances.

Approximately half of photosynthetically produced biomass consists of cellulose.

This carbohydrate therefore plays a central role in the natural carbon cycle alongside CO₂ [Schlegel92].

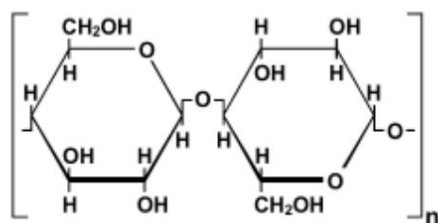


Figure 3-5: Cellulose as the basic building block of cellulose [Kögel02]

Cellulose consists of chains of 1,4-glycosidically linked β-D-glucopyranose units with a degree of polymerization (glucose units per cellulose molecule) of up to 14,000 in plants. The structurally relevant elementary unit is not glucose, but rather the disaccharide cellobiose, which is shown in Figure 3-5.

The high mechanical strength and insolubility of cellulose are achieved at the molecular level through the formation of inter- and intramolecular hydrogen bonds. The former connect the individual chains to one another, while the individual chains themselves are stabilized by intramolecular hydrogen bonds (two per glucose unit). This results in a two-dimensional network of hydrogen bonds. The strong cohesion of the individual network layers is based on van der Waals forces.

This results in a three-dimensional H-bridge network [Schlegel92].

3.2.3.2 HEMICELLULOSE (POLYOSES)

After cellulose, hemicelluloses (also known in the literature as polyoses, hemisubstances, or xylans) are the most abundant carbohydrates in nature. They are neither related to cellulose in terms of their constituent parts nor their structure, and are at least partially water- or alkali-soluble. Hemicelluloses consist of pentoses (xylose, arabinose) or hexoses (glucose, mannose, galactose) as well as uronic acids. In plants, they function as reserve or structural components. Their degree of polymerization is considerably lower (30–100) than that of cellulose, and they are also highly branched. [Schlegel92].

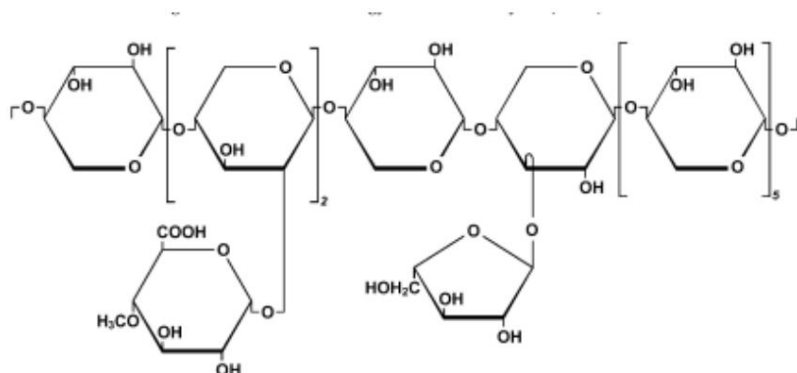


Figure 3-6: Molecular structure of polyose [Kögel02]

3.2.3.3 LIGNIN

After cellulose, lignin is, alongside hemicelluloses, the third most abundant component of plants. Lignin is encrusted in plant tissue; it is found in the secondary lamellae of the cell wall. The complex consisting of lignin and cellulose is also known as lignocellulose. Lignin is the most slowly degraded plant compound. It is therefore the main source of slowly decomposing organic substances in the soil, especially humic acids [Schlegel92].

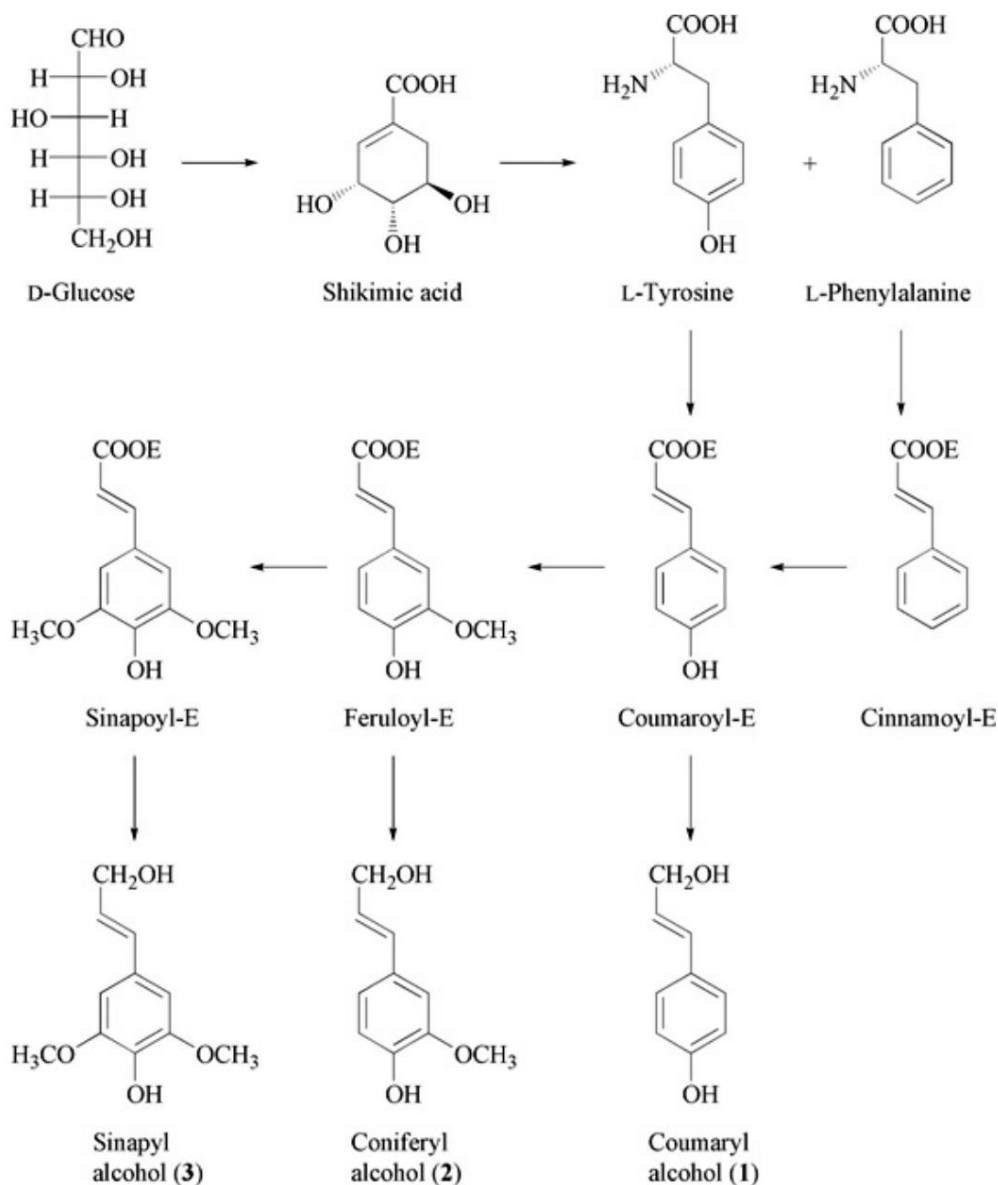


Figure 3-7: Formation of the lignin precursors sinapyl, coniferyl and coumaryl alcohol [Nimz03]

The lignin molecule has a very complex structure, which, however, can be traced back to a few monomeric basic molecules. The basic building blocks are invariably phenylpropane derivatives, predominantly coniferyl alcohol. This complexity arises from the large number of different types of bonds that can be linked together by the monomeric building blocks. This irregular structure of lignin is consistent with the idea that the enzymatic process of lignin synthesis is limited to the formation of coniferyl alcohol radicals. These radicals then spontaneously form bonds, the type and possibilities of which result from the isomeric states of the radical. A number of dimers and oligomers of coniferyl alcohol have been isolated as intermediates of lignin synthesis.

While spruce lignin consists primarily of coniferyl alcohol, broadleaf lignin contains coniferyl and sinply alcohol, and grass lignin (grasses) also contains coumaryl alcohol. The formation mechanism of these three basic building blocks is shown in Figure 3-7. The differences in composition are particularly evident in the methoxy group content: broadleaf lignin 20.5–21%, spruce lignin 15–16%, and grass lignin 14–15% of the lignin content. In lignin, the phenylpropane units are cross-linked in a variety of ways by ether and C-C bonds. The possible linkages in the lignin molecule have been investigated by various authors. Adler's model is shown in Figure 3-8 as an example. These bonds are exceptionally resistant to enzymatic attack. In plants, lignin is an inert end product of metabolism that is not re-incorporated into metabolism and only fulfills mechanical functions [Schlegel92].

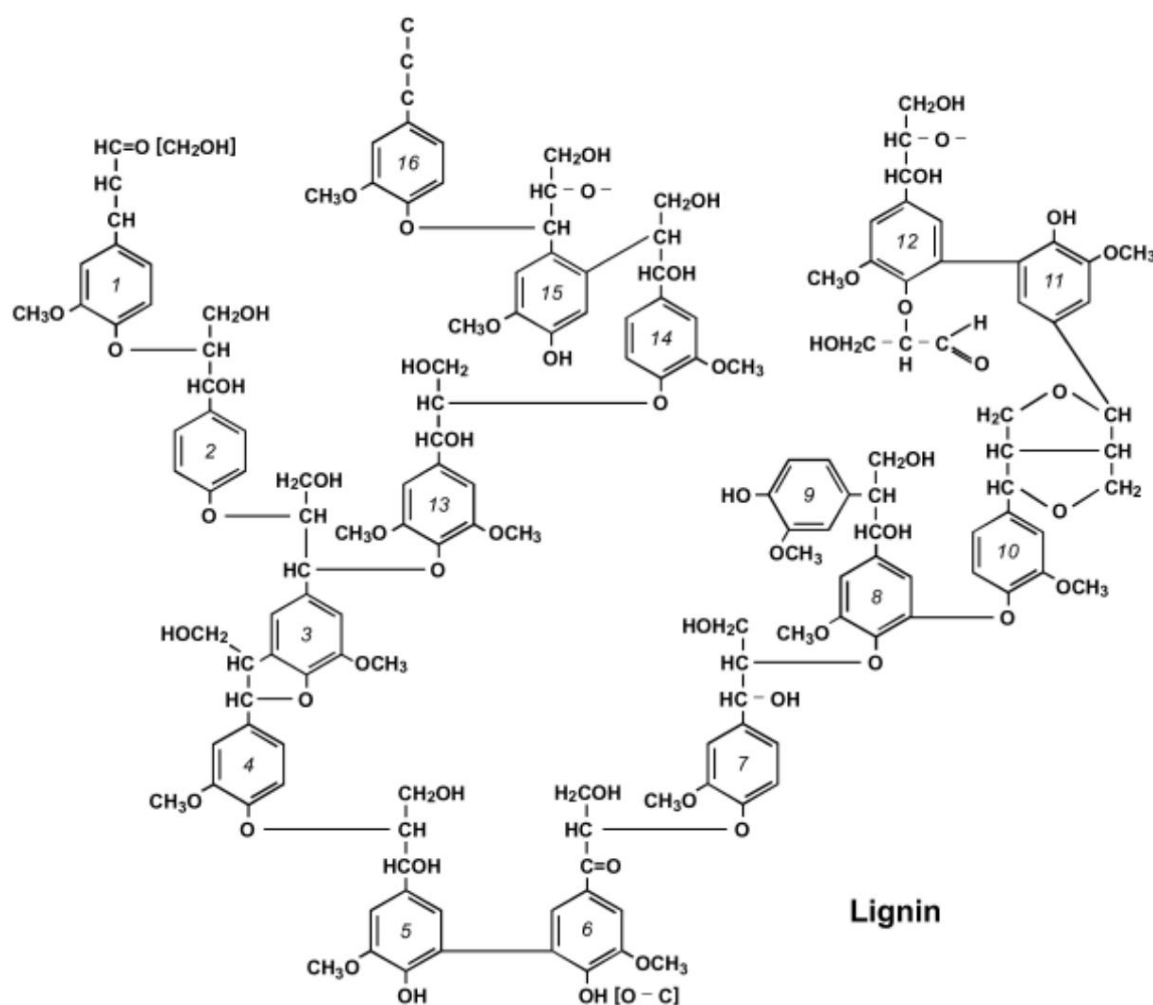


Figure 3-8: Model of spruce lignin [Adler77]

3.3 REQUIREMENTS FOR FUEL

The Tenth Ordinance Implementing the Federal Immission Control Act (10th BImSchV) was published in the Federal Law Gazette on June 24, 2004. This ordinance, concerning the composition and labeling of fuel qualities, refers to DIN EN 228 for gasoline and DIN EN 590 for diesel fuel (both in the version of March 2004).

All products derived from the direct liquefaction of biomass must fully comply with these standards if they are to be used as fuels. Meeting only part of the requirements is insufficient.

Table 3-3 for Otto and Table 3-4 for Diesel fuels provide an overview of the development over time of important parameters from these standardization documents.

Table 3-3: Development of standards for gasoline

Parameter	Basis 1995	Komm. Juni 1996	OK 2000 98/70/EG	OK 2005 98/70/EG	UBA 1995	RFG II	World-Wide Fuel Charta	
							Kat. 3	Kat. 4
Benzol v/v% max.	2,4	2,0	1,0	1,0	1,0	1,0	1,0	1,0
Aromaten v/v% max.	40	45	42	35	30	25	35	35
Schwefel ppm max.	240	200	150	50	100	40	30	5-10
T 90 °C max.	160	186	186	186	150	150	175	175
RVP kPa max.	67	60	60	60	60	60	60	60
Olefine v% max.	10	18	18	18		6	10	10
Sauerstoffgehalt m% max.	0,6	2,3	2,7	2,7		2,3	2,7	2,7

Table 3-4: Development of standards for diesel fuels

Parameter	Basis 1995	Komm. Juni 96	DK 2000 98/70/EG	DK 2005 98/70/EG	UBA 1995	schwed. EC 1	World-Wide Fuel Charta	
							Kat. 3	Kat. 4
Cetanzahl min.	51	51	51	51	54	54	55	55
Polyaromaten %m/m max.	9	11	11	11	1,0	0,1	2,0	2,0
Schwefel ppm max.	450	350	350	50	50	10	30	5-10
T 95 °C max.	355	360	360	360	310	285	340	340
Dichte g/l min./max.	843	845	845	845	825	810	820/840	820/840

3.4 REACTION CONDITIONS, DIFFERENCE FROM PYROLYSIS & GASIFICATION

In the field of direct liquefaction, as well as pyrolysis and gasification of biomass, a wide variety of reaction conditions and media can be found in the literature. Table 3-5 provides an overview of the parameter ranges found and also serves to differentiate direct liquefaction from the other two processes.

Table 3-5: Reaction conditions for thermal biomass utilization

Proceedings	solvents	Pressure	temperature	product
Direct liquefaction yes		< 1 - 240 bar	150 - 420°C	Organic liquid
Flash pyrolysis	no	< 1 - 5 bar	max. 500°C	Organic liquid
Pyrolysis/gasification: no		< 1 - 20 bar	700 - 900°C	Solid, liquid and gaseous products

Even in direct liquefaction itself, numerous reaction processes and a wide variety of reaction conditions are used. The following subdivision follows the classification of [Chornet85]:

- Solvolysis
 - Aqueous medium
 - o Acid hydrolysis
 - o Basic hydrolysis
 - o Neutral hydrolysis
 - Organic medium
 - Thermal decomposition under a reducing atmosphere.

In the following chapters or sections, these different approaches and their associated advantages and disadvantages will be presented and discussed in detail.

4 THEORETICALLY CONCEIVABLE REACTION PATHWAYS

The conversion of woody biomass (as well as peat, lignite or hard coal) into usable liquid hydrocarbons comprises the following principal steps [Chornet85]:

- Preparation of the raw material with regard to moisture content and particle size
- Introducing the raw material into a liquid phase (water – neutral, basic or acidic –, organic solvents or non-reactive heat transfer oils)
- Heating this slurry
- Application of a reducing atmosphere (e.g., hydrogen) at increased pressure
- Carrying out the cleavage and reduction reactions
- Separation of the solid residue phase and solvent from the liquid product
- Distillative separation of the liquid phase and recovery of the solvent.

Depending on the process, catalysts with a wide variety of functionalities can be added to the biomass slurry. From a chemical perspective, the following steps correspond to the process engineering steps just mentioned:

- Solvolysis of plant cells
- Depolymerization of the three main components cellulose, hemicellulose and lignin, as well as chemical transformation of the monomers or smaller fragments through interaction with the solvent with simultaneous molecular restructuring (e.g. bond cleavage, release of water or carbon dioxide); in addition, thermal bond cleavage also occurs.
- Degradation of oxygen-containing functional groups in the presence of hydrogen (either in the form of a hydrogen atmosphere under increased pressure or by a hydrogen-transferring solvent such as tetralin (1,2,3,4-tetrahydronaphthalene)).

There is a wide range of detailed knowledge regarding the individual chemical processes mentioned, specifically concerning the reactions that take place.

The degradation of cellulose or hemicellulose in aqueous media is relatively well known. Since these are poly-sugars (pentoses and hexoses), one can draw on the extensive knowledge from the paper industry and sugar chemistry. In an aqueous environment with the addition of acid, depolymerization occurs depending on the substrate and temperature (hemicelluloses between 120 and 180°C, cellulose from 240°C), followed by ring cleavage or... Rearrangement of the monomeric sugars.

Figure 4-1 shows an exemplary series of steps and intermediates that can be observed during the degradation of such sugar monomers in an acidic aqueous medium. The large number of different degradation products, characterized by a multitude of oxygen-containing functional groups, is clearly recognizable. Furthermore, it can be seen from these molecules that a simple release of carbon dioxide and thus a reduction of the oxygen content is not to be expected. Only a very small number of the visible functional groups are capable of such direct chemical degradation. This illustrates the crucial role of hydrogen in the degradation of functional groups and thus in preventing the repolymerization of the degradation products. Such repolymerization can occur, for example, through the formation of an ester from an acid group (-COOH, "acid" in Figure 4-1) and an alcohol group (-OH, e.g., in glucose). If degradation molecules possess several such functional groups, three-dimensional cross-linking and ultimately the formation of solid residues can occur.

Lignin also undergoes extensive breakdown in the solvents used. This process produces a large number of differently substituted phenols. An example from the paper industry will serve here – the sulfuric acid pulping of wood (Figure 4-2).

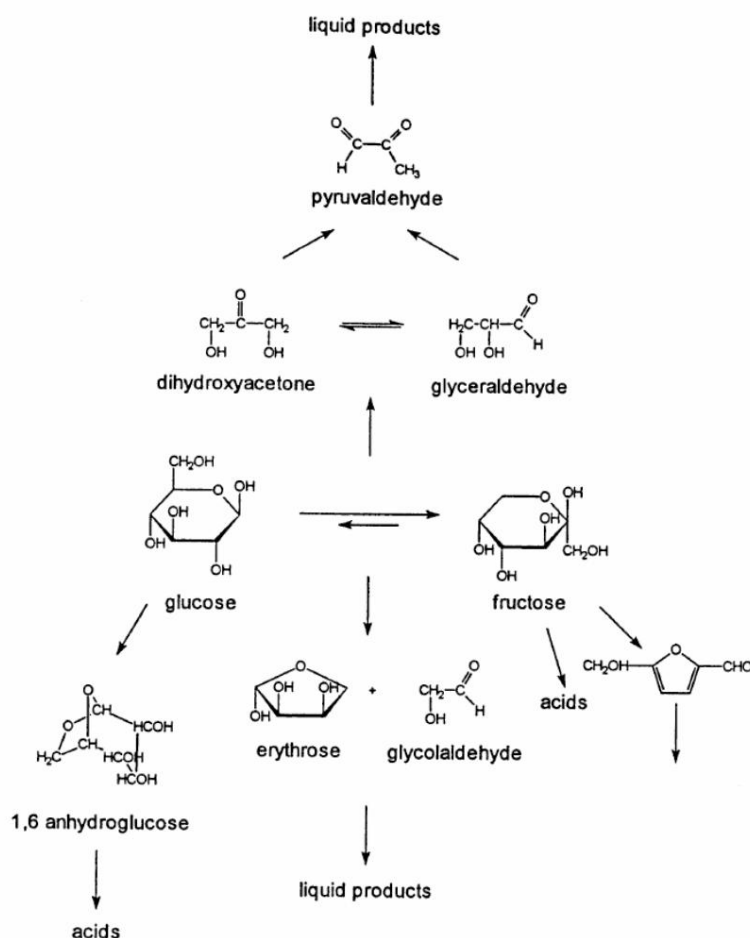


Figure 4-1: Sugar degradation reaction in acidic medium [Kruse03]

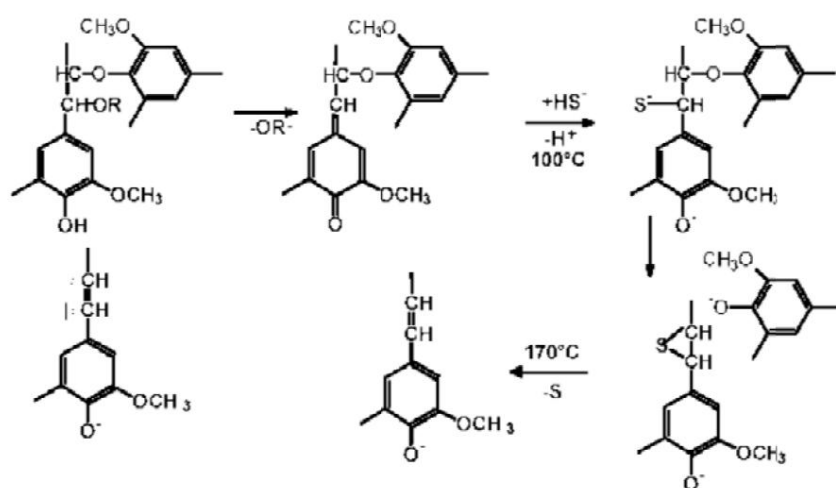


Figure 4-2: Individual reactions in the sulfuric acid degradation of lignin

Here too, the large number of functional groups on the phenol molecules would very quickly lead to repolymerization through reactions analogous to the degradation of glucose described on the previous page, without a corresponding degradation by hydrogen.

5 EXPERIMENTALLY DETERMINED REACTION PATHWAYS

A small number of studies on direct liquefaction deal with the analysis of intermediate and final products and the development of reaction pathways.

The review articles [Chornet85, Bouvier88b] mainly provide information on the depolymerization of macromolecules (lignin, cellulose, and hemicellulose) depending on the medium used. A more detailed description of all other possible reaction pathways is not possible without limiting ourselves to specific special cases.

Further reaction steps are described in works that specifically deal with a liquefaction process under certain conditions [Fang04, Kruse03, Huber04, Huber05, Kabyemela99, Lin97b, Lin01b]. These are essentially limited to four different types of processes.

- Liquefaction of cellobiose and lignin model components in phenol [Lin97b, Lin01b, Lin04]
- Liquefaction of cellulose in subcritical water [Appell71, Fang04, Kruse03]
- Liquefaction of Kraft lignin (model components) into tetralin [Connors80, Vuori88a, Vuori88b]
- Hydrodeoxygenation (HDO) of lignin model components using H₂ [Petrocelli85]

The investigations into reaction mechanisms and kinetic considerations are exclusively based on model substances that are in a homogeneous phase. Even the analysis of the reaction steps of Kraft lignin is considered too complex [Connors80, Petrocelli85].

Experiments with model components cannot be easily transferred to reaction networks of real biomass [Kruse03], since the biomass itself contains various salts that significantly influence the reaction pathways. Furthermore, the large number of organic molecules produced during the liquefaction of biomass, with their diverse functional groups (e.g., alcohols, aldehydes, acids, ethers, etc.), will undergo a wide range of reactions with one another.

No studies could be found that consider the reaction pathways of this mutual influence.

The reaction steps for the above-mentioned processes will be examined in more detail below.

The work of Huber et al. [Huber04, Huber05] is a special case, as it does not deal with direct liquefaction in the true sense, but carries out the liquefaction of cellulose using many intermediate stages.

5.1 OVERVIEW – GENERAL STATEMENTS

[Chornet85, Bouvier88b, Fengel84] provide general information on the reactions that occur during the liquefaction of the main components. A distinction is made here according to the medium in which the liquefaction takes place. Thus, liquefaction can occur in acidic, alkaline, and neutral media.

As already shown in section 3.2, the three main components each have a characteristic structure that plays an important role in the following discussion.

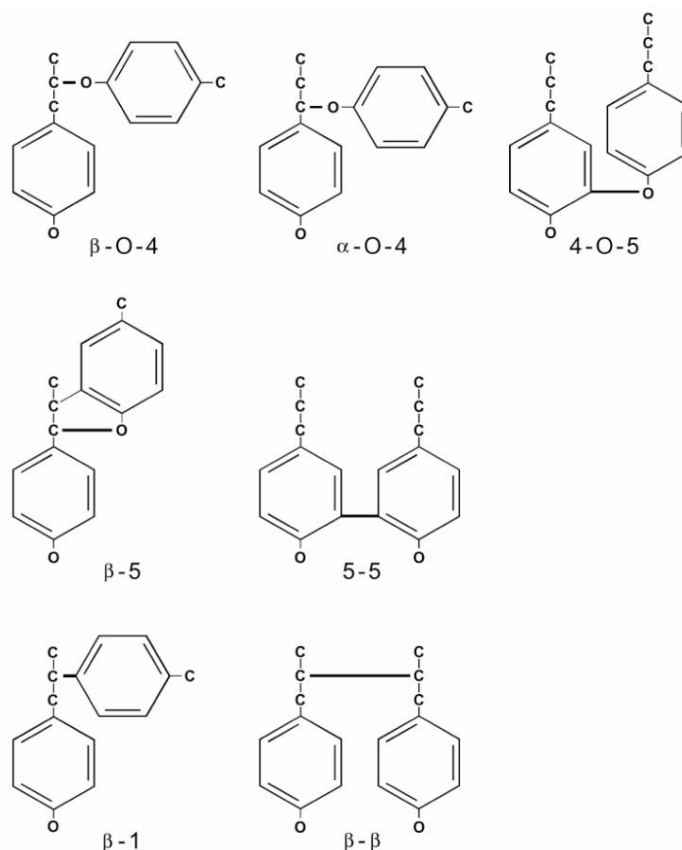


Figure 5-1: Main bond types of lignin [Kögel02]

In general terms, the following goal can be formulated [Chornet85, Bouvier88b]:

- Solvolysis into micelle-like substructures,
- Breaking down the macromolecules of wood,
- Stabilizing the reactive species,
- Reduce oxygen levels and
- Increase the H/C ratio.

Two pathways representing depolymerization are possible:

- Sequential dissolution of macromolecules via the exploitation of physicochemical properties Properties (papermaking) and
- integral dissolving, which refers to the parallel (simultaneous) dissolving of the macromolecules.

The following analysis examines only the integral pathway, assuming that it can be described by considering the reaction pathways of the individual macromolecules during liquefaction. Interactions between the macromolecules and their intermediates are neglected. Generally, the hydrolysis reactions of carbohydrates and polysaccharides proceed more slowly in basic media than in acidic media.

Section 5.1.4 presents two methods for the so-called upgrading of an aromatic, oxygen-rich “bio-oil”.

5.1.1 HYDROLYSIS IN AN ACIDIC MEDIUM

The rate of polysaccharide cleavage depends on the acidic medium used and the properties of the slurry. Water-miscible solvents (e.g., ethanol or dioxane) do not necessarily behave the same. Unlike dioxane, ethanol also acts as a reactant under otherwise identical conditions [Fengel84].

5.1.1.1 REACTION PATHWAYS OF CELLULOSE

The glycosidic bonds of cellulose are broken only at higher temperatures (200-220°C), but also at low acid concentrations. The depolymerization leads mainly to the formation of glucose units [Bouvier88b]. These further degrade to hydroxymethyl furfural [Chornet85].

Uncontrolled acid hydrolysis at higher temperatures leads to a complex mixture of aldehydes and acids, which then react further at higher temperatures in pyrolytic decomposition sequences (and hydrogenolysis if H₂ and catalyst are present).

5.1.1.2 REACTION PATHWAYS HEMICELLULOSE

Depolymerization of hemicellulose already takes place at temperatures < 120°C [Bouvier88b]. In this process, the hemicellulose molecules are cleaved into monosaccharides [Chornet85]. The selectivity of the hemicellulose depolymerization depends on the solvent used and the pH value. The resulting monosaccharides are further hydrolyzed to furfural and acid derivatives. Further transformations occur through thermal decomposition sequences.

5.1.1.3 LIGNIN REACTION PATHWAYS

β-OH and β-O groups are cleaved to form benzylium ions [Chornet85]. At 160-180°C in a weak acidic medium (sulfite salts), β-ether groups are cleaved [Chornet85, Bouvier88b].

Two competing pathways for the benzylium ion occur during digestion:

- Sulfonation •

Condensation through the so-called "Carbonium Ion Nucleophilic Site Interaction".

In aqueous acidic media, similar processes are assumed, whereby sulfonation is replaced by the addition of the conjugated base pair of the acid.

5.1.2 Hydrolysis in an Alkaline Medium

5.1.2.1 REACTION PATHWAYS CELLULOSE / HEMICELLULOSE

The cleavage of glycosidic bonds begins at T > 140°C [Bouvier88b]. The decomposition products of cellulose/hemicellulose during basic hydrolysis are organic acids: metasaccharinic acid, 2-C-methylglyceric acid, 3-deoxy-2-C-hydroxymethylpentanoic acid (gluco-isosaccharinic acid), lactic acid, 2,5-dihydroxypentanoic acid, xylo-isosaccharinic acid, and 2-Hydroxybutyric acid. Up to 30% of the total carbohydrates are lost during alkaline cooking.

Further degradation reactions occur at higher temperatures when crystalline cellulose is attacked by alkalis.

5.1.2.2 LIGNIN REACTION PATHWAYS

OH- groups promote delignification by cleaving ether bonds. β-Ether bonds (as in phenylcoumarane) lead to stilbene structures. Methoxyl groups remain as methanol in the presence of hydroxyl anions (OH⁻).

Condensation reactions also occur, leading to diarylmethane structures, and ultimately chromophoreic groups (unsaturated structures such as quinones) are formed by oxidation.

5.1.3 ORGANIC MEDIUM

The reactions that occur are strongly dependent on solvent-substrate interactions. The solvent should be chosen to interact strongly with cellulose. Ideally, it should also be a product of the liquefaction. Examples include phenols, phenolic derivatives, simple alcohols, and polyalcohols. The homolytic cleavage of the CO and C-C bonds leads to short-chain hydrocarbons. The reaction can be steered towards deoxygenation by adding reducing gases (H_2 , CO, H_2/CO).

5.1.4 UPGRADING

Starting with an aromatic, oxygen-rich "organic oil," various upgrading processes are available to further process this highly viscous, thermally unstable, and corrosive oil. Upgrading primarily involves reducing the oxygen content.

Two processes will be briefly outlined here. One is based on zeolites as catalysts.

No reducing gas is added here, and the oxygen is released as CO_2 and H_2O . The product retains its aromatic character and only small amounts of hydrocarbons.

A major disadvantage of this process is the deactivation of the catalyst through coking. The second method is hydrodeoxygenation (HDO), which consists of two steps. The first stabilizing step takes place at low temperatures and prevents the polymerization of oxygen-containing components and the coking of the catalyst. The second step involves the release of oxygen with the consumption of hydrogen at higher temperatures. A detailed description of the processes involved and their technical implementation can be found in Section 6.4.1.

5.2 Investigations on Model Substances

The reaction pathways currently found in the literature will be presented below. First, the results of investigations on lignin model substances will be presented, followed by those on cellulose.

5.2.1 LIGNIN

A series of publications on biomass dissolved in phenol can be found [Lin97a, Lin97b, Lin01a, Lin01b, Lin04]. These studies examined not only cellobiose but also lignin model substances in detail. A distinction is made between acid-catalyzed liquefaction and liquefaction without the use of a catalyst.

First, the complexity of the reaction steps during biomass liquefaction should be emphasized. A wide range of intermediate and end products are formed during liquefaction, which in turn depend on numerous influencing factors. An example will illustrate this. Figure 5-2 [Lin01b] shows a detailed analysis of the intermediate and end products in the acid-catalyzed solvolysis of a model substance for lignin (guaiacylglycerol β -guaiacyl ether) in phenol with sulfuric acid, and the corresponding reaction pathways are depicted.

The background is the production of polymeric materials. In the case of lignin, 28 products are formed, and when using cellobiose, eight products are produced. Due to the choice of phenol as the solvent, it is no longer possible to distinguish the specific products, which explains the aromatic character of the reactants. In any case, it is clear that the product range contains a significant amount of oxygen.

Less extensive studies regarding the reaction pathways have been carried out for the liquefaction of lignin model substances in which tetralin was used as a solvent and H₂ donor.

[Connors80] describes investigations into the hydrocracking of p-ethylguaiacol and dehydrodihydrodiisoeugenol. Since the Kraft lignin product range appears too complex, investigating individual steps is deemed unfeasible. For the model component ethyl guaiacol, however, two pathways for oxygen cleavage were identified (see Figure 5-3) (methyl-O cleavage and ring-O cleavage), while for dehydrodihydrodiisoeugenol, three pathways were observed (1- $\ddot{y}$ cleavage, $\ddot{y}$ - $\ddot{y}$ cleavage, and $\ddot{y}$ -5' cleavage). Further investigations are not conducted here. and while

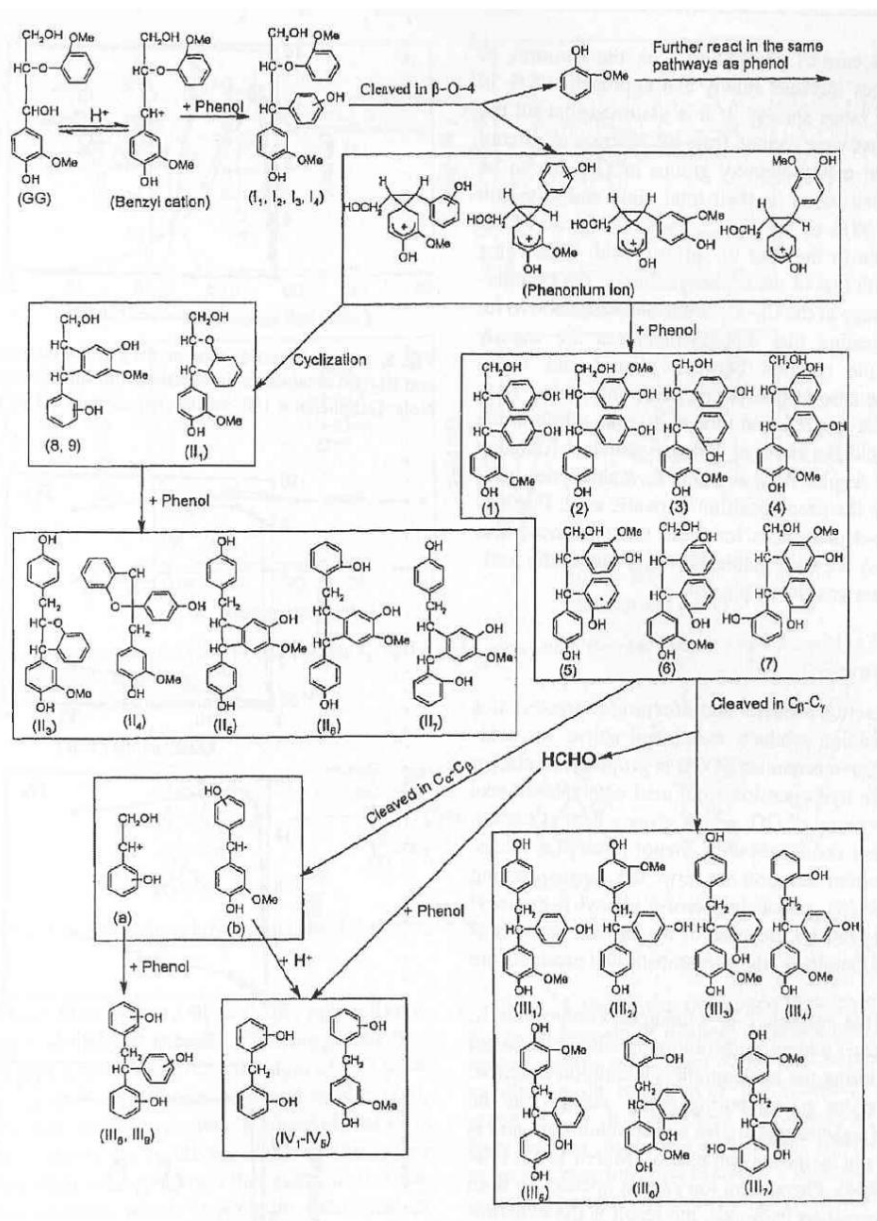


Figure 5-2: Product spectrum of the acid-catalyzed cleavage of guaiacylglycerol- γ -guaiacyl ether (lignin model substance) in phenol [Lin01b]

Another interesting aspect regarding the reaction pathways was investigated by Petrocelli and Klein [Petrocelli85]. Hydrodeoxygenation is commonly used as a downstream upgrading process in the context of biomass liquefaction (see Section 6.4.1).

However, this work focuses on investigating the effect of hydrodeoxygenation of lignin model substances directly under liquefaction conditions and not as a processing step.

They found that the oxygen content in lignin prevents the thermal conversion of lignin to short-chain products, resulting in large proportions of repolymerized long-chain components. Therefore, they investigated hydrodeoxygenation to reduce the oxygen content. n-Hexadecane was used as the solvent and $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$, pretreated with H_2S and H_2 , as the catalyst. A pressure of 34.5 bar was applied using H_2 .

Under these reaction conditions, the yield of benzene and cyclohexane is significantly increased compared to that of phenols. This results from the release of oxygen and the secondary reactions of the phenols to hydrocarbons via catalytic dehydroxylation.

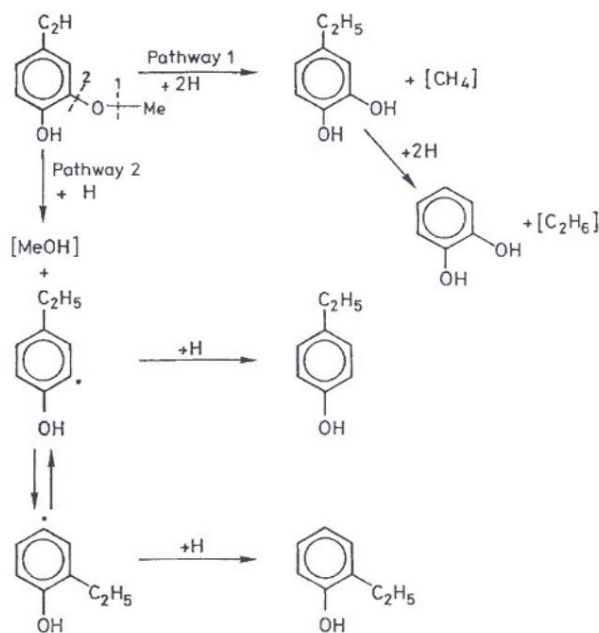


Figure 5-3: Hydrocracking of ethyl guaiacol via methyl oxygen (path 1) and ring oxygen Split (Path 2) [Connors80]

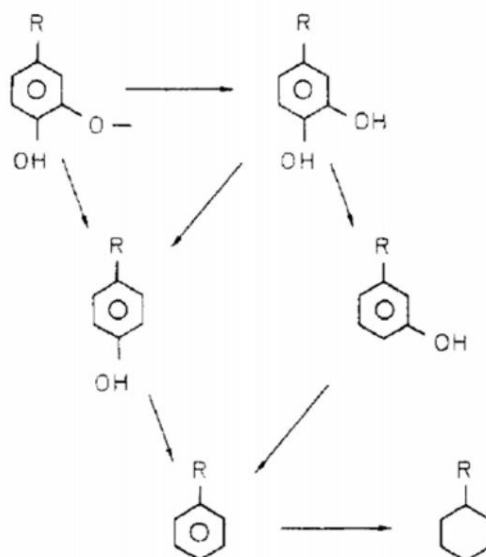


Figure 5-4: Methoxyphenol-HDO reaction pathway [Petrocelli85]

4-Methylguaiacol, 4-methylcatechol, eugenol, and vanillin were investigated, and their reaction pathways are shown in Figure 5-4. These reactants behave very similarly; they first demethylate the aromatic methoxyl groups, followed by dehydroxylation to monohydroxyl-substituted intermediates, which are then further dehydroxylated to hydrocarbons.

As a result of this work, it can be stated that the substituted guaiacols (4-methylguaiacol, eugenol) and catechols (4-methylcatechol, vanillin) used react mainly to form alkylated phenols and single-ring hydrocarbons, and that repolymerization can be reduced. Furthermore, it was shown that the use of o,o'-biphenol, o-hydroxydiphenylmethane, and phenyl ethers resulted in catalytic activity in the direction of hydrocracking of the ring bonds between the aromatics. In addition, the release of oxygen was also observed in this case.

5.2.2 CELLULOSE / GLUCOSE

The first studies on the reaction steps of cellulose in subcritical water in the presence of soda (Na_2CO_3) were carried out by [Appell71]. Building on this, there are further studies that have dealt with the same problem [Kabyemela99, Kruse03, Fang04].

There is general agreement on the reaction steps of cellulose in subcritical water (Figure 5-5) [Kabyemela99, Kruse03, Fang04]. Here, only the gray hatched box labeled "Homogeneous Phase" at high heating rates is relevant for liquefaction. of interest.

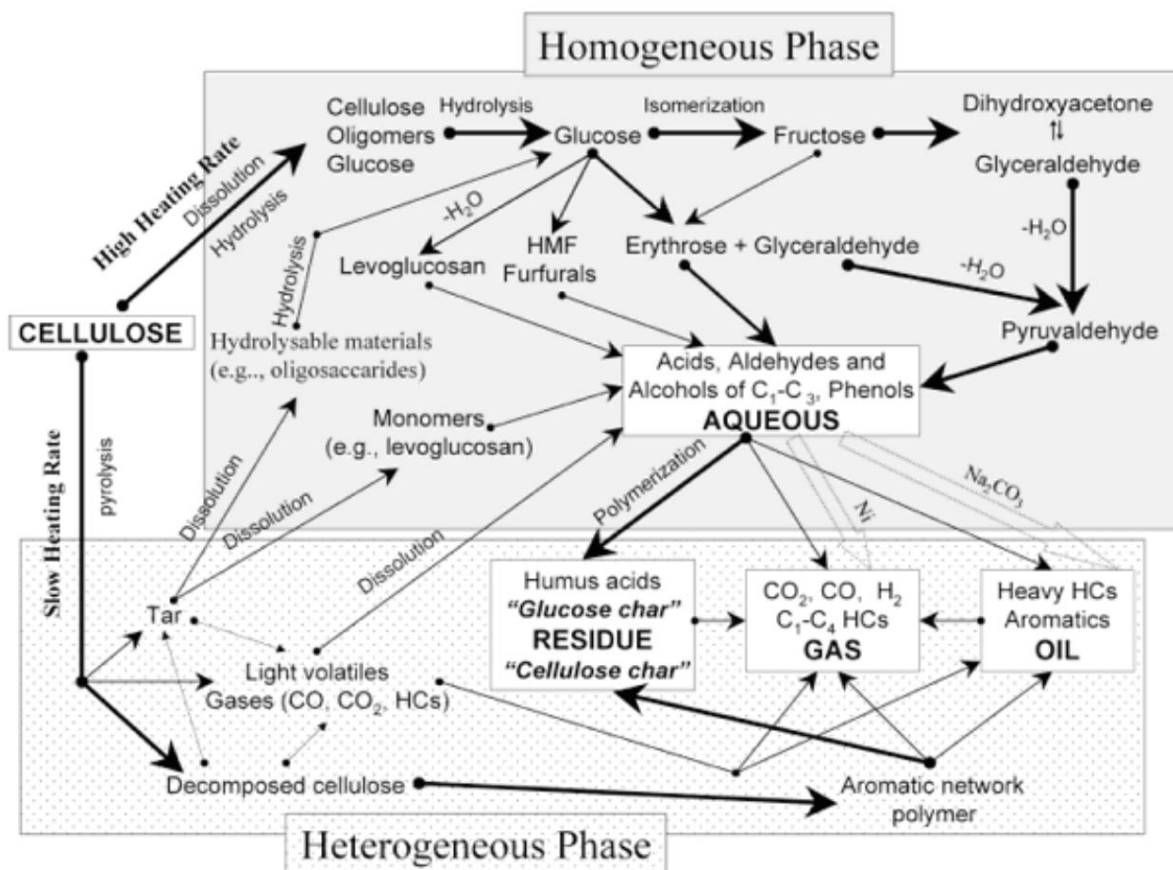


Figure 5-5: Product spectrum during the liquefaction of cellulose in aqueous medium [Fang04]

The reaction pathways for the hydrolysis of glucose in aqueous medium are straightforward (Figure 5-6). The aldol hydrolysis of glucose or fructose yields dihydroxyacetone and glyceraldehyde, which exist in equilibrium via tautomeric isomerization. These two components readily eliminate water, forming pyruvaldehyde, which reacts to form liquid products. Furthermore, the aldol hydrolysis of glucose and fructose produces erythrose and glycolaldehyde, which then react further to form non-liquid components.

The "liquid products" consist, among other things, of organic acids (levulinic acid, acetic acid, formic acid, lactic acid), aldehydes (acetaldehyde, formaldehyde) and alcohols, all of which contain a not insignificant amount of oxygen.

[Fang04] observed that without the use of a catalyst, a high proportion of a so-called glucose coke is formed from these liquid components, while in the presence of soda (Na_2CO_3) predominantly oily products are formed and in the presence of Ni high proportions of gaseous products are formed.

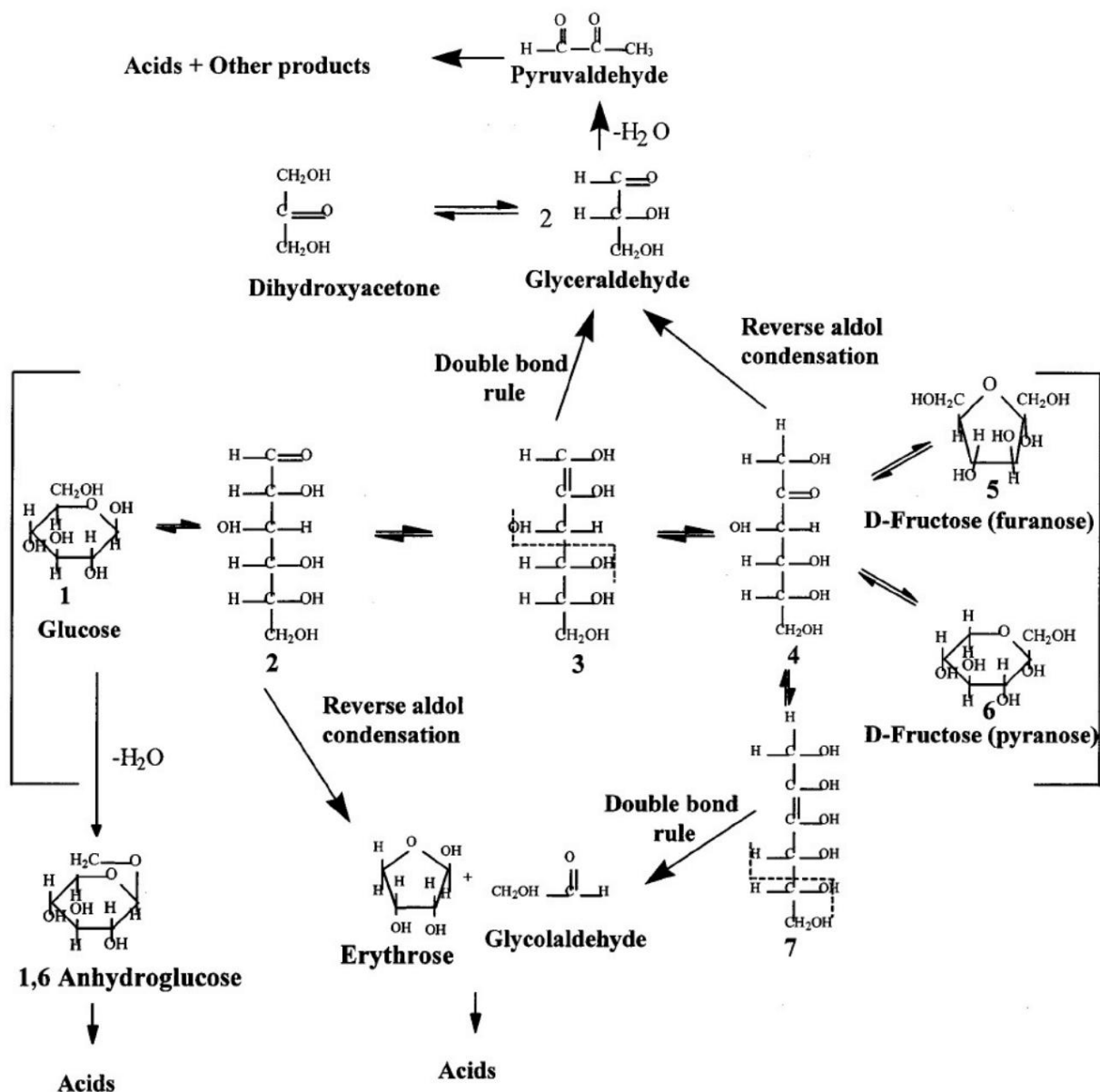


Figure 5-6: Hydrolysis of glucose [Kabyemela99]

Recent work by [Huber04, Huber05] presents reaction pathways in whose product spectrum alkanes appear.

In [Huber05], the steps for the liquefaction of carbohydrates produced from biomass are described. The aim is the production of liquid alkanes (C_7 to C_{15}). The starting materials used (furoin, furfural + acetone, HMF + acetone, HMF + acetone + furfural) are first condensed via aldol condensation at room temperature using Mg-Al oxide and NaOH catalysts. These are then hydrogenated in an autoclave with a Pd/Al₂O₃ catalyst using methanol or water, or methanol/water.

The actual reactor system is a 4-phase reactor system, composed as follows:

- an aqueous influx consisting of water-soluble organic reactants,
- a hexadecane influx,
- an influx of H₂ and
- a solid catalyst.

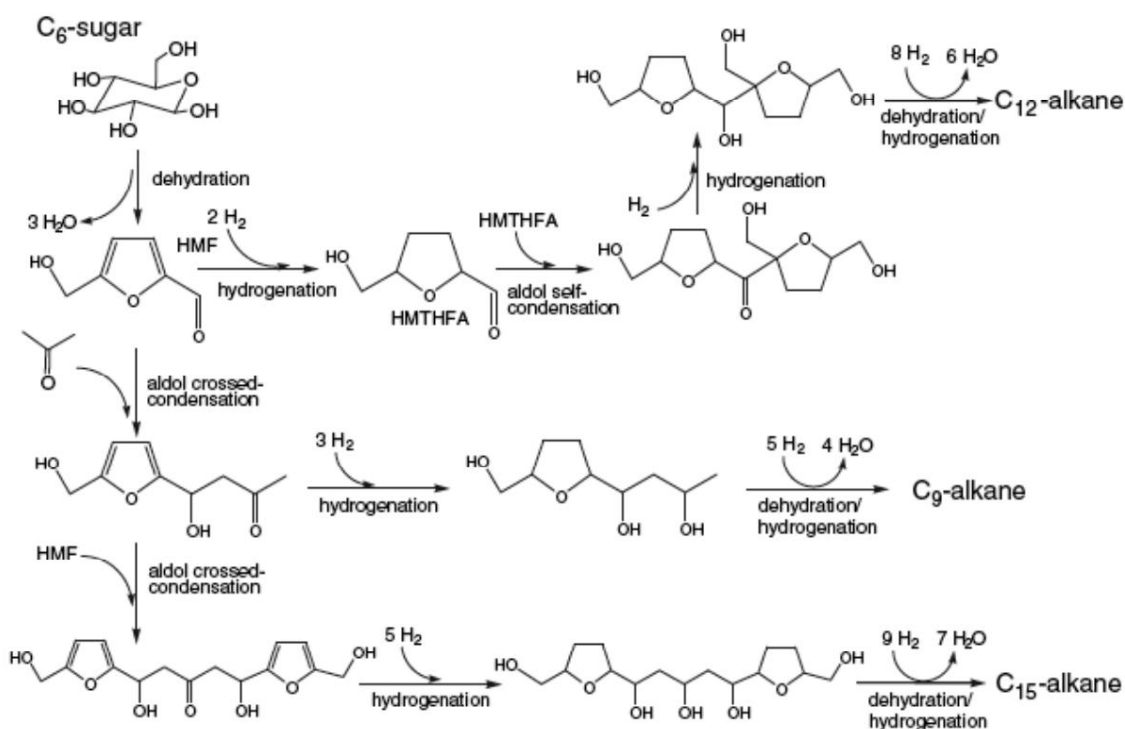


Figure 5-7: Reaction pathways for the production of liquid alkanes from glucose [Huber05]

The reactions that occur are dehydration and hydrogenation reactions. During this reaction, the aqueous organic reactant becomes increasingly hydrophobic. These hydrophobic species are removed from the catalyst with the help of hexadecane, preventing them from further reacting to form coke. In addition to these reactions, basic-catalyzed aldol condensation reactions also take place to form larger organic components. These molecules are then converted into liquid alkanes via dehydration and hydrogenation reactions over bifunctional catalysts.

The process presented in [Huber05] is described in detail here because, on the one hand, it is the only reaction pathway that actually leads to liquid alkanes as products, and on the other hand, it reflects the complexity of such a process for the production of diesel. Pretreatment of the reactants is necessary, and furthermore, the process cannot proceed without the addition of H₂.

5.2.3 SUMMARY – INVESTIGATION OF MODEL SUBSTANCES

Experiments found in the literature to determine reaction pathways in the liquefaction of biomass are generally limited to investigations of individual model substances. Some research groups have determined the intermediate and end products of liquefaction in detail and identified the corresponding reaction pathways. However, the detailed steps presented do not allow for a direct generalization to biomass.

If hydrogen is used in liquefaction to saturate reactive intermediates (e.g., to remove oxygen-containing functional groups) and if a larger number of further processing and purification steps are carried out, it is possible to produce alkanes with specific size distributions in a targeted manner. This is an important prerequisite for the production of standard-compliant liquid fuels.

If no hydrogen is used, the intermediate and final products contain high proportions of ring-shaped components. Further steps are necessary to convert these to straight-chain hydrocarbons. The reaction pathways shown without hydrogen clearly demonstrate that the product range contains a significant proportion of oxygen atoms. The oxygen content in the various components is considerably higher (10-20%) compared to crude oil, resulting, among other things, in a lower calorific value of the product oil. Furthermore, this increased oxygen content means that the resulting oil is highly reactive and prone to decomposition or undesirable subsequent reactions. Further processing (so-called upgrading) is therefore essential.

5.3 PARAMETERS INFLUENCE YIELD

In the field of direct liquefaction of biomass, there are basically two different types of experimental investigations: On the one hand, reaction pathways are investigated (as shown in the preceding section 5.2), and on the other hand, there are studies that determine the yields of gaseous, liquid and solid products as a function of various parameters, without going into the exact material composition of the three resulting phases.

The results of the second group of experimental investigations will be summarized below.

First, differences in experimental methodology and their consequences will be highlighted. Next, the qualitative influences of biomass properties and various chemical and physical parameters on product distributions will be presented. Following this, elemental analyses of the product oil from different research groups will be summarized. Finally, the results of the so-called BLTF project, the most comprehensive systematic experimental study to date on the direct liquefaction of biomass, will be presented.

5.3.1 INFLUENCE OF PROCESSING AND PREPARATION STEPS USED

This section aims to illustrate differences in the methodologies of the various working groups. It will become clear that the product distributions reported in the various publications are only comparable to a very limited extent.

5.3.1.1 DEFINITION OF PROFIT

Generally, yield is defined as the ratio of the product mass to the input biomass. However, in many cases, it is not specified whether the water contained in the biomass is also included in the reference quantity. Different yield values are obtained depending on whether the product mass is related to the anhydrous or moist biomass. In any case, the moisture content of the input biomass should be specified, which is often omitted.

Furthermore, the liquid product yield is sometimes defined incorrectly. [Mun01], for example, assumed that the liquid yield consisted of all material that did not remain as a solid residue after liquefaction. However, this neglects the fact that a significant proportion of the processed biomass passes into the gas phase. Therefore, the data provided by this working group regarding "liquefaction yield" are of limited significance.

As a rule, two liquid phases are formed during liquefaction: a hydrophobic and a hydrophilic phase. Usually, only the mass of the hydrophobic (i.e., oil-rich) phase is used to determine the oil yield. However, sometimes a distinction is made between the two.

No distinction is made between the liquid phases, and the entire mass of the liquid phase is included in the oil yield. This is also not appropriate.

5.3.1.2 TYPE OF REACTOR

Most liquefaction experiments were conducted using autoclaves (isochoric). However, a considerable number of studies have also been carried out using an open Erlenmeyer flask (isobaric). Experiments have also been conducted with a fixed-bed flow reactor. It can be assumed that the reactor type influences the yield. A comparative study on this has not yet been performed.

5.3.1.3 PRESSURE MEASUREMENT

As already mentioned, most investigations were carried out using autoclaves. While volumes and temperatures were generally reported in these cases, the pressure during liquefaction was usually not specified. It is to be expected that heating the reaction mixture would be accompanied by a significant pressure increase (due to the gases and vapors produced). This relationship is illustrated below by measurements from two research groups.

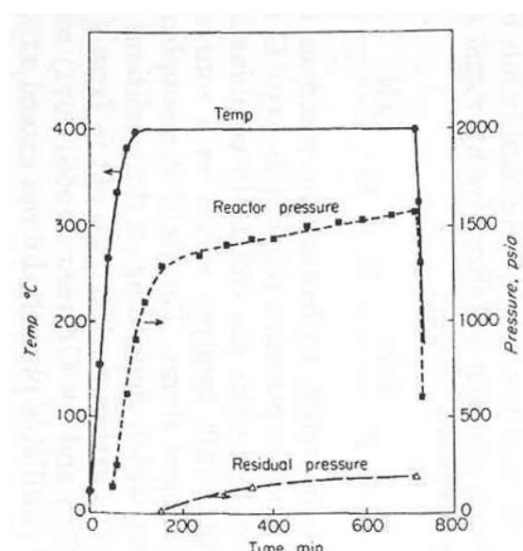


Figure 5-8: Pressure profile during liquefaction in an autoclave [Connors80]

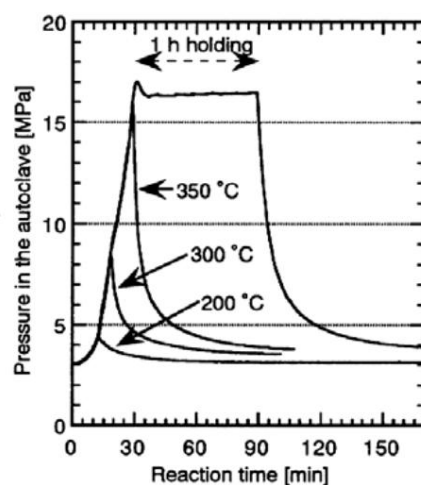


Figure 5-9: Pressure profile during liquefaction in an autoclave [Minowa97]

Naturally, the pressure during liquefaction affects the yield. Without information on the pressure, the results cannot be compared with other studies.

5.3.1.4 PRODUCT REPROCESSING

Another significant methodological difference between the work of various authors lies in the treatment of the product mixture. This mixture can contain—in addition to the desired liquid product (hereinafter referred to as "product oil")—other components: residues of the unreacted solvent, the (usually liquid) catalyst, solid residue (which can, in principle, consist of unreacted solid biomass or repolymerization product), and possibly a second liquid (usually water-rich) phase. The desired product oil must be separated from the other components. This separation can be achieved in a variety of ways. The techniques employed encompass the entire spectrum of process engineering treatment steps: filtration, extraction (with various extraction solvents), sedimentation, or distillation. Each research group uses its own method for separating the product mixture. To illustrate this, a representative selection of eight product treatment flow diagrams is presented below (Figures 5-10 to 5-17).

A clean separation of the product mixture components is impossible with the separation operations employed. Parts of the product oil will also be present in all other phases. Conversely, the separated product oil will also contain traces of the remaining components. Often, for example, the product oil still contains significant amounts of the solvent used. The total amount of contaminants in the product oil cannot be readily estimated. Furthermore, these amounts will vary from process to process.

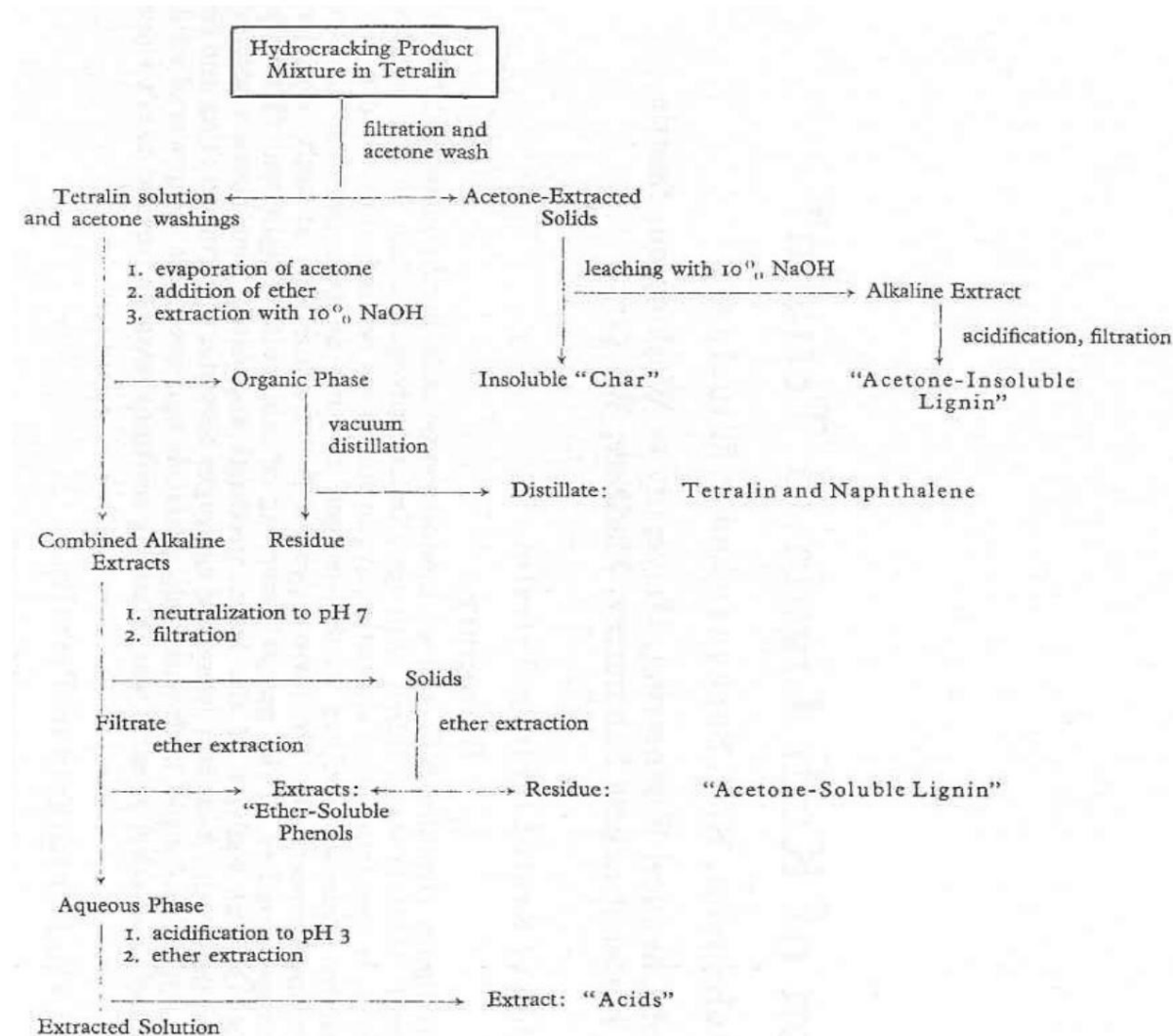


Figure 5-10: Preparation of the product mixture [Connors80]

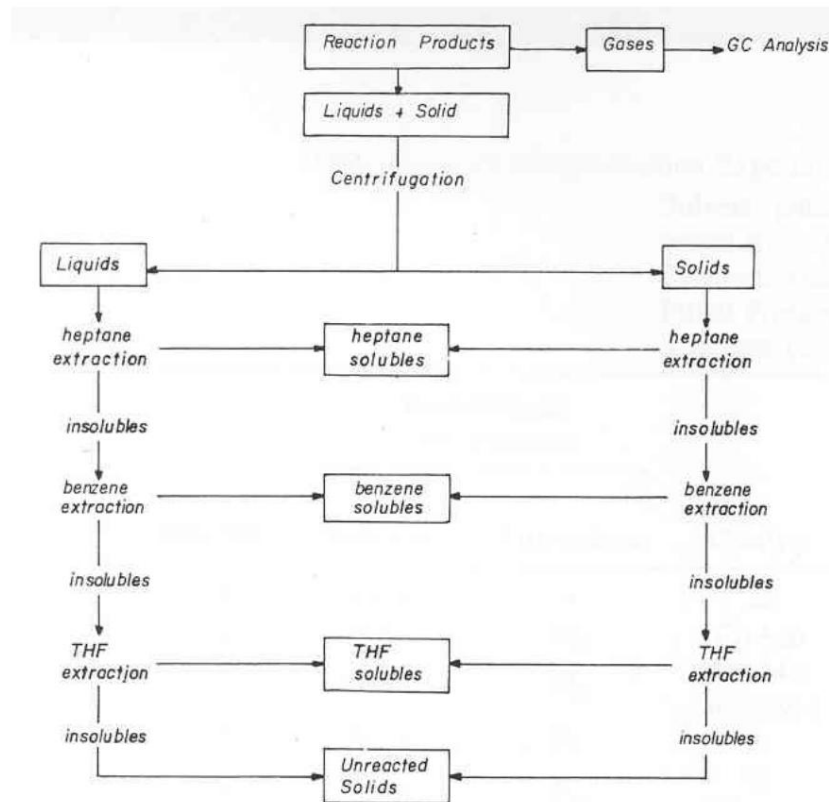


Figure 5-11: Preparation of the product mixture [Araya86]

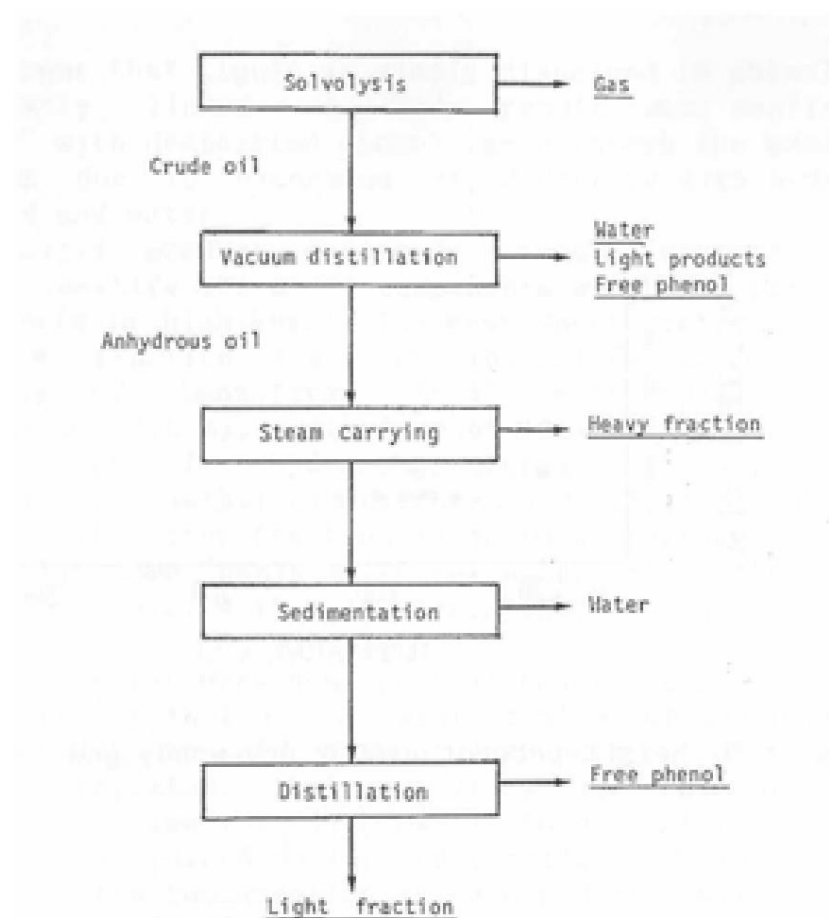


Figure 5-12: Preparation of the product mixture [Bouvier88b]

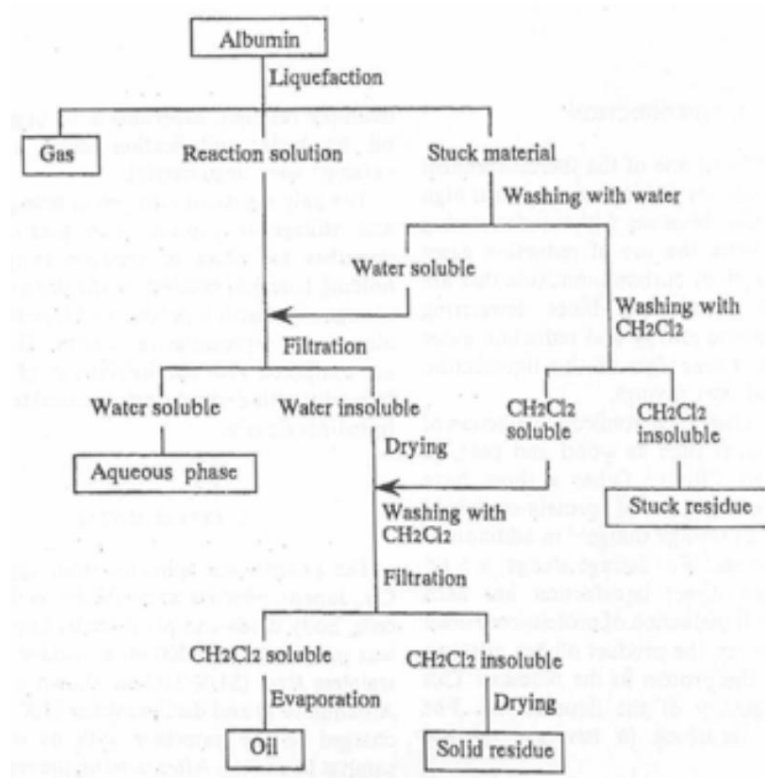


Figure 5-13: Preparation of the product mixture [Dote96]

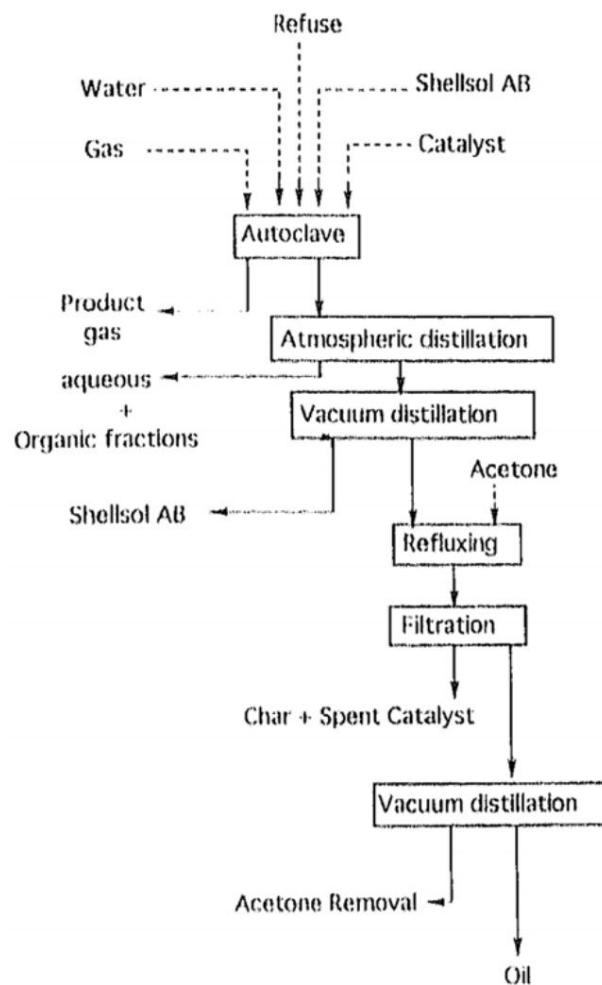


Figure 5-14: Preparation of the product mixture [El-Gayar97]

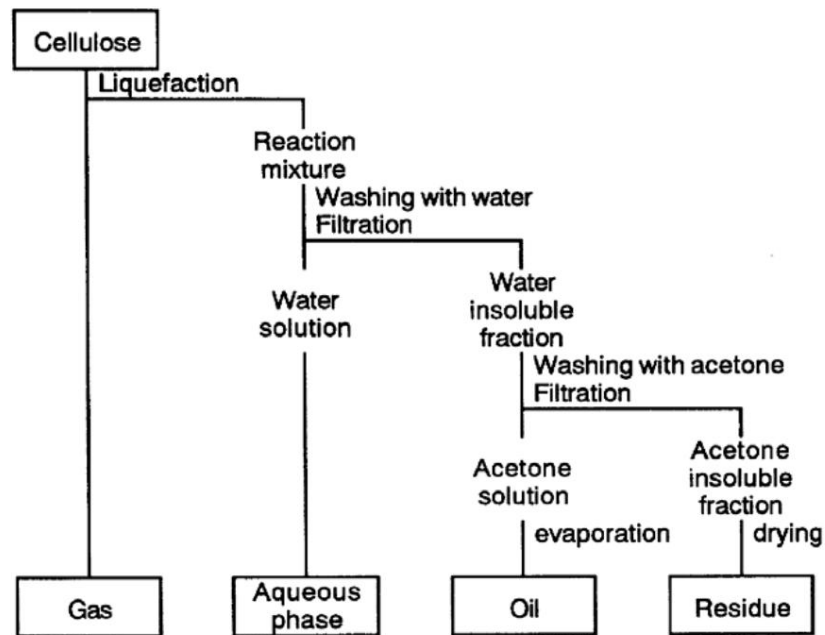


Figure 5-15: Preparation of the product mixture [Minowa97]

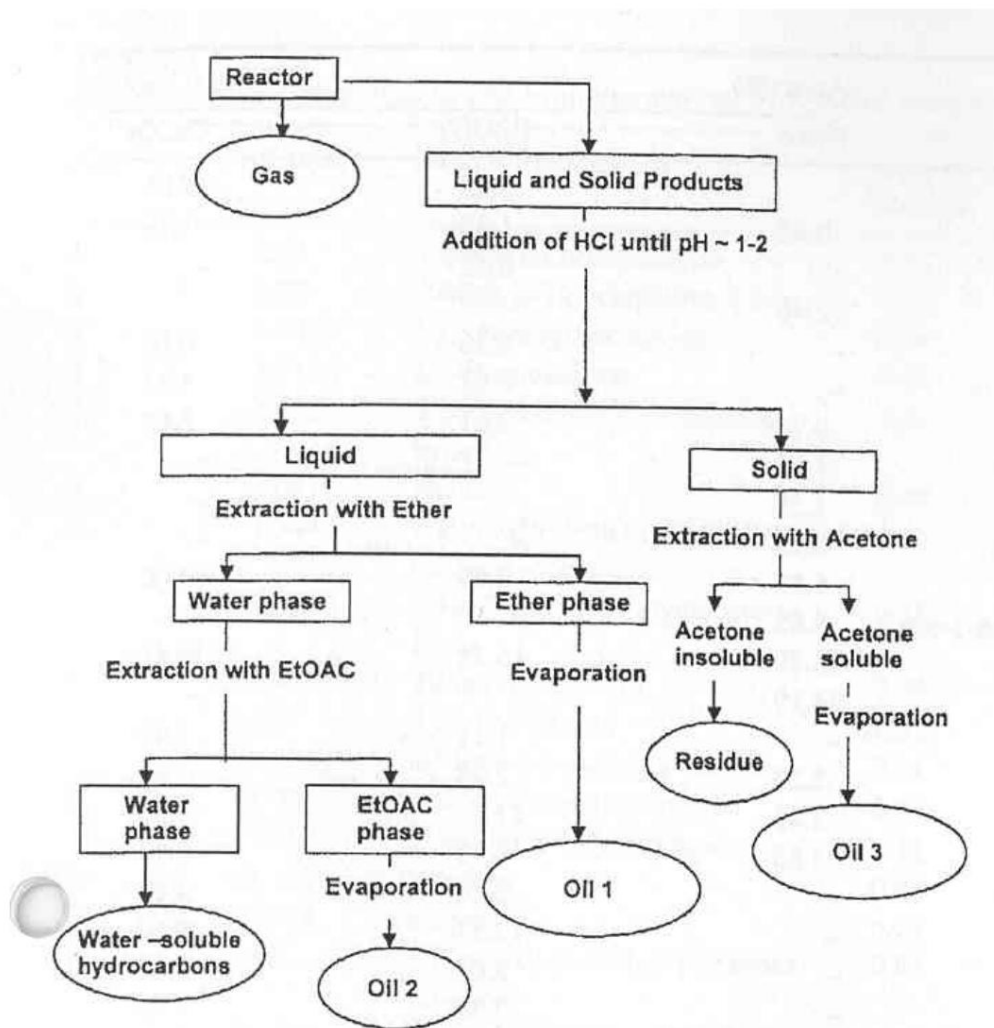


Figure 5-16: Preparation of the product mixture [Karagöz04]

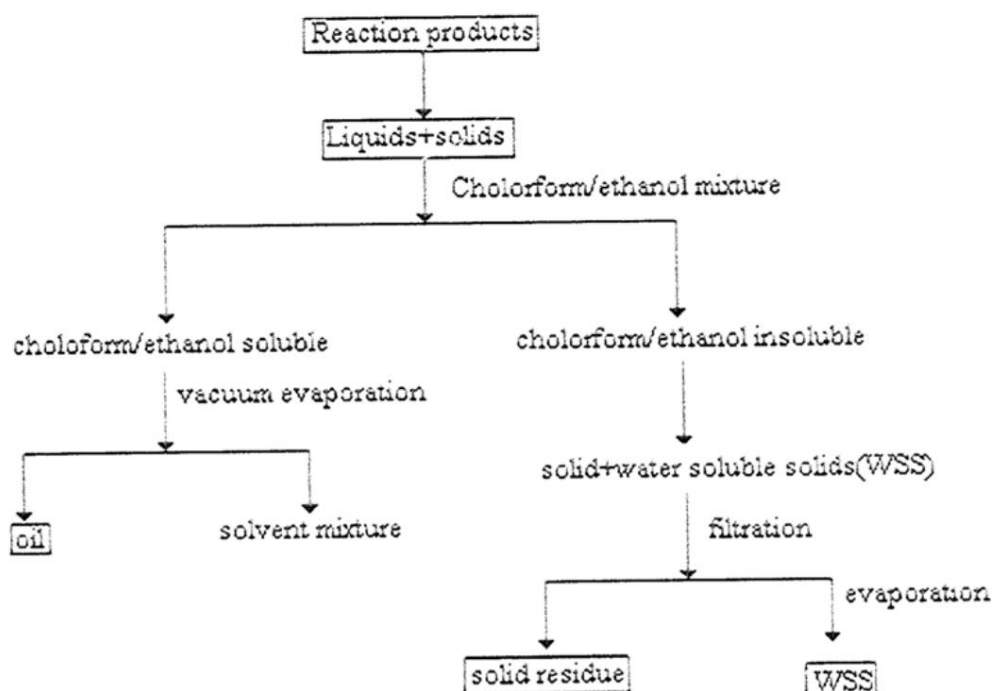


Figure 5-17: Preparation of the product mixture [Yilgin04]

5.3.1.5 CONCLUSION ON THE PROCESSING AND PREPARATION STEPS

The differences in the methodology of the experiments carried out, as described in the preceding sections, lead to the conclusion that a meaningful quantitative comparison of the stated yields of product oil is only possible in the rarest of cases, namely when the methodology largely agrees.

5.3.2 INFLUENCE OF CHEMICAL PARAMETERS

For the reasons already mentioned and because of the large number of relevant parameters, making general quantitative statements regarding expected yields is virtually impossible.

The research results can only be evaluated with regard to qualitative relationships, which will be done in the following sections. In the following figures, LM/B indicates the mass ratio of solvent to biomass at the beginning of the reaction.

5.3.2.1 COMPOSITION OF BIOMASS

The different types of biomass differ primarily in their proportions of cellulose, hemicellulose, and lignin. Two research groups independently investigated the influence of lignin content in biomass on product distribution.

Experimentally determined reaction pathways

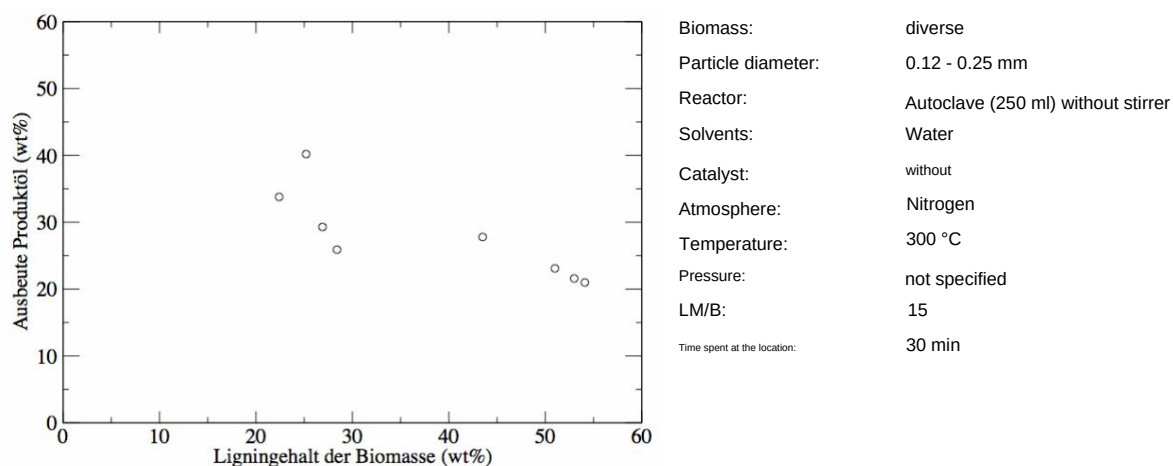


Figure 5-18: Influence of the lignin content of the biomass on the oil yield [Demirbas00]

These results suggest that a low lignin content is advantageous for liquefaction.

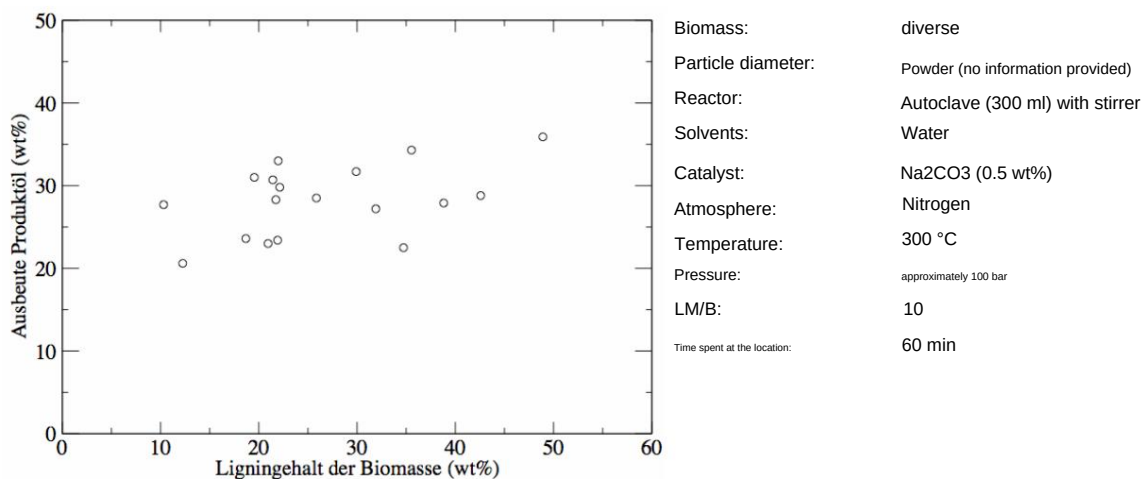


Figure 5-19: Influence of the lignin content of the biomass on the oil yield [Minowa98]

These results do not confirm the findings of [Demirbas00]. One reason for this could be that [Minowa98] distinguished between a water-rich and an oil-rich phase, while Demirbas only obtained a liquid phase and declared this as product oil. Furthermore, Demirbas treated the biomass with an alcohol-benzene mixture before liquefaction (without providing reasons).

Therefore, based on the available results, it is not possible to say to what extent the composition of the biomass affects the oil yield.

5.3.2.2 SOLVENTS

Naturally, the solvent has a decisive influence on the liquid yield. Several studies have tested various solvents. The most comprehensive investigation on this topic was carried out by [Mun04b]. In this study, 5.5 g of the substances listed in Figure 5-20 were added to 1 g of phenol and 1 ml of water. This ternary mixture served as the solvent.

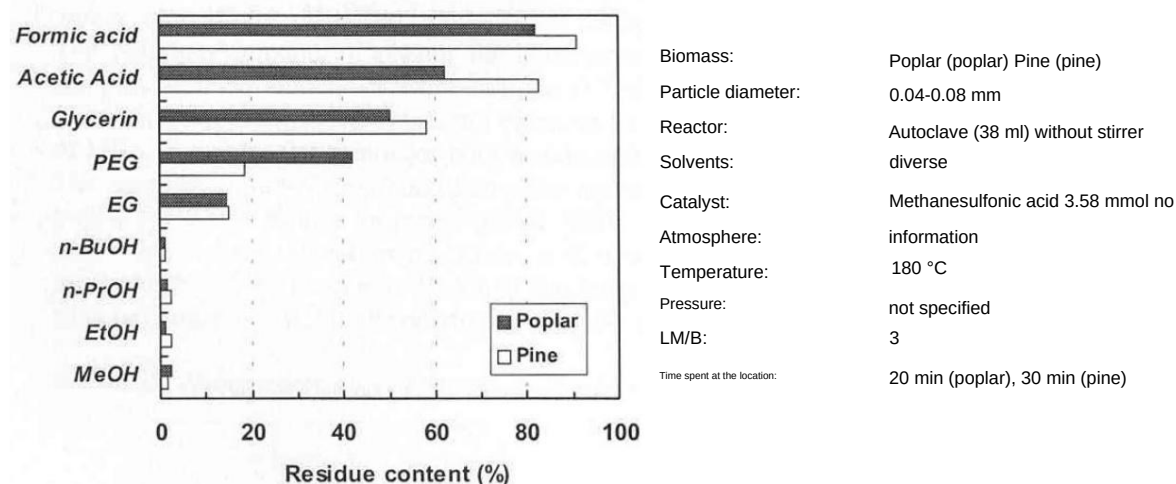


Figure 5-20: Proportions of solid residue in the product mixture when using different solvents [Mun04b]

The smallest residues appear to occur when simple alcohols are added. However, the disadvantage of simple alcohols is their relatively low boiling points. Polyalcohols and organic acids have higher boiling points, but are less effective solvents.

A similar study was conducted by [Krzan05]. The chestnut wood used was previously extracted with tannin, and only the residue was used for liquefaction. Propylene glycol (PG), ethylene glycol (EG), and diethylene glycol (DEG) were used as solvents.

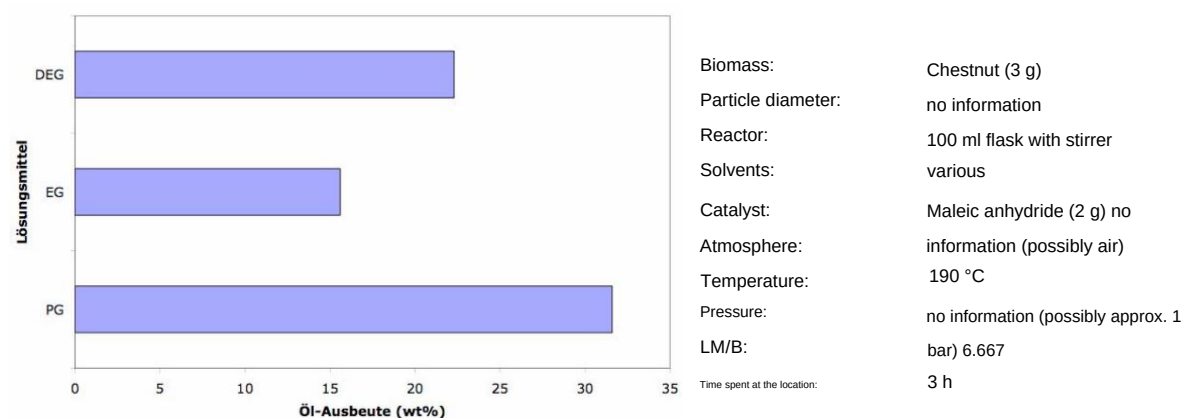


Figure 5-21: Oil yields when using three different polyalcohols as solvents [Krzan05]

Although the three substances used are quite similar, the oil yields differ considerably.

5.3.2.3 CATALYTIC CONVERTER

[Araya86] tested various metals as catalysts, which they dispersed in the reaction mixture. The diagram below shows that the metals used exhibit practically no catalytic effect with regard to liquefaction. Raney nickel, known as a hydrogenation catalyst, accelerates gas production but even has a negative effect on liquefaction. Presumably, Raney nickel primarily hydrogenates the already liquefied components to gaseous substances.

Experimentally determined reaction pathways

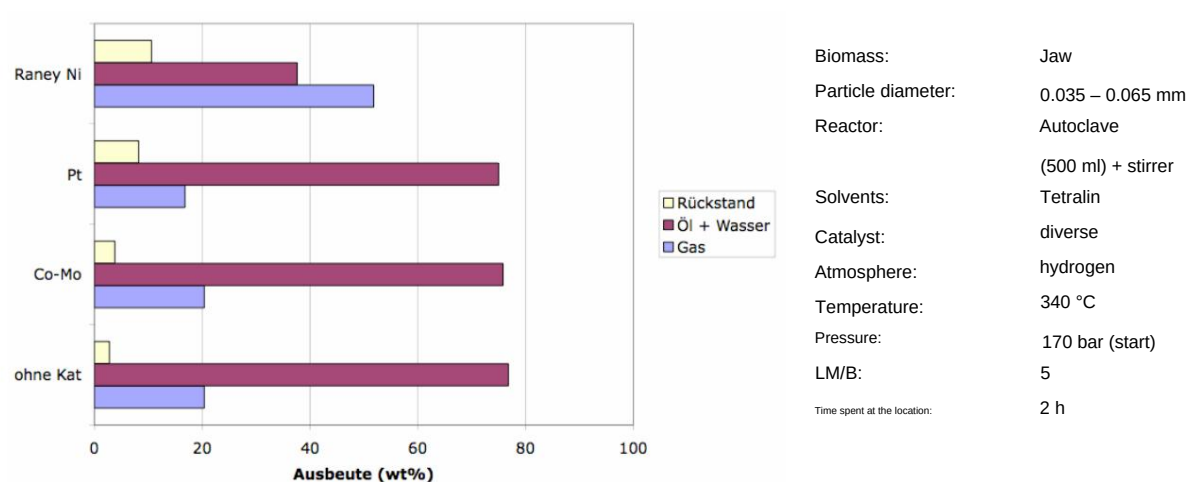


Figure 5-22: Yields when using different metallic catalysts [Araya86]

Similar results were obtained by [El-Gayar97], who tested Raney nickel, another nickel-based catalyst (Harshaw), and nickel olate dissolved in xylene as catalysts.

The results can be seen in Figure 5-23 .

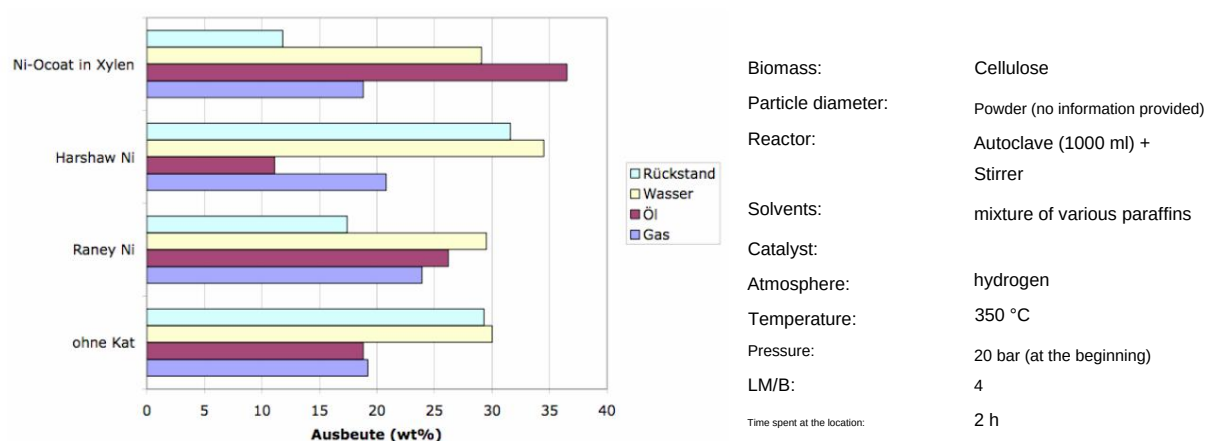


Figure 5-23: Yields when using different nickel-containing catalysts [El-Gayar97]

It is noteworthy that the homogeneous catalyst (Ni olate) achieves significantly better liquefaction results compared to the two heterogeneous catalysts. It can be assumed that solid catalyst particles penetrate the biomass less effectively than homogeneous catalyst substances. Therefore, the latter should be more successful at depolymerizing the biomass. Consequently, the following discussion will focus on homogeneous catalysts.

Most studies used either alkalis or acids as catalysts. Unfortunately, only [Funazukuri90] conducted a direct comparison, which was inadequately documented.

Both the acid and the base exhibit catalytic activity. The fact that the difference compared to the experiment without a catalyst is so small is most likely due to the relatively short residence time. However, this single study does not provide a definitive answer as to whether bases or acids are generally better liquefaction catalysts.

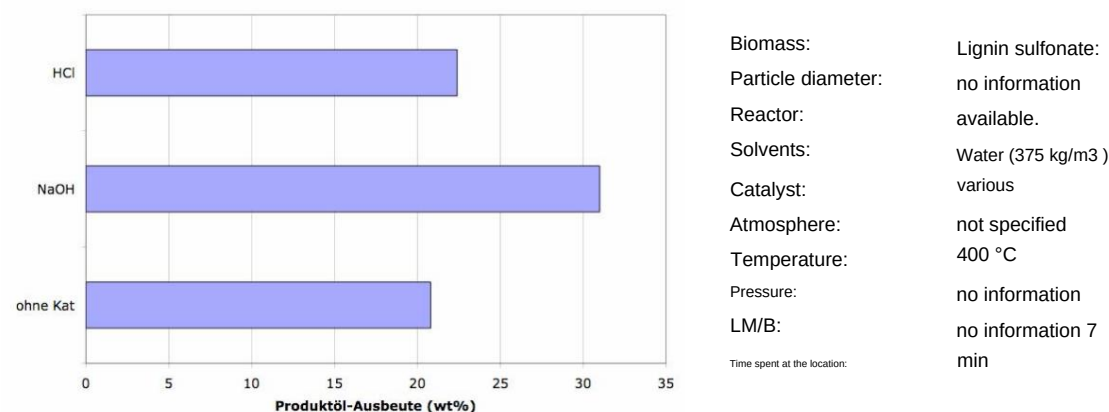


Figure 5-24: Oil yields when using different homogeneous catalysts [Funazukuri90]

[Mun04a] compared the catalytic activity of various acids. These were sulfuric acid (SA), hydrochloric acid (HCl), methanesulfonic acid (MSA), p-toluenesulfonic acid (PTSA), naphthalenesulfonic acid (NSA) and phosphoric acid (PA), all of which were presented at the same concentration.

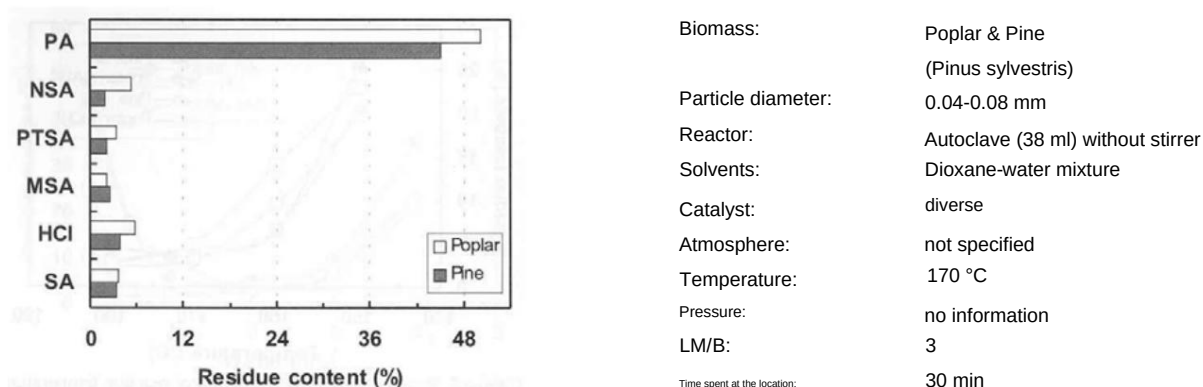


Figure 5-25: Proportions of solid residue in the product mixture when using different acids as Catalysts [Mun04a]

Organic acids (MSA, PTSA, NSA) tend to lead to lower proportions of solid residues than mineral acids (SA, HCl and PA), with phosphoric acid in particular leading to significant amounts of solid residues and therefore being unsuitable as a catalyst.

[Alma98] tested a number of salts for their catalytic activity. It was found that at 250°C none of the salts used produced less residue than sodium hydroxide, as shown in the diagram below.

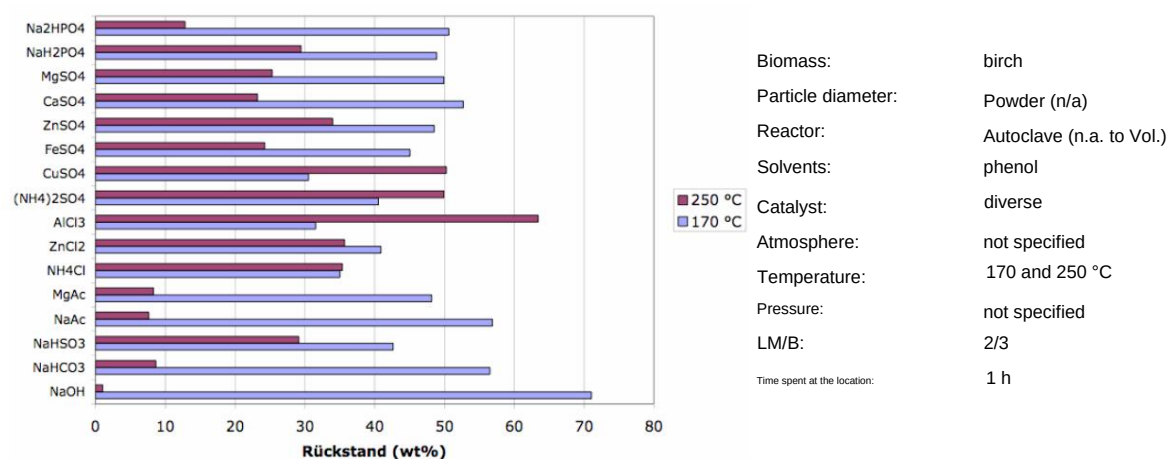


Figure 5-26: Proportions of solid residue in the product mixture when using different salts as Catalysts [Alma98]

5.3.2.4 ATMOSPHERE

Three different research groups [Araya86, Vuori88a, El-Gayar97] compared yields under nitrogen and hydrogen atmospheres. The results are summarized below.

There is no universally valid answer to the question of whether an inert or reducing atmosphere is advantageous for liquefaction. The reducing capacity of the atmosphere appears to be less important than the reducing capacity of the solvent or the catalyst.

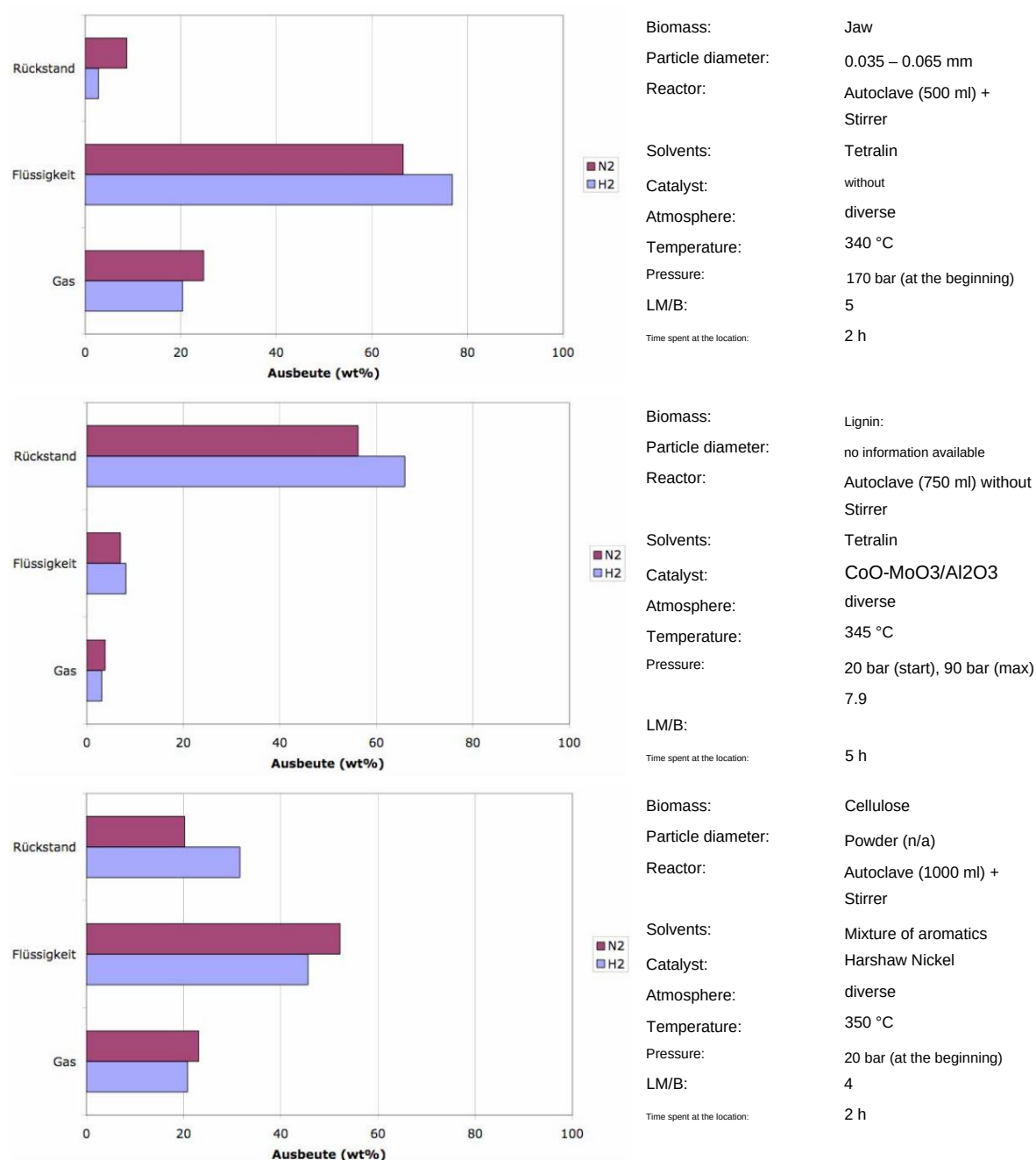


Figure 5-27: Yields under different atmospheres [Araya86, Vuori88a, El-Gayar97] (from top to bottom)

5.3.3 INFLUENCE OF PHYSICAL PARAMETERS

5.3.3.1 TEMPERATURE

The temperature dependence of liquefaction results has been investigated by several research groups. A common pattern emerges, which is illustrated by the following diagram summarizing results from studies by five different authors.

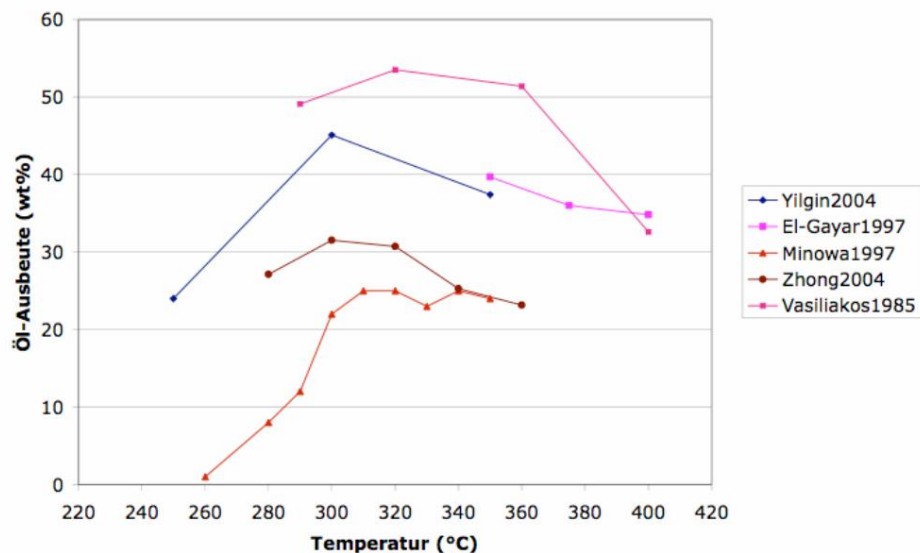


Figure 5-28: Oil yield as a function of temperature

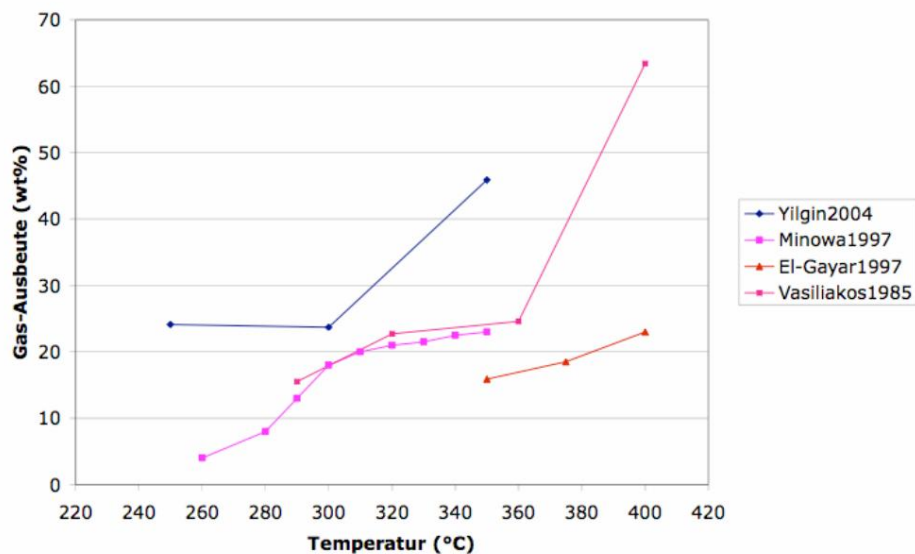


Figure 5-29: Gas yield as a function of temperature

Despite the fact that the four presented measurement series were obtained with widely varying parameters, it is clear that the oil yield does not increase monotonically with rising temperature, but rather reaches a maximum at temperatures between 290 and 330°C. The fact that the oil yield decreases at even higher temperatures is presumably due to the gasification of liquid components, which is dominant under these conditions. In four of the five studies mentioned, gas yields were also measured in addition to the oil yields. These results can be found in Figure 5-29.

5.3.3.2 PRINT

Very few research groups have investigated the pressure dependence of liquefaction.

In general, it can be stated that higher pressure should lead to a greater oil yield, as the vaporization of liquid components is suppressed. This relationship has also been experimentally confirmed, as shown in Figure 5-30.

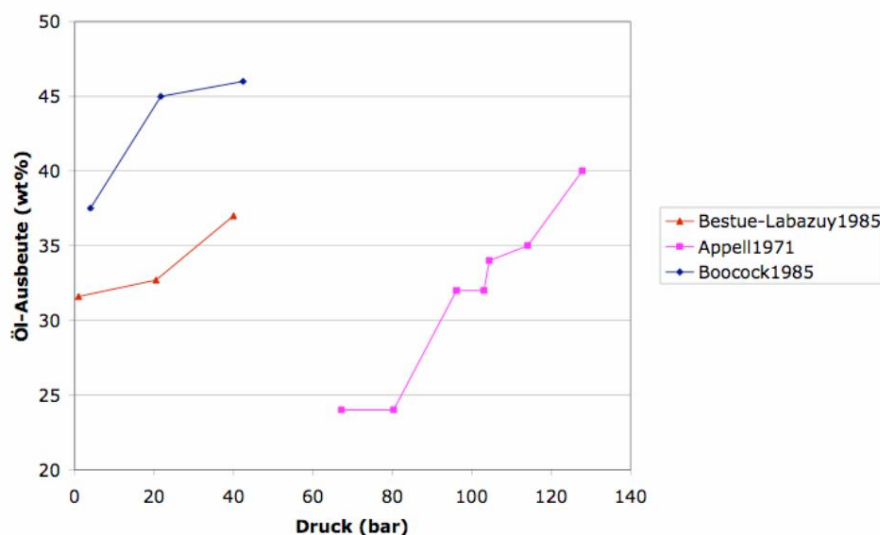


Figure 5-30: Oil yield as a function of pressure

5.3.3.3 SOLVENT : BIOMASS MIXTURE RATIO

Unfortunately, most research groups have only investigated the effects of this parameter on the liquefaction results with regard to the residue. It was generally found (except in [Maldas97]) that the residue decreases with increasing solvent/biomass mass ratio (see Figure 5-31).

The more solvent is available, the more monomers can dissolve in the liquid phase. Against this background, it seems plausible that the residue decreases (asymptotically) with increasing solvent concentration. In [Maldas97], no interpretation is given for the finding, which contradicts the other results and which they observed in several experimental series. A plausible explanation cannot be provided here either.

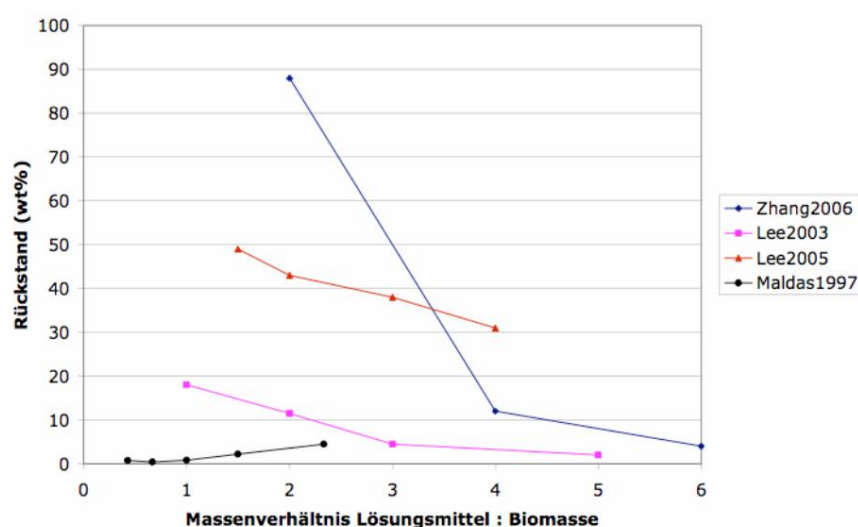


Figure 5-31: Proportion of solid residue in the product mixture as a function of the mass ratio Solvent/Biomass

[Boocock85] was the only research group to determine the oil and gas yield as a function of the solvent/biomass mass ratio. Their results were as follows:

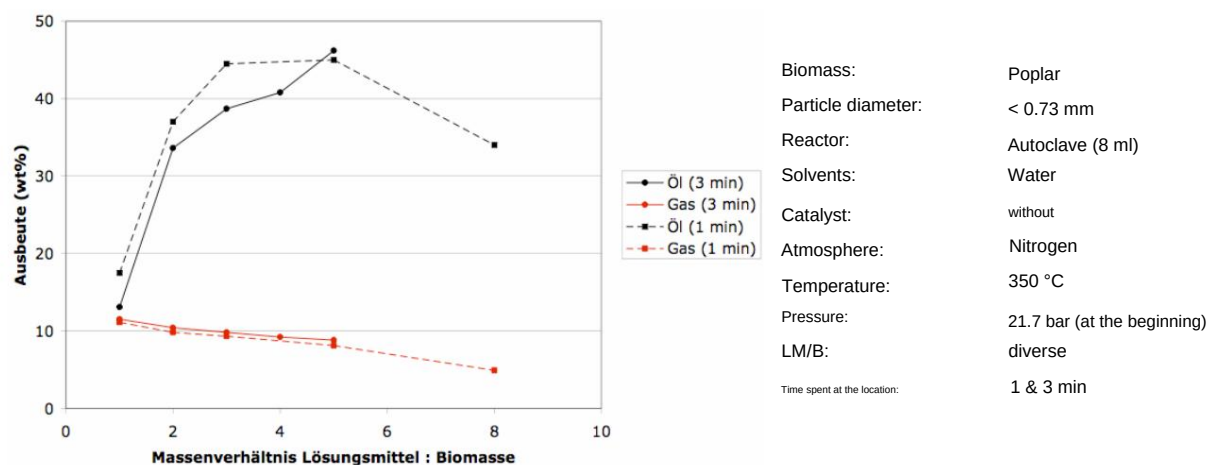


Figure 5-32: Oil and gas yields as a function of the solvent/biomass mass ratio

[Boocock85]

Due to the limited solubility of the monomers, the oil yield is expected to increase with increasing solvent concentration and then decrease asymptotically. Why, after a residence time of one minute, does the yield decrease again with increasing solvent concentration after reaching a maximum?

The decrease cannot be explained. Interestingly, the gas yield decreases with increasing solvent content.

5.3.3.4 HOMOGENEITY OF THE MIXTURE

[Boocock85] compared oil and gas yields for continuously dispersed and stationary reaction mixtures. As expected, a more homogeneous reaction mixture is advantageous, as illustrated by the following figure.

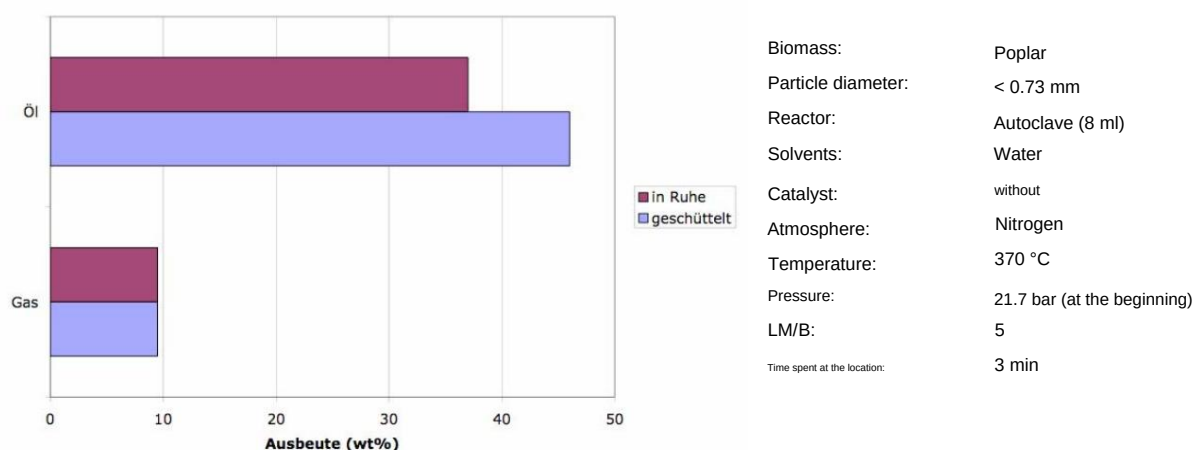


Figure 5-33: Oil and gas yields with stationary and shaken reaction vessel [Boocock85]

5.3.3.5 CATALYTIC CONCENTRATION

Section 5.3.2.3 showed that it is advantageous to use homogeneous rather than heterogeneous catalysts. These homogeneous catalysts can now be introduced in different concentrations (mass of catalyst relative to mass of solvent). The dependence of the residue on the catalyst concentration was investigated by [Maldas96b] and [Mun01,

Mun04a] was investigated in several experimental series. The same qualitative relationships were consistently observed. Two representative measurement series are shown in the following diagram.

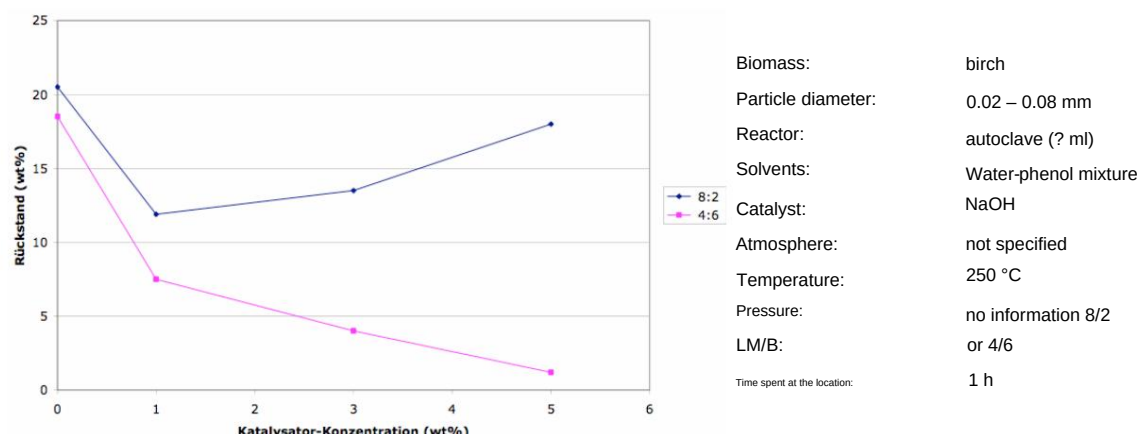


Figure 5-34: Influence of catalyst concentration on the mass fraction of solid residue in the Product mixture [Maldas96b]

It was observed that the residue either decreases monotonically with increasing catalyst concentration or passes through a minimum. It is quite possible that the observed monotonic curves also pass through a minimum with further increasing catalyst concentration. It would be interesting to investigate the catalyst/biomass ratio, rather than the catalyst/solvent ratio, as an independent parameter, since the latter is more relevant for liquefaction. Unfortunately, the data provided by Maldas and Shiraishi, as well as by Mun et al., are not detailed enough to allow for such a conversion.

A qualitative confirmation of the results presented above is provided by the work of [Ogi85], who determined the oil yield as a function of the catalyst concentration, as shown below.

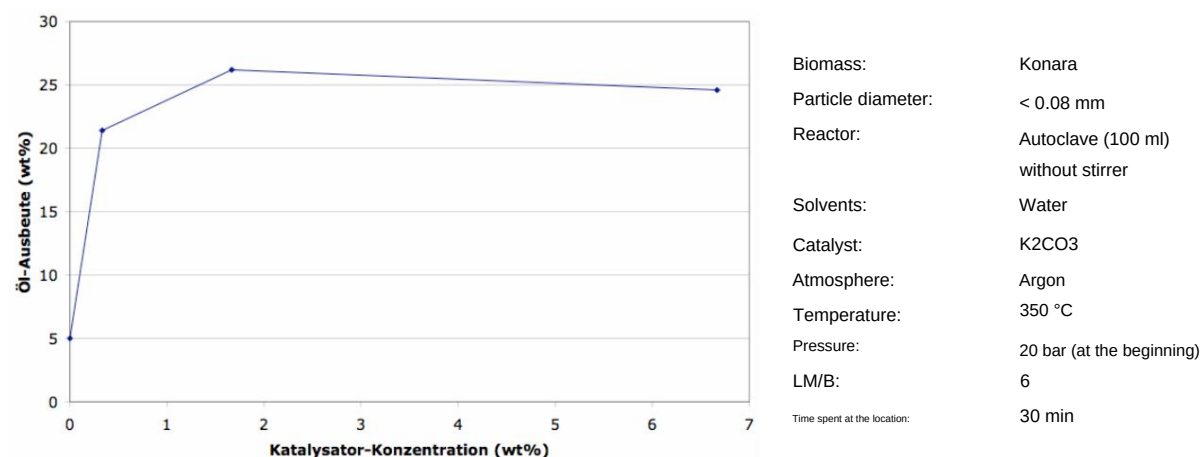


Figure 5-35: Influence of catalyst concentration on oil yield [Ogi85]

It appears that above a certain optimal catalyst concentration, the repolymerization of the monomers proceeds faster than the depolymerization of the solid phase.

5.3.3.6 DISTANCE TIME

The dependence of liquefaction yields on residence time has been investigated by several research groups. The results show qualitatively the same relationship as in the case of catalyst concentration. The results of [Yilgin04] are representative of all results obtained and are presented below.

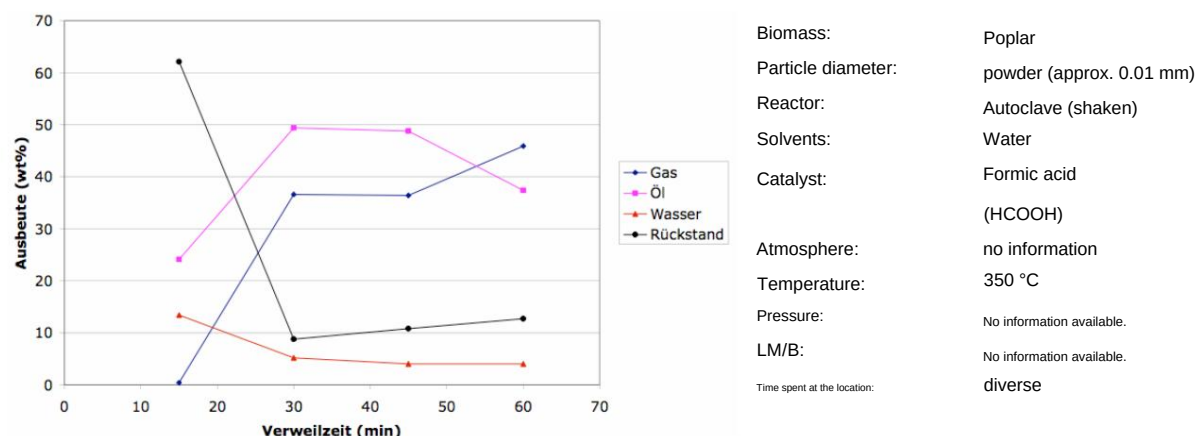


Figure 5-36: Influence of residence time on yield [Yilgin04]

The oil yield reaches a maximum. The fact that it does not increase monotonically is due, firstly, to the repolymerization of monomers formed and, secondly, to the further decomposition of the liquid components into gaseous substances. Therefore, the gas yield increases continuously with the residence time. The proportion of unreacted biomass should decrease steadily with the residence time. However, the observation that the residue increases again after a minimum is due to the fact that no distinction is made between solid repolymerization product on the one hand and unreacted biomass on the other. Both components are subsumed under the term "residue." After a certain residence time, more substance is repolymerized than depolymerized, which in total leads to an increase in the solid residue.

These fundamental qualitative relationships are found in almost all publications on liquefaction. In cases where the oil yield does not reach a maximum or the residue does not reach a minimum, it can be assumed that the necessary residence time has not yet been reached.

5.3.4 SUMMARY – YIELD PARAMETERS INFLUENCED

The expected yields from direct liquefaction depend on various physical parameters. Qualitatively, higher product oil yields can be expected at higher pressures, a larger mass ratio of solvent to biomass, and the best possible homogeneity of the reaction mixture. Optimal values for temperature, residence time, and concentration of the homogeneous catalyst must be determined experimentally.

The influence of chemical parameters is less clear. Whether the proportions of cellulose, hemicellulose, and lignin in the biomass used have a significant impact on the yield cannot be determined at present due to conflicting results in the literature. The solvent used also influences the yield, but here, too, no definitive statement can be made as to which solvents are generally best suited for direct liquefaction. Regarding the catalysts used, homogeneous catalysis allows for higher product oil yields than heterogeneous catalysis. The use of acidic or basic catalysts has no clear influence on the yield. Furthermore, no consistent trend in yield was observed when using a reducing (hydrogen or carbon monoxide) or non-reducing (nitrogen) atmosphere in the reaction vessel. However, the type of atmosphere does have a clear influence on the oxygen content of the product oil.

Typically, product oil yields range from 35 to 55% by mass (based on the biomass used).

5.4 COMPOSITION OF THE PRODUCT OIL

Several research groups have analyzed the elemental composition of the product oil. These results are interesting because a key objective of liquefaction is the removal of oxygen from the biomass. Figure 5-37 shows the mass ratios in the product oils in the same way as Pier did for coal liquefaction. Representative data for wood and gasoline are also included for comparison.

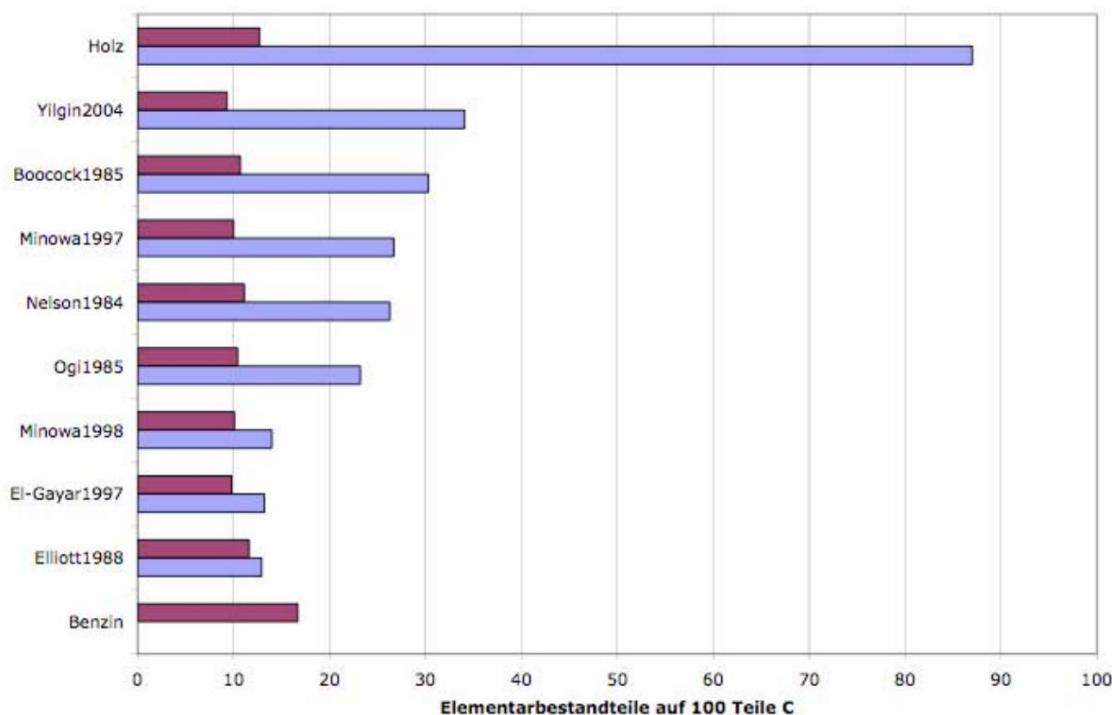


Figure 5-37: Results of the elemental analysis of product oils from different working groups

In summary, it can be stated that the oxygen content is reduced by a (single-stage) Direct liquefaction can significantly reduce the oxygen content compared to the starting material, but according to a review of the literature, it does not appear possible to reduce the oxygen content in a single process step to such an extent that a diesel fuel-like mixture of hydrocarbons is obtained, regardless of whether hydrogen is present in the atmosphere. While liquefaction does considerably reduce the oxygen content compared to wood, the mass ratio of oxygen to carbon in the product oil is still at least 1:10.

5.5 THE BLTF PROJECT

The largest project to date for the systematic experimental investigation of biomass liquefaction was conducted in the early 1980s by four members of the International Energy Agency (IEA): Canada, Sweden, Finland, and the United States. Under the project name "Biomass Liquefaction Test Facility" (BLTF), various liquefaction processes were investigated. The six participating laboratories used identical starting material (Canadian poplar wood, HHV: 27.8 MJ/kg, oxygen content: 23.7 wt%). An overview of the investigated processes can be found in the following table.

All product mixtures were analyzed in a single laboratory, which greatly facilitates, indeed makes possible, the comparability of the results. Analysis of the product mixtures revealed oil yields ranging from 38 to 53 wt% (based on the biomass used). The calorific values of the product oils range from 29 to 36 MJ/kg. The oxygen content of the product oils ranged from 9 to 25 wt% [Beckmann85].

Table 5-1: Overview of the liquefaction processes used in the BLTF project [Beckmann85]

Laboratory	Process	Feed	Reaction conditions				Reactor type
			Temp. (°C)	Press. (MPa)	Catalyst	Gas	
University of Saskatchewan, Saskatoon, Canada	Liquefaction via screw-feeding	Wood fibres	360	28	Na ₂ CO ₃	CO or N ₂	Screw-fed tubular
University of Sherbrooke, Sherbrooke, Canada	Liquefaction via solvolysis	Wood powder	330	8.3	None	H ₂	Tubular
University of Toronto, Toronto, Canada	Wood liquefaction	Wood powder	350	20.7	NiCO ₃	H ₂ or N ₂	CSTR
University of Toronto, Toronto, Canada	Aqueous phase liquefaction	Wood sticks	350	24	None	N ₂ flush	Tubular (batch)
Biomass Liquefaction Experimental Facility Albany, U.S.A.	Wood liquefaction in a recycle oil (PERC)	Wood powder	340	20	Na ₂ CO ₃	CO/H ₂	Tubular
Lawrence Berkeley Laboratories, Berkeley U.S.A.	Liquefaction via acid pretreatment	Wood powder	350	22	Na ₂ CO ₃	CO or CO/H ₂	CSTR
British Columbia Research, Vancouver, Canada	Supercritical extraction	Wood chips	360	10 to 28	None	Supercritical acetone	Fixed bed

6 CURRENT LOGGING METHODS

6.1 INTRODUCTION AND OVERVIEW

The following is an overview of the approaches currently known in Germany for the liquefaction of various feedstocks. The process parameters are sometimes not disclosed by the process providers, so this compilation is incomplete (Table 6-1).

The data are supplemented with relevant information on several internationally known processes and described in detail. In Finland, Sweden, and several other European countries, as well as in the USA and Canada, a number of research activities in the field of biomass liquefaction have already taken place.

Work in the USA dates back to the late 1960s (Bruceton, PA, US Bureau of Mines [Appeal 71]). Based on this work, the predecessor organization of the Department of Energy, ERDA, commissioned a large pilot development unit (PDU) for biomass liquefaction in Albany, OR, in 1974. Its operation had to be discontinued in the 1980s for economic reasons. Because the research facility in Bruceton, PA, was called the Pittsburgh Energy Research Center (PERC) at that time, this process became known as the PERC process (see Section 6.3.1). By the end of the 1970s, this pilot plant was still not fully operational, as some of the intended process components were still not functioning as designed. The Lawrence Berkeley Laboratory, CA, proposed an alternative process at that time (LBL process, see section 6.3.2) [Schaleger82], which enabled the first significant quantities of oil to be extracted from wood in 1979.

The following two figures compare historical and current methods for direct liquefaction. In Figure 6-1, the methods are sorted according to the reaction conditions used, while in Figure 6-2, the institutions or working groups behind the respective methods are named.

Current methods for liquefaction

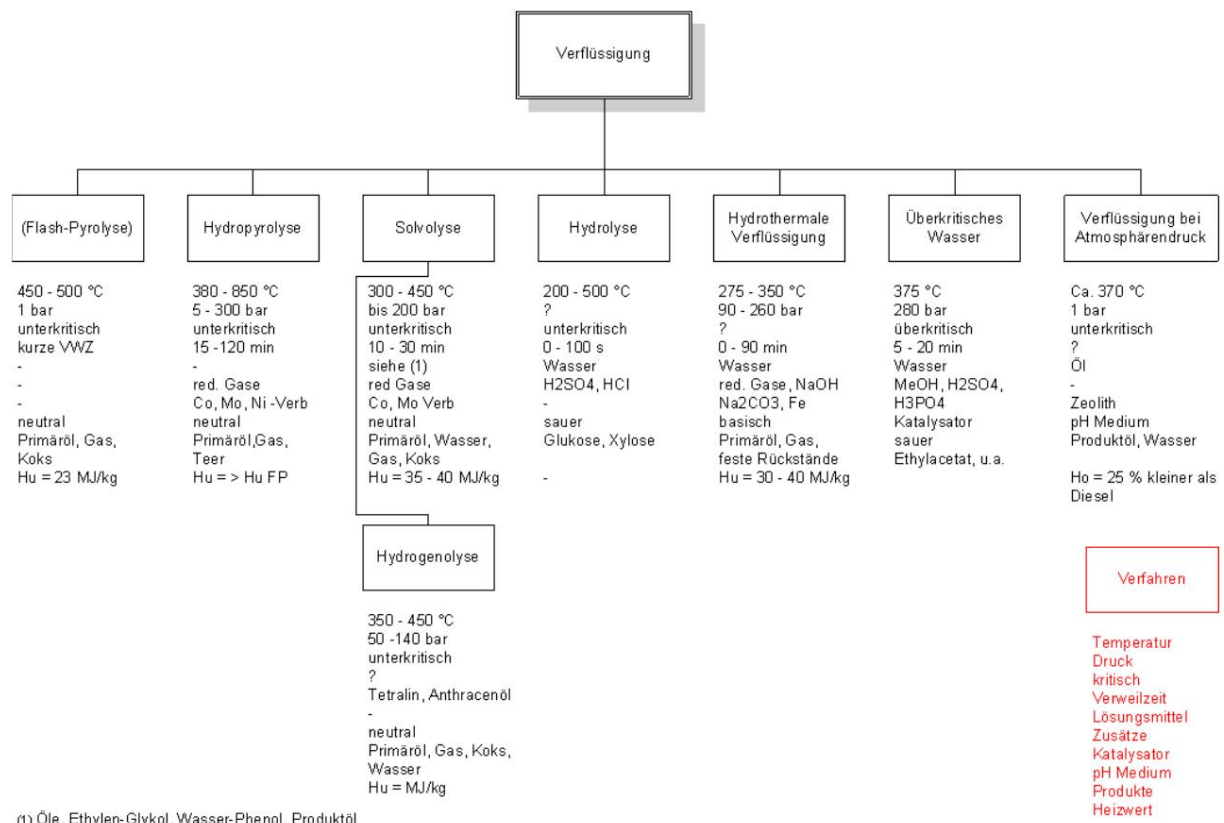


Figure 6-1: Classification of liquefaction processes - reaction conditions

Although flash pyrolysis is not strictly one of the direct liquefaction processes included in this study, it is presented for comparison purposes. Some of the direct liquefaction processes show significantly better results with plastics than with biomass.

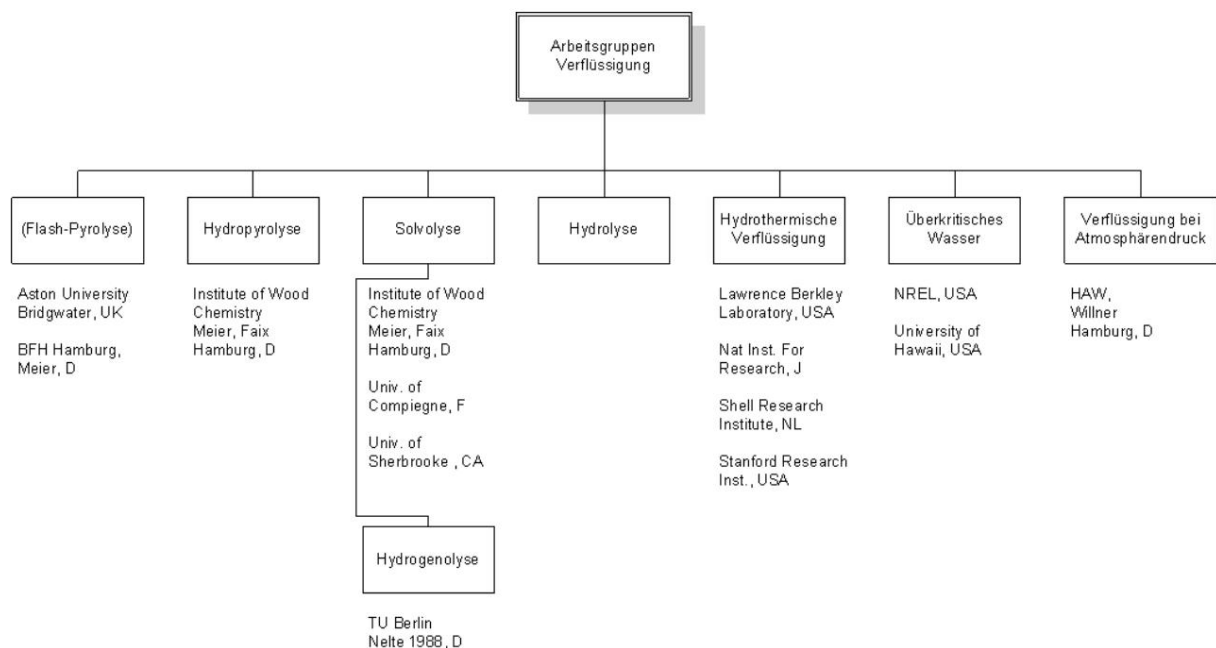


Figure 6-2: Classification of liquefaction processes - working groups

Current methods for liquefaction

The following sections describe in more detail the processes listed in Table 6-1 and discuss and evaluate the reaction conditions and the results obtained (where published). The information on the products, their quality, and quantity is based on data provided by the process owners.

Table 6-1: Process providers for the liquefaction of plant and animal biomass, plastics, and waste oils

MATERIAL SUPPLIERS		PROCEDURE- DESIGNATION	T/°C	P/BAR	H ₂	CAT. REMARK
Plant Biomass	FZK, Future energy, Lurgi AG, D	Bioliq- Proceedings	1200	80	no	No, two-stage.
	Pytec GmbH, Bulkau, D	BtO procedure 475		30-50	no	no Ablative Flash pyrolysis
	Pittsburgh Energy Research Center, USA	PERC process	330-370	200	Yes	Yes Recycled oil H ₂ supplier, Na ₂ CO ₃
	Lawrence Berkeley Laboratory, CA	LBL process	330-360	170-240	yes	Yes CO/ H ₂ Alkali carbonates
	Shell Research Institute, NL	HTU	265-350	180	no	no
	BFH, Meier, Hamburg, Germany	BFH proceedings 380		100	Yes	no 3 autoclaves in Row
	Alphakat Future energies, Buttenheim, D	KDV	270-350	1.0	no	Yes
	HAW, Willner, Hamburg, Germany	KDV	370	< 1	no	Yes
	HAW, Willner, Hamburg, Germany	DOS	350-500	80	Yes	no
Animal Biomass, Sewage sludge	T. Müller, S. Bothur, Wildenhain, D	B/M procedure Mueborit	< 220	6	no	no Exploration solution, KCO ₃
	University of Tübingen, Gießen University of Applied Sciences, E. Stadlbauer, D	NTK	400	1.0	no	Yes Sewage sludge, animal Fats, PE, PP, rapeseed, Tar sands
	HAW, Willner, Hamburg, Germany	KDV	370	< 1	no	Yes
Plastics (pure/ mixed)	Ozmoenergy, AUS, Envosmart, NL	Ozmoenergy	390-420		no	Yes PE, PP, PS, Mix
	Gossler Envitec Gutknecht GmbH Reinbek, Germany	KS Recycling Gossler	350-400	no pressure		Yes PE, PP, PS, PET Mix
	Alphakat Future energies, Koch, Buttenheim, D	KDV	270-350	1.0	no	Yes
	Clyvia Technology GmbH, Wegberg- Wildenrath, D	Clyvia CL500	380-420	0.2-0.3	no	no Additives: Hydrated lime, soda
Waste oil, rinsing oil	Clyvia Technology GmbH, Wegberg- Wildenrath, D	Clyvia CL500	380-420	0.2-0.3	no	no Additives: Hydrated lime, soda
	HAW, Willner, Hamburg, Germany	KDV	370	< 1	no	Yes

Table 6-2 provides an overview of the suppliers of liquefaction processes in Germany documented in this study.

Table 6-2: Overview of suppliers / developers of liquefaction processes in Germany

Unternehmen / Institution / Organisation	Verfahren	Ansprechpartner	Anschrift		Telefon
Alphakat Zukunftsenergie Ges. für katalytische Aufbereitungstechnologien mbH	Alphakat, KDV	Dr. Christian Koch	96155 Buttenheim	Schulstr. 8	09545-208
Bundesforschungsanstalt für Forst- und Holzwirtschaft Hamburg	BFH	Dr. Dietrich Meier	21031 Hamburg-Bergedorf	Leuschner-str. 91	040-73962517
Clyvia –Technology GmbH	Clyvia CL500	Esther Stölzer	41844 Wegberg	Friedrich List Allee 10	02432-893626
Fachhochschule Gießen-Friedberg FB 06 MNI	NTK-Verfahren	Prof. Dr. Ernst Stadlbauer	35390 Gießen	Wiesenstr. 14	0641-309-2322
Gossler Envitec GmbH	KS-Recycling Gossler	Michael Gutknecht, Dr. Henryk Zmuda	21462 Reinbeck	Borsigstr. 4-6	040-72709250
HAW Hochschule für Angewandte Wissenschaften Hamburg	KDV, DoS	Prof. Thomas Willner	21033 Hamburg	Lohbrügger Kirchstr. 65	040-7600547
Müborit	B/M-Verfahren Müborit	Stefan Bothur, Thomas Müller	01561 Wildenhain	Hohe Str. 25	03522-507749, 0351-2878942
PYTEC Thermochemische Anlagen GmbH	Ablative Flash-Pyrolyse	Stefan Scholl	21037 Hamburg	Durchdeich 10	040-73430808

6.2 PROCEDURES IN INDIVIDUAL CONSULTATION

6.2.1 FLASH PYROLYSIS

Flash pyrolysis is a variant of conventional pyrolysis in which biomass is heated very rapidly at temperatures of approximately 475 °C in the absence of oxygen. The released, predominantly primary pyrolysis products condense after rapid cooling into a reddish-brown liquid that has about half the calorific value of conventional heating oil.

Compared to normal pyrolysis, the yield of liquid products is maximized rather than the yield of charcoal (see Figure 6-3) [Kaltschmitt01].

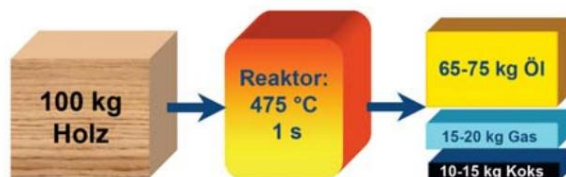


Figure 6-3: Schematic of flash pyrolysis [Meier06a]

Unlike other liquid energy carriers from fossil sources, pyrolysis oils are hydrophilic, meaning they are miscible with water up to a concentration of approximately 35%. At higher concentrations, the oil separates into an aqueous and a tar-like phase. The normal water content is between 20 and 30%, originating partly from the residual moisture of the wood and partly from the water of reaction. Some properties of the resulting pyrolysis oils are summarized in Table 6-3.

Table 6-3: Typical properties of pyrolysis oils [Pytec06]

Characteristics	Average values
Water content	20-35%
PH value	2-3
density	1.2 g/cm ³
carbon	56%
hydrogen	7%
oxygen	37%
Nitrogen	0.1
Viscosity (40°C, 20% H ₂ O)	40-100 cP
fine particles	<0.3%
calorific value	16-18 MJ/kg

The special features of flash pyrolysis are:

- very high heating and heat transfer rates (small particle size of 2-3 mm necessary)
- Good temperature control is necessary, narrow temperature range of approx. 475-500°C • Increase in energy density (from wood with 8 GJ/m³ to product oil with 20 GJ/m³)
- Residence time of the pyrolysis products in the reaction zone < 1 s
- Rapid cooling and separation of the products to avoid secondary reactions, which would lead to losses in yield and quality of the pyrolysis oils.

To meet these technical requirements, stationary and circulating fluidized bed reactors are widely used and well-suited for larger plants, as they enable high heat transfer rates with short residence times. A disadvantage is the high grinding effort required for the biomass to achieve the small particle sizes. However, reactors with ablative action and vacuum reactors are also used. An overview of the most important processes is shown in Figure 6-4.

In the field of technical implementations of flash pyrolysis, there are currently only a few plants. Apart from one commercially operated plant with a throughput of 45 t/d biomass for the production of liquid smoke in Canada, all other plants listed below are either operating on a pilot scale or have not yet been commissioned:

- Fortum, Finland, 500 kg/h
- Wellman, England, 250 kg/h, no operating permit
- BTG ("Rotating Cone"), Holland, 50 t/d
- ENEL, Italy, 300 t/d
- Ensyn ("RTP"), USA, 70 t/d
- Dynamotive ("BioTherm"), Canada, 100 t/d [Bridgwater06]
- FZ Karlsruhe ("bioliq"), Germany, 12 t/d
- PYTEC ("BTO"), Germany, 6 t/d.

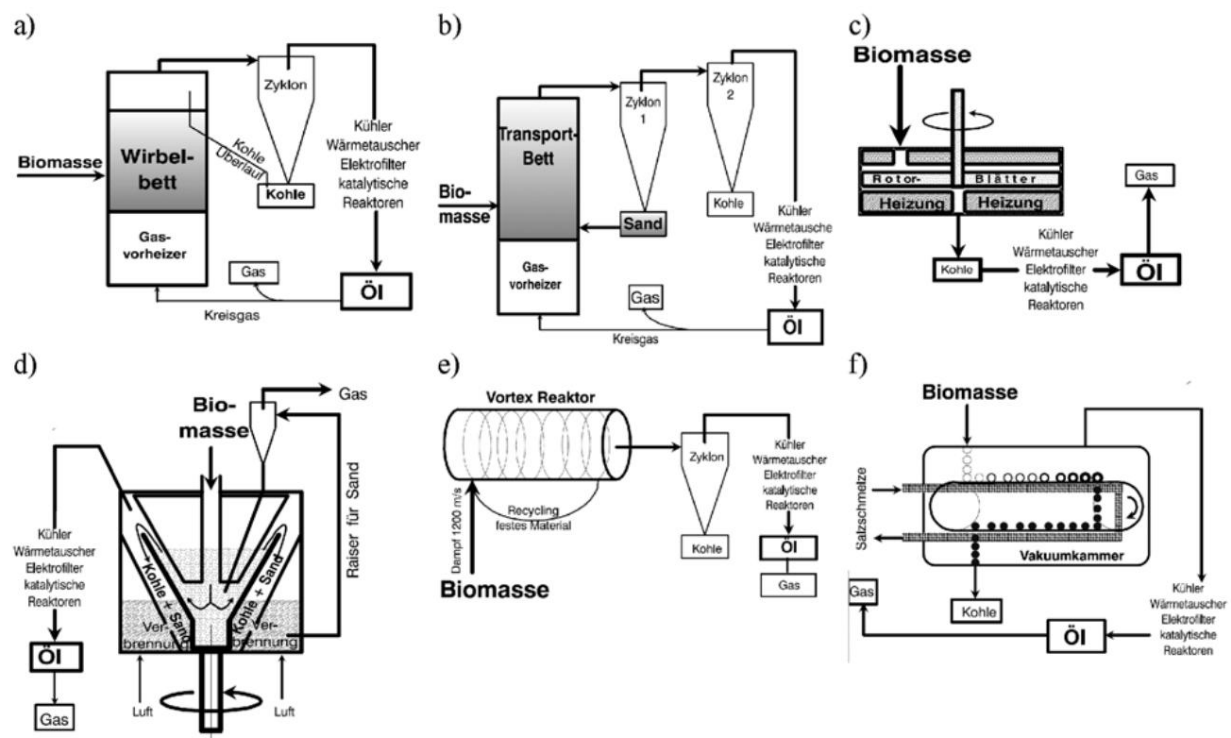


Figure 6-4: Reactors for the flash pyrolysis of biomass: a) reactor with stationary fluidized bed, b) with circulating fluidized bed; c, d, e) with ablative effect, f) reactor under vacuum, according to [Kaltschmitt01]

6.2.1.1 Pneumatic Fluidization (Fluid Layer Technology)

At the Finnish research center VTT in Fortum, the production of pyrolysis oil from forestry waste (including bark and needles) is planned. The bio-oil is intended to replace light heating oil in a Wärtsilä diesel engine with 1 MW of electrical output for combined heat and power generation. So far, all trials have proceeded according to plan.

The Wellman plant in England is not operational. Stringent environmental regulations imposed by the permitting authorities have so far prevented its commissioning.

Within the framework of the EU research project "Bio Fuel Oil for Power Plants and Boilers," bio-oils are to be produced in larger quantities (300 t/d), characterized, and then refined or used for energy production. Production takes place in Italy at the energy company ENEL, which operates a demonstration plant. In Germany, at the Institute for Wood Chemistry and Chemical Technology of Wood of the Federal Research Institute for Forestry and Forest Products in Hamburg, the bio-oils are chemically and physically characterized, and investigations into their long-term stability are carried out. The oils are stored under various conditions, with particular attention paid to the influence of temperature and light. Measurements include not only global parameters such as acid value, bromine value, pH value, water content, viscosity, etc., but also changes in individual substance classes and components [Meier03].

6.2.1.2 Rotating Reactor

The Dutch plant of the Biomass Technology Group (BTG) is operational and is being used for pilot tests. The plant design differs significantly from other fluidized bed reactors, as the sand is fluidized mechanically by a cone-shaped, rotating reactor and not by a gaseous medium.

6.2.1.3 THE BIOLIQ PROCESS

Another reactor with mechanical fluidization and a fuel capacity of 3 to 5 t/h is currently being investigated at the Karlsruhe Research Center. It is based on the LR twin-screw reactor (LR = Lurgi-Ruhrgas), in which the heat transfer medium, sand, is mixed with the biomass by two co-rotating twin screws and conveyed axially. In a cross-flow process, the product gases are extracted and the oil is condensed.

Two companies are significantly involved in the "bioliq" process of the Karlsruhe Research Centre: Lurgi AG from Frankfurt am Main supplies the process for rapid pyrolysis developed for petrochemical residues, and Future Energy from Freiberg, a subsidiary of the Swiss company Sustec, is a leader in the field of entrained flow pressure gasification.

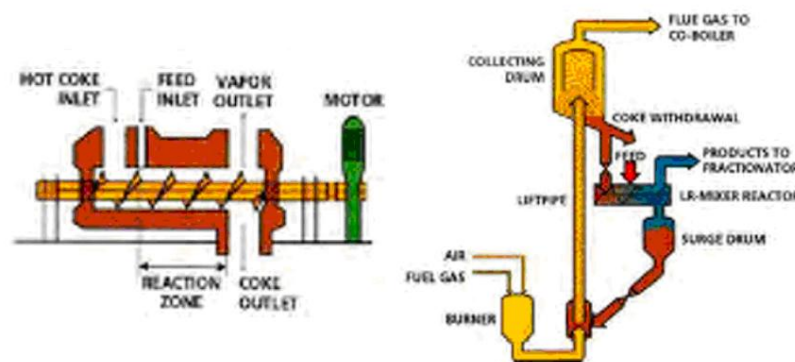


Figure 6-5: The Lurgi-Ruhrgas reactor of the bioliq process [Meier06b]

Conceptually, flash pyrolysis is an important step here, but in the overall concept it does not serve to directly produce liquid hydrocarbons, but rather to provide

Economically transportable intermediate products, which are then converted to synthesis gas in central plants in a flow-through gasifier at temperatures around 1200°C and pressures of 80 bar and ultimately fed to a Fischer-Tropsch or methanol synthesis.

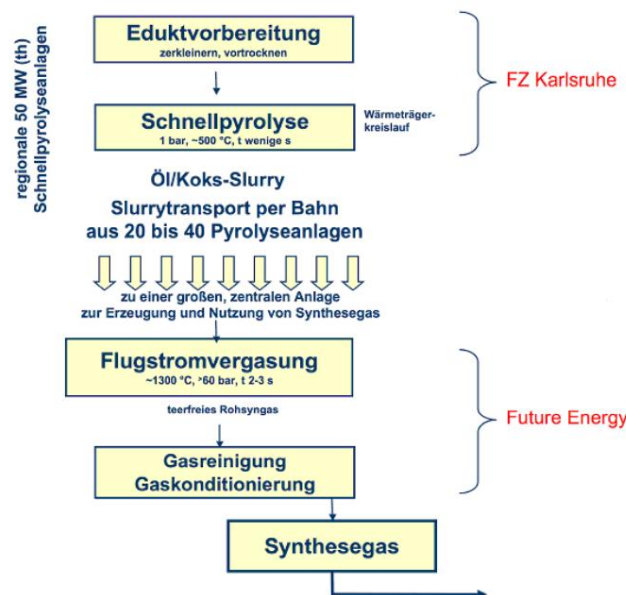


Figure 6-6: The bioliq concept of FZ Karlsruhe and Future Energy [Meier06b]

6.2.1.4 CONTACT WITH HOT SURFACE (ABLATIVE REACTOR, VACUUM REACTOR)

Process developer:

PYTEC Thermochemical Systems GmbH

Contact: Stefan Scholl, Durchdeich 10, 21037 Hamburg, 040/73430808

In ablative flash pyrolysis, there is no fluidized heat transfer fluid. Biomass is melted directly at a hot contact surface. Relative movement between the hot medium and the biomass is necessary to ensure high melting rates. The resulting liquid film evaporates immediately and can be condensed as pyrolysis oil. With this process principle, comminution is no longer strictly necessary; the reactor geometry alone determines the size of the biomass particles.

To date, ablative reactors have only been operated on a laboratory scale. A primitive "hot mill" was developed at the Colorado School of Mines, USA, in which biomass particles were pyrolyzed between two hot grinding discs. Building on these results, facilities were constructed at Aston University in Birmingham, UK [Bridgewater96], and the CNRS, Nancy [Lede00], in which the biomass is moved relative to the reactor wall. The Aston reactor, with a capacity of 5 kg/h, uses a horizontal heating disc on which the biomass is pushed by a rotating vane rotor. CNRS uses a cyclone reactor, which, however, must be operated with small particle sizes. In Germany, the company PYTEC Thermochemische Anlagen GmbH, Hamburg, operates a reactor with a vertical heating disc, the so-called BtO plant. The heating disc rotates, with up to four solid wooden slats (area 10x47 mm) being pressed against it by compressed air-controlled cylinders. Melting rates between 2 and 5.5 mm/s were achieved at contact pressures between 30 and 50 bar [Meier03].

According to PYTEC, they successfully used bio-oil directly as fuel in a modified 450 kW Mercedes-Benz diesel engine of a combined heat and power (CHP) plant during a 12-hour trial. With a consumption of 140 liters/hour of bio-oil, an average of 300 kWh of electricity was produced.

Figure 6-7 schematically shows the BtO plant in Bülkau of the company PYTEC with the four process steps for generating electricity from wood chips in a CHP unit.

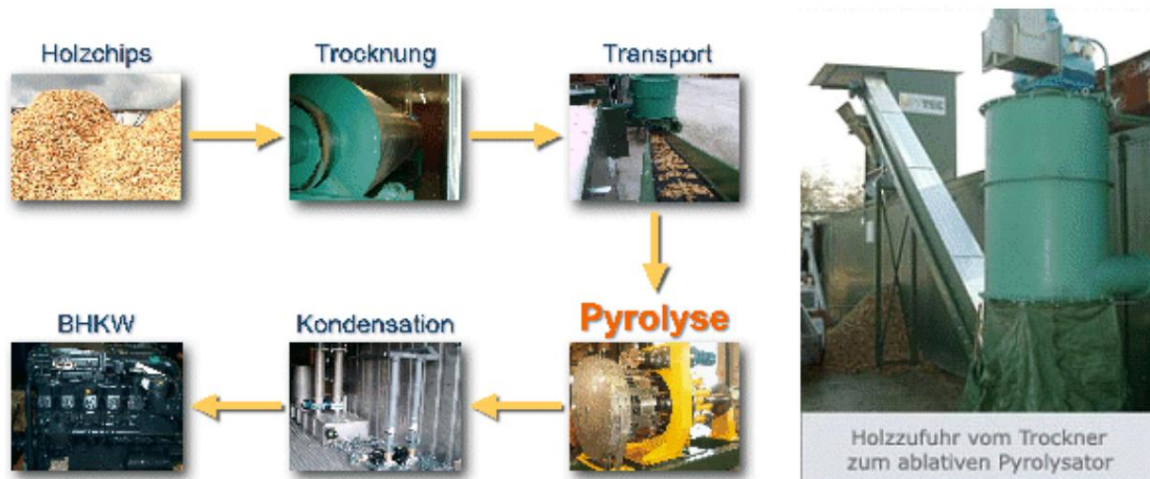


Figure 6-7: Schematic diagram of the ablative flash pyrolysis plant of the company PYTEC for Wood liquefaction [Meier06a, Pytec05]

At PYTEC, bio-oil production through condensation of the hot product gas stream is achieved using a combination of jet scrubbers and electrostatic precipitators. The gases are combusted, and the heat is used to dry the feedstock. The charcoal is removed via a cyclone, combusted, and the released energy is used to heat the reactor [Pytec05].

The expected yields of flash pyrolysis, depending on the reaction temperature, are approximately 75% oil based on the dry raw material, as well as valuable byproducts charcoal (10-15%) and gas (15-20%), with ash remaining as the residue (see Figure 6-8).

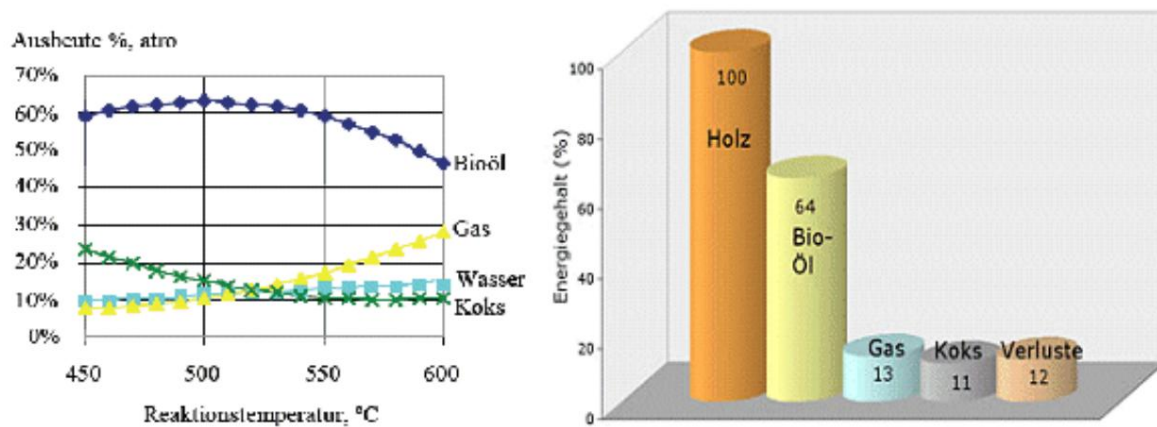


Figure 6-8: Influence of reaction temperature on yield and percentage distribution of the Energy content of the products in flash pyrolysis [Meier06a, Pytec05]

6.3 HISTORICAL DIRECT LIQUEFICATION METHODS

Against the backdrop of the two oil price crises, work on direct liquefaction was intensified. The PERC process (Pittsburgh Energy Research Center, Pittsburgh, USA) and the LBL process (Lawrence Berkeley Laboratory, Berkeley, USA) were developed. Both processes utilize a gas mixture of CO₂ and H₂ derived from the gasification of the biomass used.

Both processes were abandoned after considerable development effort, primarily for economic reasons. The high oxygen content of the biomass, the increased formation of reaction water during hydrogenation, and the strong competition from pyrolysis proved to be disadvantages.

6.3.1 PITTSBURGH ENERGY RESEARCH CENTER (PERC)

The feedstocks used are wood flour and processed product oil. The mixture is pumped through a tubular reactor and remains there for approximately 10 to 30 minutes at temperatures of 330 to 370°C and a pressure of 200 bar. The oil yield is approximately 45 to 55% based on the dry mass of organic material used. The recycled oil serves as a hydrogen source.

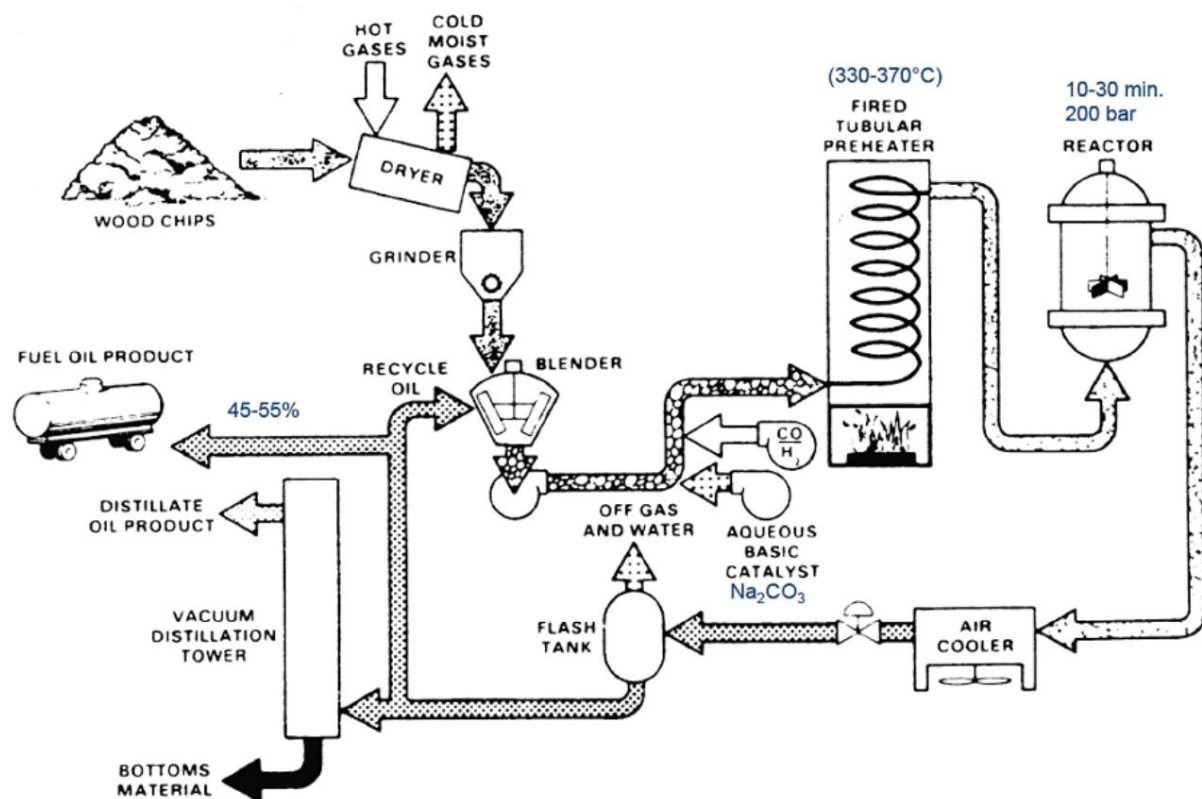


Figure 6-9: Direct catalytic pressure liquefaction of biomass (PERC process) [Meier06a]

6.3.2 LAWRENCE BERKELEY LABORATORY (LBL)

In the LBL process, the biomass is first hydrolyzed with sulfuric acid and then neutralized with sodium carbonate. The mixture is homogenized in a refiner. The aqueous slurry, with a solids content of 16 to 20%, is pumped through a tubular reactor and liquefied at 170 to 240 bar and 330 to 360°C (see Figure 6-10).

The addition of alkali carbonates promotes the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) at high pressure and in the presence of water and CO₂. The hydrogen produced serves to saturate free radicals. The crude product from direct liquefaction using the LBL process is a liquid, bitumen-like material with very high viscosity and a density of 1.1 to

1.2 kg/m³. Elemental analysis revealed 15–19% oxygen, 6.8–8% hydrogen, and 74–78% carbon. The calorific value is 34 MJ/kg.

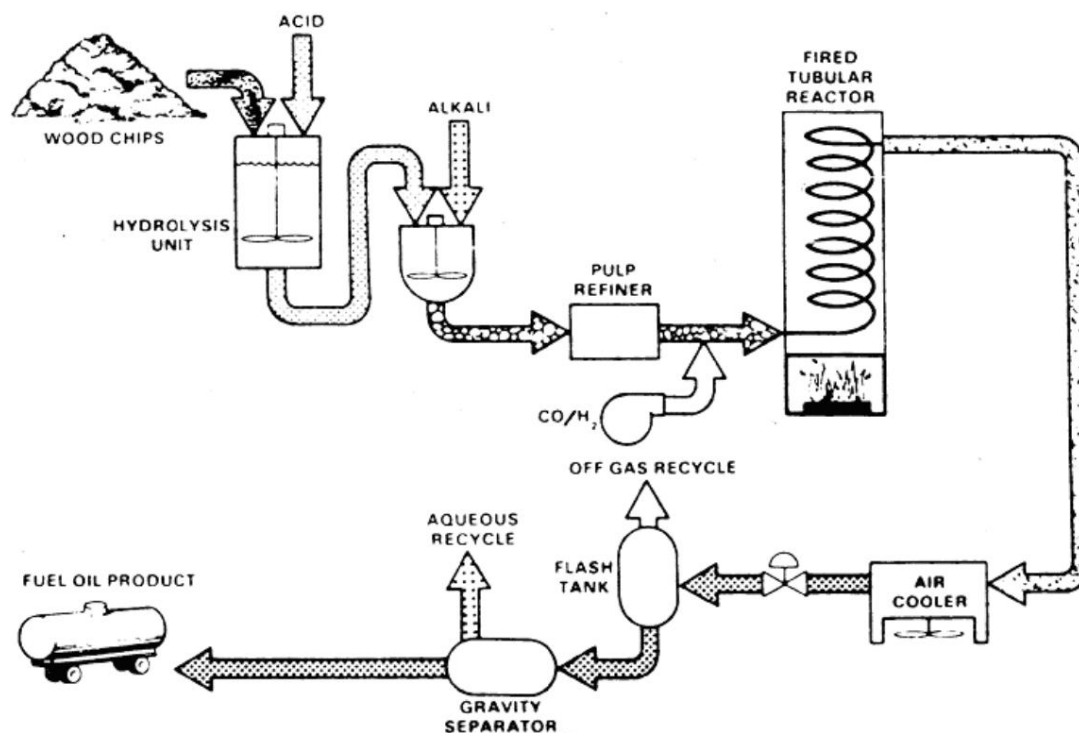


Figure 6-10: Direct catalytic pressure liquefaction of biomass (LBL process) [Meier06a]

6.4 Current methods for direct liquefaction

6.4.1 Hydrolytic Processes - HTU Process (Shell)

The process presented here has been under development since 1982. From 1982 to 1988, development and fundamental research were conducted at the Shell Research Laboratory in Amsterdam under the direction of Goudriaan. After a brief interruption, a techno-economic evaluation of the process was carried out between 1994 and 1997, followed by a process development project between 1997 and 2000. The commissioning of a demonstration plant with an annual throughput of 25,000 t/a is planned for 2008/2009. The following information is taken from the presentations [Naber04, Naber05].

The HTU (Hydrothermal Upgrading) process can be used to liquefy many different biomasses (even those with high moisture content) under pressure. The process diagram is shown in Figure 6-11. Pre-drying is not required. Liquid water is present in the system during the reaction. The biomass is suspended and introduced into the reactor via a high-pressure pump. At temperatures of 300–350°C and pressures between 120 and 180 bar, a so-called "biocrude" is produced after a residence time of 5–20 minutes. The oxygen contained in the biomass is removed from the system as water and CO₂. The product contains 45% biocrude (mass percentage of the starting material, dry and ash-free), 25% gas (>90% CO₂), 20% water, and 10% dissolved organic substances such as acetic acid and ethanol. Biocrude is a heavy organic liquid that solidifies at 80°C. It has a calorific value of 30–35 MJ/kg, a hydrogen/carbon ratio of 1:1, and an oxygen content between 10 and 18%. It is immiscible with water. The thermal efficiency for one variant of this process is given as 74.9% (theoretical maximum of 78.6%) [Naber04].

This product can be further separated into light and heavy fractions, which can then be used for energy generation in various applications. It is also possible to generate oil fractions through processing using the HDO process (HDO – Hydro-Deoxygenation).

This processing method is similar to the refinery processes "first stage hydrocracking," HDS, and HDN. Laboratory tests conducted at Shell Research in 1983 showed that O, N, and S could be removed to low concentrations with a hydrogen consumption of approximately 5% by mass. The products were fractionated. In tests at the Shell Products Laboratory in Great Britain, the gas oil fraction exhibited better ignition properties than the comparable fossil fraction.

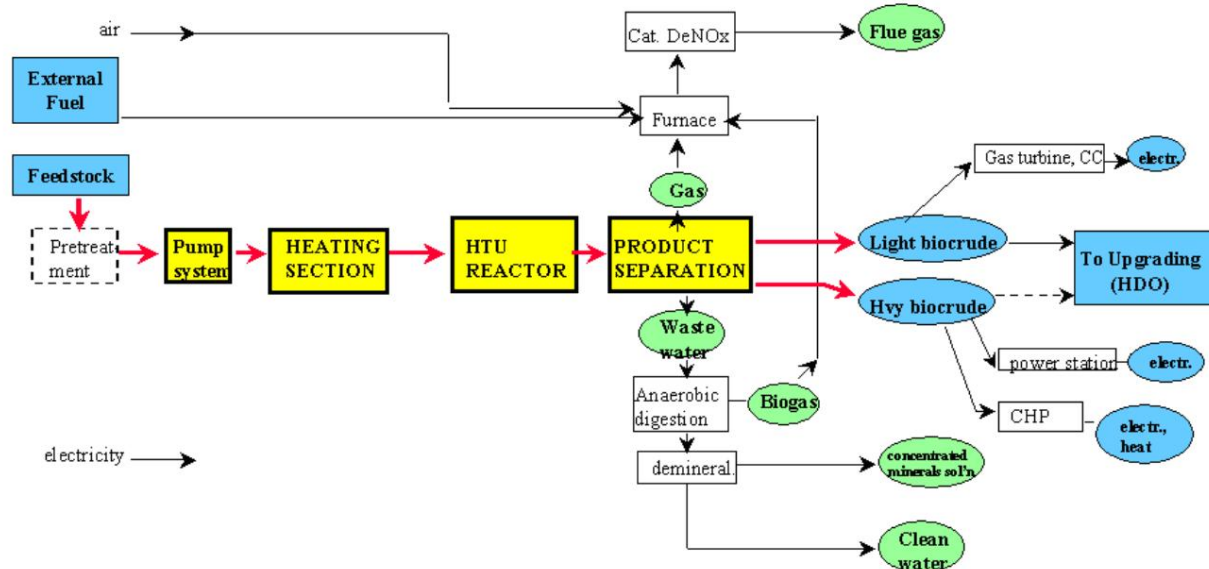


Figure 6-11: HTU-Upgrading Process Flowchart [Naber04]

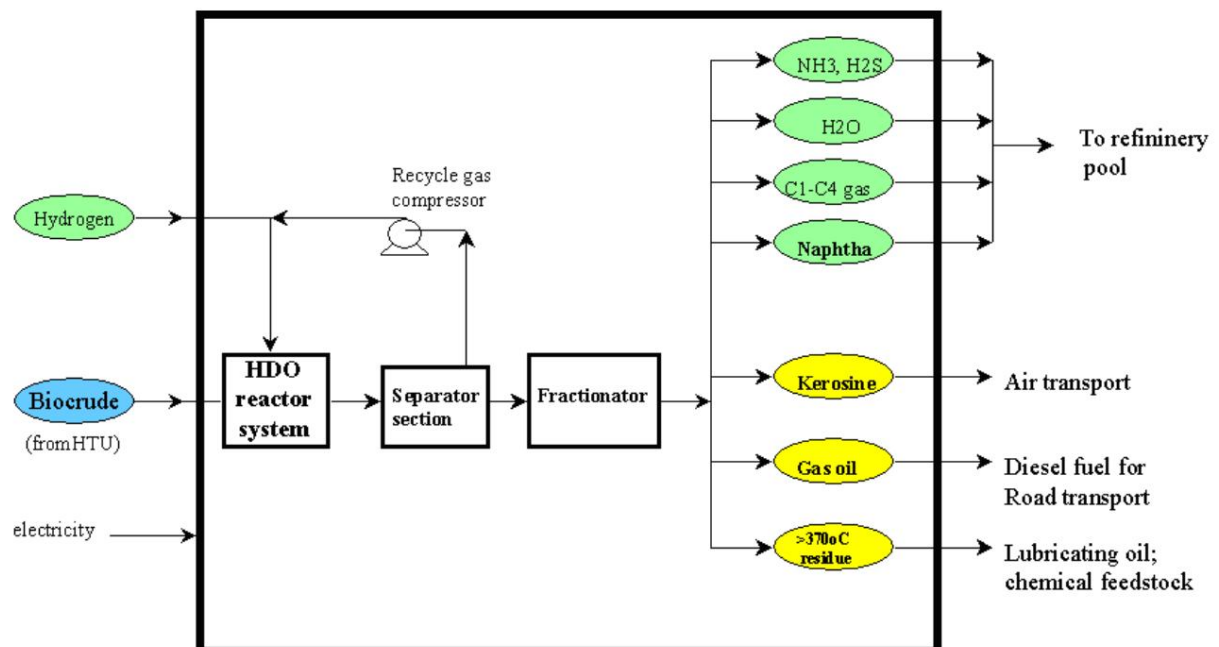


Figure 6-12: Procedure diagram HDO-Upgrading [Naber04]

6.4.2 DIRECT CATALYTIC PRESSURE LIQUEFICATION – BFH PROCEDURE

Process developer:

Federal Research Institute for Forestry and Forest Products (BFH)

Contact: Dr. Dietrich Meier, Leuschnerstraße 91, 21031 Hamburg-Bergedorf, 040/73962517

In the 1980s, intensive fundamental research was conducted in the laboratories of the Bern University of Applied Sciences (BFH) on the conversion of lignocellulosic raw materials and residues into liquid products through thermal pressure treatment (FE project 81NR006, BMFT). In addition to reaction time, temperature, and pressure, experimental parameters such as solvent, catalyst, and reducing gases in the reaction system were also varied. Three interconnected autoclaves were used as the reactor system, allowing for rapid heating of the aqueous/organic solvent and rapid cooling of the reaction mixture. In 1984, a semi-continuous process for the liquefaction of lignocellulosic substances was developed.

The most promising process in terms of yields, carbon and energy balances was catalytic hydrogenolysis, with the components hydrogen / precious metal catalyst / oil.

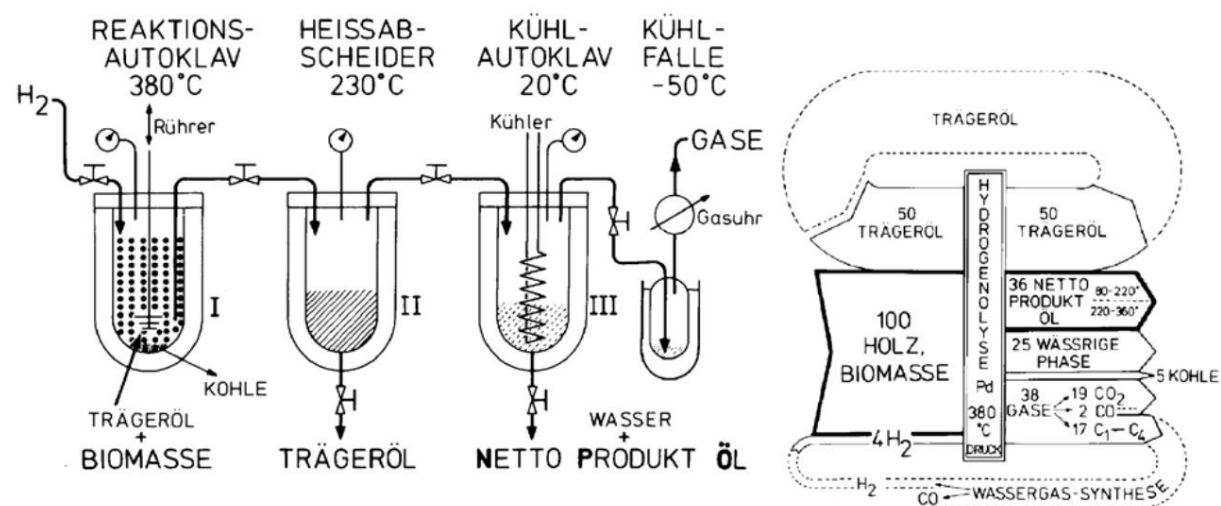


Figure 6-13: Left: Direct catalytic pressure liquefaction of biomass; right: Mass balance [Meier06a]

Figure 6-13 (left) shows the experimental setup for direct catalytic pressure liquefaction. Hydrogen is used as a reducing gas in the reaction autoclaves, along with the substance contained in the...

The oil collected in the hot separator was added back in after each experiment. After a residence time of 15 minutes, the conversion products passed through the hot separator into the cooling system, where they were depressurized. Under these conditions, wood flour could be hydrogenated in the presence of palladium.

Figure 6-13 (right) shows the mass balance for the process described above. From 100% wood, 36% oil is obtained as liquid wood tar, which is miscible with water, 50% carrier oil, which is recycled back into the process, 5% coal, and 25% aqueous phase.

The optimization of the BFH process for direct catalytic pressure liquefaction was not pursued further due to the more promising technology of flash pyrolysis and the associated EU financial support.

6.4.3 CATALYTIC PRESSURELESS OILING (KDV PROCESS)

6.4.3.1 VARIANT ACCORDING TO KOCH

Process developer:

Alphakat Future Energy - Company for Catalytic Processing Technologies Ltd.

Contact: Dr. Christian Koch, Schulstr. 8, 96155 Buttenheim, 09545/208

The quotations and technical details in the following presentation are based on the information in: <http://www.alphakat.ch/KDV%20Technik.htm> (as of 21.04.06) www.alphakat.de/Das_Prinzip/das_prinzip.html (as of 09.05.06).

Catalytic pressureless oleation (CPE) is intended to convert biogenic or petroleum-based, as well as hydrocarbon-containing, raw materials and residues into diesel fuel. The patented process aims to transform anything that has ever grown or been produced from petroleum into high-quality diesel fuel using CPE.

The process developer describes his process as follows: "...The model for the new, patented process is the natural formation of petroleum. Similar catalysts to those used hundreds of millions of years ago, when turbulent seas deposited suspended clay minerals along with dead matter, are employed in the process."

This process has been further developed to meet today's requirements. It had to be taken into account that hundreds of millions of years are no longer available for the process. It must also be considered that today's residues are often mixed with problematic substances such as PVC and Teflon, meaning that the formation of dioxins and furans is possible during non-catalytic decomposition.

The process taking place in the KDV plant therefore uses, in comparison to the formation of petroleum millions of years ago: a temperature of 270 to 350°C instead of 40°C and ion-exchange catalysts made of 100% crystallized γ -catalysts¹, which are extremely active and yields high-quality diesel as the end product instead of petroleum..."

The KDV process is a closed loop, so no pollutants are released. The low process temperatures of max. 350°C are intended to prevent the formation of dioxins or furans. The process is suitable for processing a wide range of feedstocks.

- Waste oils, waxes, greases of all kinds, including transformer oils and hydraulic oils
- Plastic waste, including PVC
- Rubber, car tires, refinery residues, bitumen, tars
- Sewage sludge
- Paper sludge
- Household waste and hospital waste (sterilized, dewatered, dried)
- Agricultural residues (animal waste products, spoiled food, brewer's grains, oilseed press cake, green waste)

¹ Y-type catalyst: The synthetic zeolite of type Y with a faujasite structure is one of the important catalysts in the petroleum refining process. It consists of AlO_4 and SiO_4 tetrahedra with the following structure: $\text{M}_x/\text{n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot z \text{H}_2\text{O}$ (n = charge of M, usually 1, 2). According to http://www.mrw.interscience.wiley.com/ueic/articles/a28_475/pdf_fs.html, <http://de.wikipedia.org>, <http://www.dmg-home.de/Schule/Zeo2.doc>, accessed April 25, 2006.

- Renewable raw materials, such as corn, straw, rapeseed, sunflowers, miscanthus , etc.
- Wood, lignite (precursor to brown coal)

The yield should be 80% for petroleum-based materials such as plastics and waste oil, and at least 30% for biogenic materials, based on dry mass. A catalyst consumption of approximately 1% of the input quantity is specified.

A high yield in terms of the product's calorific value relative to the calorific value of the raw materials is claimed, which is said to be more than 80% of the hydrocarbon substance contained.

Halogens are to be separated from the product by bonding in the liquid state as a salt, although it remains unclear from the available documentation what this means.

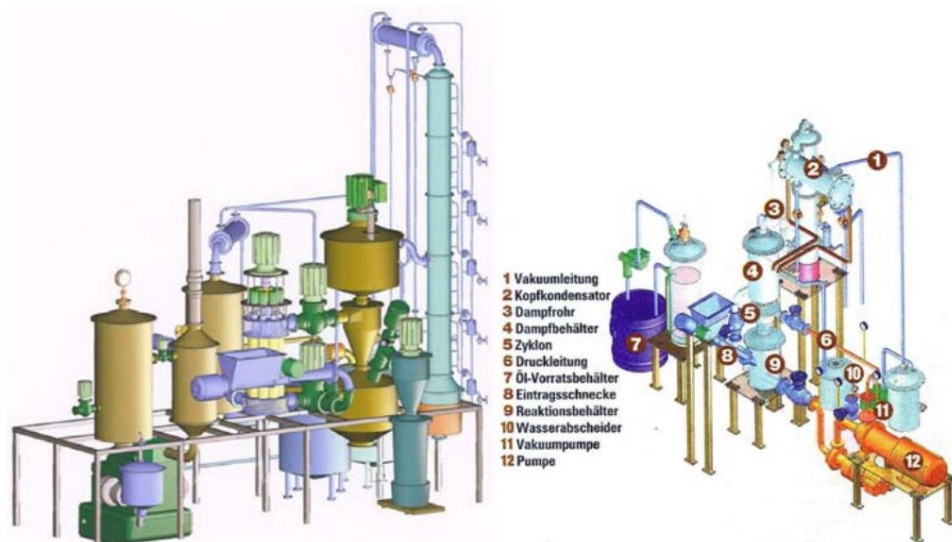


Figure 6-14: Left: 3D system diagram for pressureless catalytic oiling at 1 atm according to Alphakat, from: <http://www.fuxfax.de/onlinepartner/evk/>; right: Alphakat process [Autobild, September 2005]

According to the process developer, a first production plant in Mexico with a design capacity of 500 l/h diesel oil has been realized (Figure 6-15).

Two samples from the KDV process of Alphakat were subjected to fuel analysis by the University of Rostock in 2005 on behalf of the State Research Institute for Agriculture and Fisheries. The GC/MS analysis shows a distribution of long-chain unbranched and branched saturated hydrocarbons, as well as aromatics, typical for diesel fuels. An analysis according to EN 590 for diesel fuels reveals some significant anomalies. The sulfur content exceeds the limit of 10 or 50 ppm by up to twenty times. The flash point is too low compared to the standard, which would have consequences for safety requirements during storage. While the boiling behavior is similar to that of diesel fuel, it exhibits deviations that do not comply with the standard. The cetane number was not determined, but a low cetane index suggests a similarly low cetane number. While the content of metallic elements is generally unproblematic, the silicon content is significantly too high, which can lead to considerable problems during engine operation ("sand in the engine").

The samples examined also contained an unidentified sediment and drops of a second liquid phase.



A temperature-resistant circulating oil from BP, type Energol CS 220 208 L, was used as the starting/base oil, and an ion-exchange active aluminosilicate from Alphakat, Buttenheim, type A 407, was used as the catalyst. The catalyst powder was dried for approximately 16 hours at 200 °C before each experiment. Wood, straw, fodder beet, cellulose, and sugar (cube sugar) in granulated, lumpy form (particle size less than 5 mm) were used as raw materials and model materials for solid biomass. The wood was pre-dried to a residual moisture content of 0.8% by mass. The other raw materials were used air-dried.

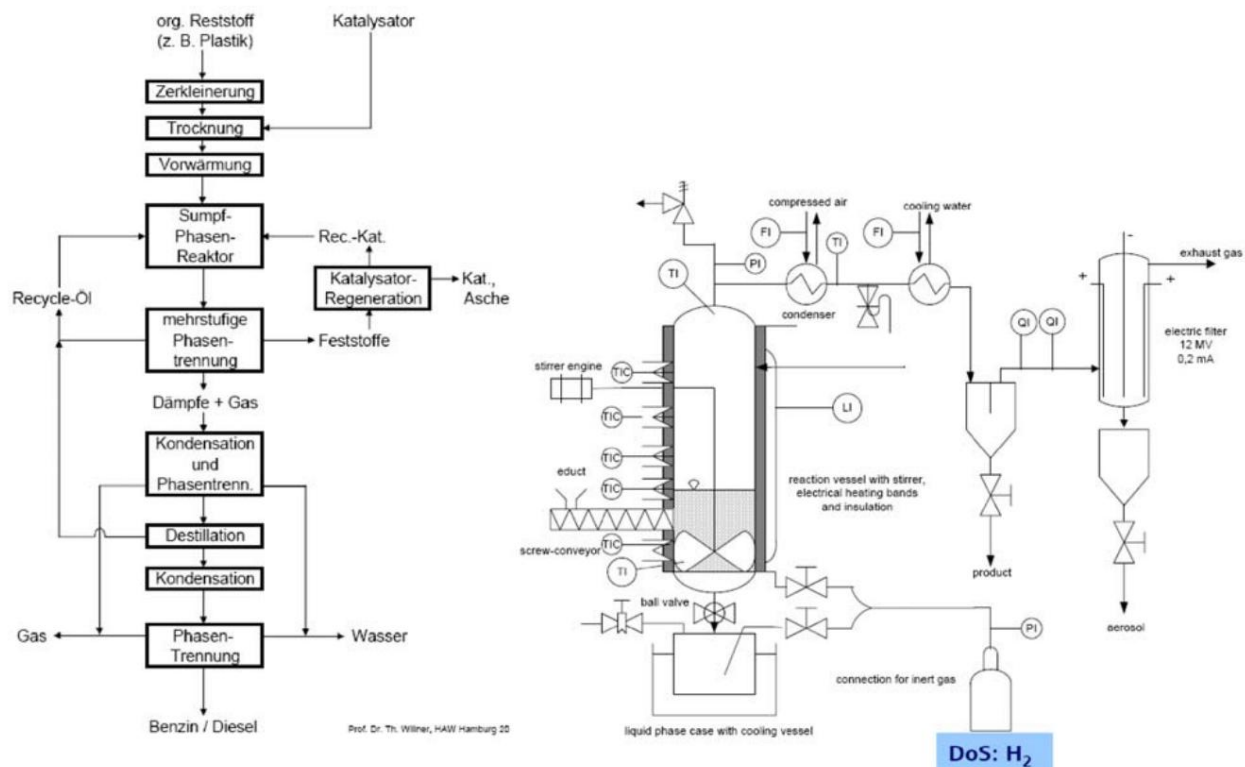


Figure 6-16: Process flow diagram for the bottom-phase cracking process using atmospheric pressure catalytic cracking
 Process for the semi-continuous laboratory plant with a throughput of 1 kg/h at 1 atm, HAW Hamburg
 [Willner06a]

According to the process operator, the following raw materials could be examined in the KDV plant at HAW Hamburg:

Plant biomass: - Wood -
 Cereals,
 cereal straw - Miscanthus -
 Fodder beet -
 Rapeseed,
 rapeseed press cake - Fermentation
 residues from biogas plants Animal biomass: - Fats and
 oils - Sewage sludge
 Waste materials: -
 Waste oil, heavy oil -
 Pure and mixed
 plastics - Cadmium-
 contaminated PE - Shredder light
 fraction - Medical waste.

The collected condensate consisted in all cases of two immiscible phases: a lighter hydrocarbon phase (product oil) and a heavier aqueous phase. The process developer commissioned gas chromatographic and mass spectrometric analyses of the product oil phase. Figure 6-17 shows examples of GC/MS analyses for product oils from wood and diesel fuel. The analysis shows that unbranched hydrocarbons in the C8 to C23 range predominate. The majority of these molecules are in the same size range as diesel fuels (C11 to C25), with a smaller portion in the C8 to C10 range .

in a size range similar to gasoline. However, this does not mean that these are fuels that meet standards.

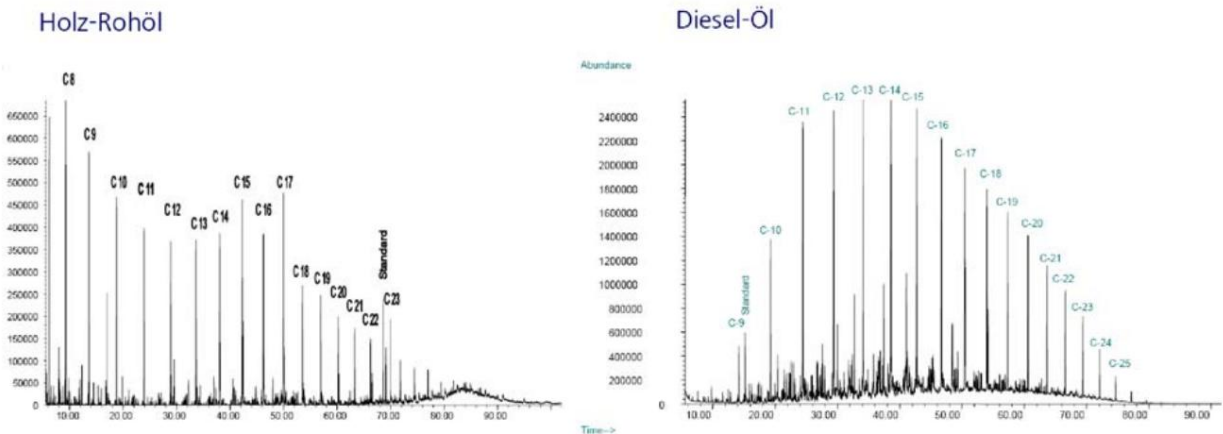


Figure 6-17: Left: Product oil from wood (internal standard fluoranthene) [Willner06]; right: Diesel fuel [Willner06a]

Figure 6-18 shows the boiling curves (boiling temperatures over the distillate fraction) of the product oils obtained from straw and sewage sludge by catalytic direct liquefaction, compared to conventional diesel.

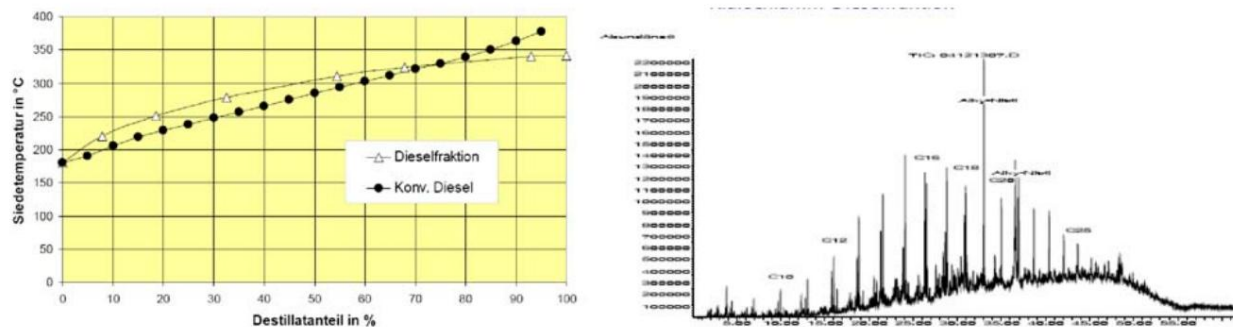


Figure 6-18: Boiling curve of the KDV product oil from sewage sludge compared to conventional diesel. [Willner06]; right: GC/MS analysis of KDV product oil from sewage sludge [Willner06a]

Some physical properties of the product oil obtained from wood or sewage sludge using the KDV process are compared in Figure 6-18 with selected properties for diesel fuel according to the EN 590 standard.

Parameter	EN 590	Synthet. Dieselöl	Einheit
C / H / N / O		84 / 13 / 0 / 3	Gew. %
H/C		1,9	
Heizwert (H _u)		42.399	kJ/kg
Dichte (15 °C)	820 bis 845	837,6	kg/m³
Kin. Viskosität (40 °C)	2,0 bis 4,5	3,3	mm²/s
Cetanzahl	min. 51	52,9	
CFPP (Sommer/Herbst/Winter)	max. 0/-10/-20	-13	°C
Koksrückstand n. C.	max. 0,3	0,05	Gew. %
PAK	max. 11	4,3	Gew. %
Gesamtverschmutzung	max. 24	18	mg/kg

Parameter	EN 590	Synthet. Dieselöl	Einheit
C/H/N/O		85,4/11,9/1,2/1,5	Gew. %
H/C		1,7	
Heizwert (H _u)		40.300	kJ/kg
Dichte (15 °C)	820 bis 845	834	kg/m³
Kin. Viskosität (40 °C)	2,0 bis 4,5	3,8-6,9	mm²/s
Cetanzahl	min. 51	48-56	
Koksrückstand n. C.	max. 0,3	<0,1	Gew. %
Diaromaten		2,7-2,9	Gew. %
Tri(+)aromaten		1,2-1,6	Gew. %

Figure 6-19: Fuel properties of KDV product oils from wood (left) and sewage sludge (right) [Willner06a]

Recent analyses of fuel characteristics, using wood-derived product oil as an example, show that the requirements of the standard are met by the analytical values given in parentheses for the following points: cetane number (52.9), density at 15°C (838 kg/m³), kinematic viscosity at 40°C (3.3 mm²/s), total contamination (18 mg/kg), Conradson coke residue (0.05%), and polyaromatics (4.3%, of which tri-aromatics 0.8%). No information is provided regarding flash point or sulfur content (catalyst poison).

Figure 6-20 shows the concept for a technical implementation of catalytic direct liquefaction (CDF) in continuous operation with a capacity of 5 kg/h, developed by Alphakat GmbH, Eppendorf/Saxony, which is to be built at Hamburg University of Applied Sciences (HAW Hamburg) in the near future. This plant will be used to verify whether the results achieved so far can be confirmed in stable, steady-state operation. Furthermore, the plant will serve to ensure mass and energy balances. A product oil yield of approximately 40% and an energy efficiency of approximately 70% are expected.

In this planned plant, the sump phase is processed in a separation cycle to remove excess solids. The solids, removed along with sump oil, are to undergo a multi-stage downstream purification process involving mechanical oil de-oiling, thermal oil evaporation, and incineration of the solid and high-boiling organic residues. The separated oil components are recycled back into the process, leaving only mineral residues, consisting primarily of catalyst and raw material ash.

The cracked product vapors are fed directly from the reactor into a rectification column (multi-stage distillation) and separated there into different boiling ranges. The heavy oil fraction is recirculated, i.e., returned to the reactor for further cracking and to increase the product yield. The non-condensable product gas is discharged overhead and can contribute to meeting the process energy requirements. The electrical energy and heat required for the process are generated in an integrated combined heat and power plant [Willner05a].

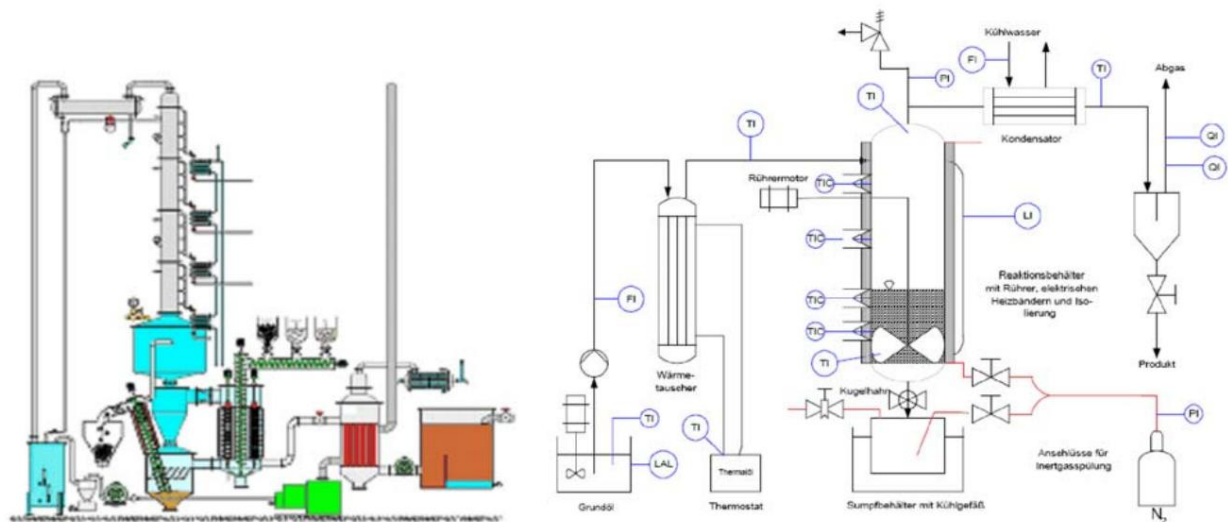


Figure 6-20: Concept of a continuous technical plant for the catalytic direct liquefaction of organic raw materials and residues with a throughput of 5 kg/h [Willner05a]

6.4.4 Pressure Hydration Process / DOS

Process developer:

HAW - Hamburg University of Applied Sciences

Contact: Prof. Dr.-Ing. Thomas Willner, Lohbrügger Kirchstraße 65, 21033 Hamburg, +49 40 7600547

The DoS process is described as a thermochemical conversion process under a pressure of 80 bar and at temperatures between 350 and 500°C. It is a bottom-phase cracking process with rapid pyrolysis followed by solvolysis into a product oil. High-molecular-weight organic substances are directly converted into liquid products through cracking and refining reactions, optionally supported by catalysts, i.e., without intermediate gasification. Neither foreign materials as reactants nor external thermal energy are required for the process. The process's hydrogen demand is met by hydrogen production from the byproducts coal and water via parallel steam gasification with carbon monoxide conversion. The pressurized hydrogen serves to saturate and stabilize the cracking products and to bind oxygen components. According to the operator, the overall process, illustrated in Figure 6-21, is completely energy and hydrogen self-sufficient and can be operated without wastewater. The overall thermal efficiency is over 70%, based on the calorific value of the input material [Meier03, Willner05b].

The hydrogenating pressure treatment according to the DoS process is based on semi-continuous laboratory tests at the Hamburg University of Technology (TUHH). The system was designed for the direct, single-stage liquefaction of lignin-rich biomass such as wood, miscanthus, and cereal straw.

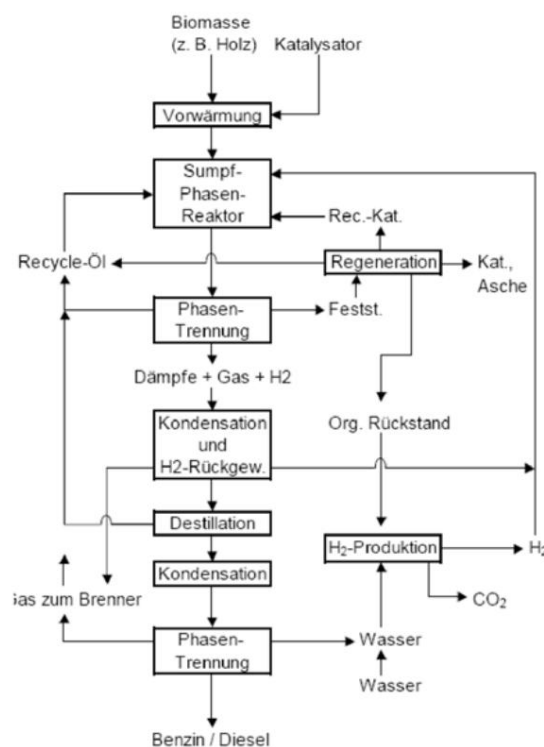


Figure 6-21: Process flow diagram (left) for hydrating pressure treatment according to the DoS process, 80 bar, HAW Hamburg [Willner06b]

The laboratory reactor shown in Figure 6-22 was used at the Hamburg University of Technology (TUHH) as part of a doctoral dissertation on wood liquefaction under the influence of hydrogen and water [Willner93]. The experimental results served as a basis for further research in this field.

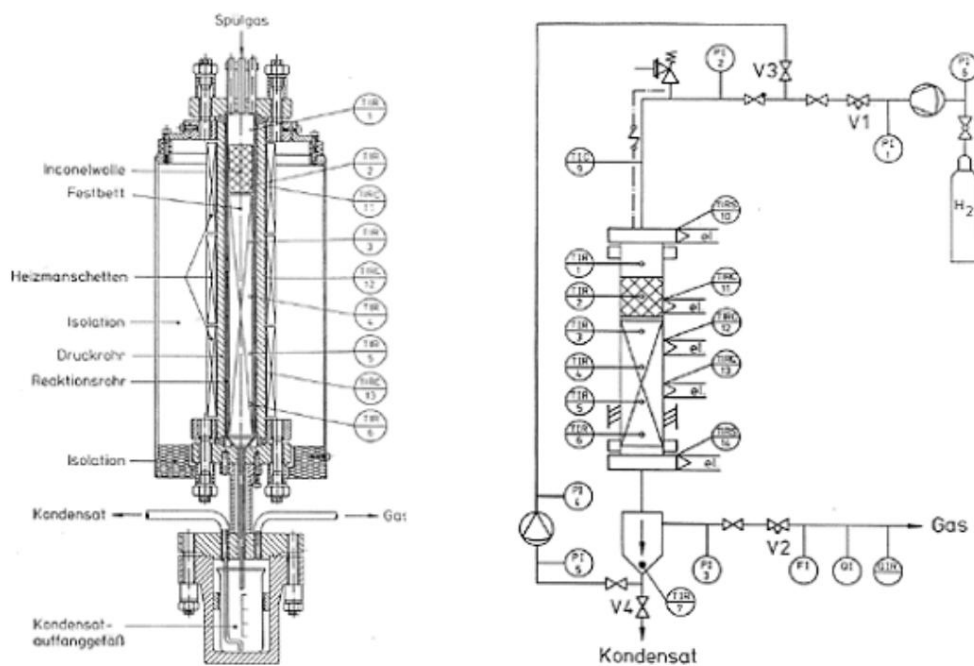


Figure 6-22: Laboratory reactor: Purge gas flow through wooden fixed bed, DoS at 80 bar [Willner06b]

In a sludge-phase reactor (see Figure 6-23), the shredded and dried biomass, fed via an extruder, is converted into the product groups oil, water, coal, and gas under hydrogen pressure. Product oil and water are discharged as vapor via the gas/vapor phase and, after condensation, gas separation, and expansion, are fed to multi-stage distillation for fractionation. A corresponding product oil analysis in comparison to crude oil is shown in Figure 6-24. This demonstrates that the DoS oil exhibits similar properties to crude oil. A residue analysis is necessary to evaluate the overall process.

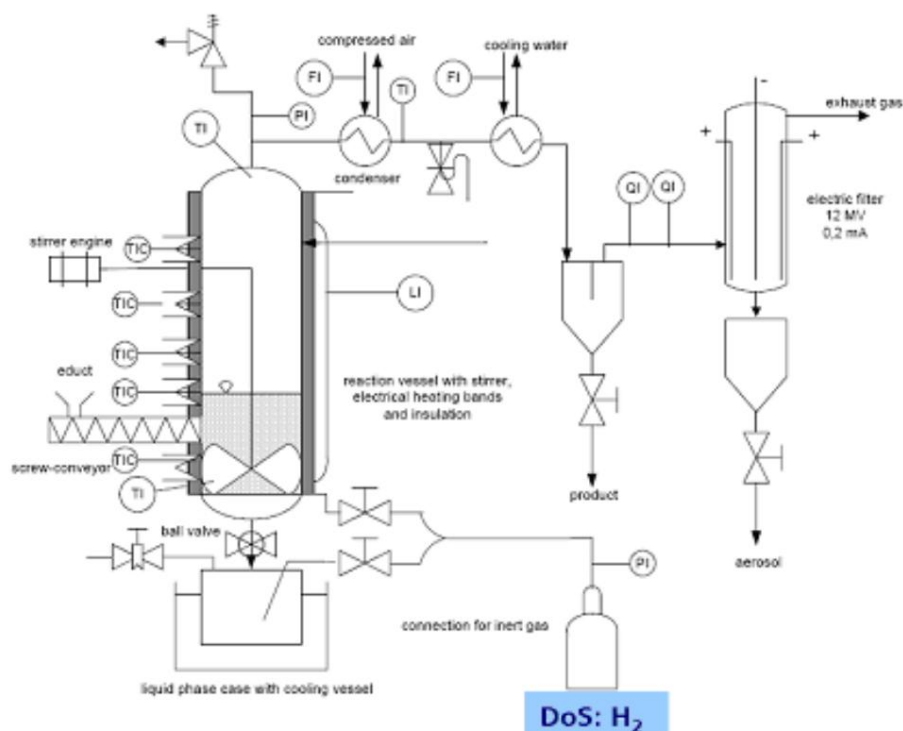


Figure 6-23: Hydrating pressure treatment using the DoS method, 80 bar, HAW-HH [Willner06a]

	Erdöl	DoS Öl
C-Gehalt	81 - 87 Gew. %	85,90 Gew. %
H-Gehalt	10 - 14 Gew. %	10,30 Gew. %
O-Gehalt	0 - 7 Gew. %	3,80 Gew. %
O/C-Verhältnis	0 - 0,06	0,033
H/C-Verhältnis	1,4 - 2,1	1,44
Dichte bei 20°C	845 kg/m³	932 kg/m³
Asphaltgehalt	5,00 Gew. %	17,00 Gew. %
Aschegehalt	0,80 Gew. %	0,30 Gew. %
Wassergehalt	0,04 Gew. %	0,20 Gew. %
Schwefelgehalt	0,001 - 8 Gew. %	0 Gew. %
Benzinschnitt (bis 180°C)	27,00 Gew. %	25,00 Gew. %
Gasölschnitt (180 bis 350°C)	36,00 Gew. %	55,00 Gew. %
mittlere Molmasse	200 g/mol	182 g/mol
Viskosität bei 20°C	10 mm²/s	5 mm²/s

Figure 6-24: Laboratory reactor: Product oil produced using the DoS process compared to crude oil [Willner06b]

The solids, consisting of raw material minerals and coal, are removed via the tailings phase and subsequently separated from the oil content of the tailings phase, which is also recycled. The tailings phase consists of heavy oil components that are formed as an intermediate product from the solid macromolecules of the respective organic raw material during the cracking process and, according to the operator, are involved in the conversion reactions of the raw material in an unknown manner.

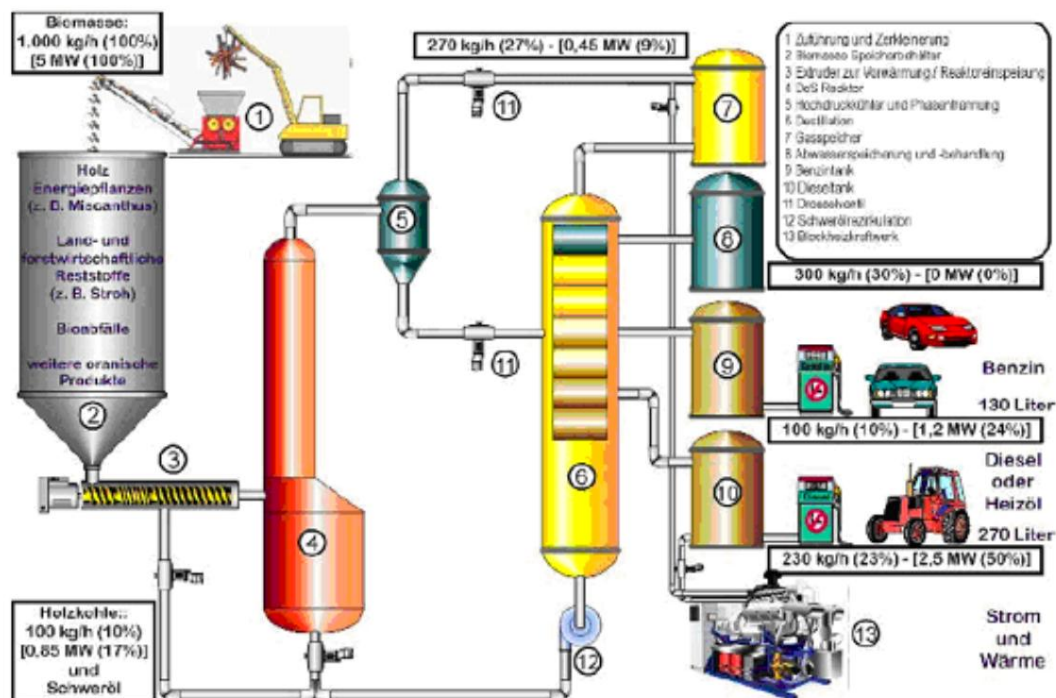


Figure 6-25: Planned plant according to the DoS method (80 bar) by Vanselow IBH [Willner06b]

A 50 kg/h DoS pilot plant in Rhineland-Palatinate, operated by IBH Ingenieurgesellschaft Ludwigshafen, is currently under construction and is scheduled to go into operation in the third quarter of 2006 (Figure 6-25). It will serve as the basis for a subsequent DoS plant with a capacity of 500 kg/h, which is to be built and commissioned at the same location by the end of 2007.

6.4.5 SUMMARY – KDV AND DOS PROCEDURES

In contrast to other known catalytic and pyrolytic low-temperature conversion processes, both catalytic cracking using the KDV process and hydrogenating pressure treatment using the DoS process are not carried out "dry", i.e. in a gas/vapor atmosphere, but in a liquid oil phase, the so-called sump phase.

Key advantages of sludge phase cracking over "dry" pyrolysis are seen by the Process developer

- in the extremely rapid heating of crushed raw material particles to reaction temperature avoiding unwanted side reactions during the heating phase,
- in maximizing product oil yield and
- in an improvement in product oil quality.

The reaction temperatures between 350 and 500°C are about 50 to 100°C higher than in the case of catalytic conversion, because the lignin component of the biomass reacts significantly slower than the carbohydrate components cellulose and hemicellulose, as kinetic studies on the individual components lignin, cellulose and hemicellulose have shown according to Willner [Willner05b].

6.4.6 ECONOMIC CONSIDERATIONS OF KDV AND DOS PROCEDURES

Willner claims the following energy and mass balance for wood liquefaction using the DoS process without internal hydrogen production [Willner06a].

Energy balance: (Wood 18 MJ/kg, Oil 38 MJ/kg, Coal 32 MJ/kg, Gas 9 MJ/kg)

100 e% wood + 7 e% H₂ + 5 e% primary energy consumption
= 80 e% oil + 18 e% coal + 12 e% gas + 2 e% V

Mass balance:

100% wood + 1% H₂ = 38% oil + 29% water + 10% coal + 24% gas

If internal hydrogen production (60 MJ/kg H₂) is assumed during wood liquefaction using the DoS process, these balances change as follows.

Energy balance: (Wood 18 MJ/kg, Oil 38 MJ/kg, Gas 9 MJ/kg) 100 e%

wood + 12 e% primary energy consumption = 80 e% oil + 12 e% gas + 20 e% V

Mass balance:

100 m% wood = 38 m% oil + 24 m% gas + 38 m% CO₂

These balances are based on a number of assumptions, at least some of which are questionable. The energy balance is calculated using calorific values, which is unusual (normally the heating value is the relevant parameter) and must be taken into account when comparing with other balance analyses. The calorific value of the wood is that of anhydrous wood; the energy required for the drying process is not considered. An elemental balance (C, H, O) is missing. This is problematic because the material flows within the plant are not fully considered, and thus it remains unclear how much of the so-called initial mash oil is ultimately removed with the product oil.

The terms oil, gas, and coal are not defined in any way, making it impossible to understand the basis for the accounting. The definition of "coal" should be better formulated as a solid, carbon-rich residue, which in turn should be specified in terms of its elemental composition.

Describing the byproducts is important for a plausible presentation of the overall system, as this can significantly influence the economic viability of the process. Information on the type and composition of the gas and the residues (C/O/H distribution) is lacking, so the question of whether these residues could pose a disposal problem cannot be answered.

Figure 6-26 shows a comparison of single-stage (KDV and DoS processes) and two- or multi-stage processes for the production of liquid fuels from biomass. The products listed, methanol and FT diesel, represent multi-stage processes via gasification with subsequent synthesis, ethanol represents saccharification and fermentation, and RME (rapeseed oil methyl ester) represents biodiesel. The data for the known processes largely originate from a 2002 study by Daimler-Chrysler. The direct liquefaction data assume an annual biomass yield of 15 t DM/ha and a biomass price of €60/t DM [Willner05b].

Prozess	Wirkungs-grad*	Ausbeute l/ha/a	H _u MJ/kg	Dichte kg/l	Ausbeute kW/ha	Kosten €/l	Kosten €/l Diesel***
Methanol	40-55 %	5.000	21,1	0,8	2,7	0,36	0,77
Ethanol	33-50 %	4.200	27,7	0,8	2,9	0,44	0,72
RME	45-54 %	1.600	37	0,9	1,7	0,55	0,60
FT-Diesel	40-47 %	2.000	42,5	0,85	2,3	0,70	0,70
KDV-Diesel	70-75 %	7.000	32	0,85	6,1	0,30	0,40
DoS-Diesel	69-74 %	6.000	38	0,85	6,1	0,31	0,35

* Wirkungsgrad (energetisch) = (Produktheizwert-Prozessfremdenergie) / Rohstoffheizwert

** 1 toe (ton of oil equivalent) = 41,87 GJ

*** €/l Diesel = €/l Dieselaquivalent = € / 36,1 MJ

KDV- und DoS-Diesel-Erträge für 15 t TS/ha a

Quelle für konventionelle Vergleichsprozesse: DaimlerChrysler-Studie Juni 2002

Figure 6-26: Biomass liquefaction: Process comparison [Willner05b]

The efficiency calculations for the DoS and KDV processes are based on anhydrous biomass, without taking drying costs into account. A discrepancy is noticeable in the calorific value data between Figure 6-19 and Figure 6-26 for the KDV process (42 and 32 MJ/kg, respectively). The respective reference years for the state of process development, and thus the basis for the cost analysis, are not specified.

Another cost calculation for the catalytic direct liquefaction of biomass using the DoS process can be found in Figure 6-27 [Willner05a, Willner05c].

An availability of 7,200 hours per year is a very optimistic estimate for a concept that has not yet proven its suitability for continuous operation outside of the laboratory. The cost calculation does not include any items for the refinery processing of the crude oil.

Landwirtschaftlicher Biomasse-Ertrag:	20 t TS/ha a
Energetischer Wirkungsgrad:	70 %
Produktölausbeute:	40 Gew.-%
Heizwert des Produktöles:	32 MJ/kg
Wirtschaftlichkeit:	
Anlagenkapazität (Biomasse):	5.420 kg TS/h
Verfügbarkeit:	7.200 h/a
Jahreskapazität (Biomasse):	39.000 t TS/a
Jahresölproduktion (Dieselsiedebereich):	18,3 Mio Liter/a
Biomassekosten:	60 €/t TS
Reststoffentsorgungskosten:	100 €/t
Investitionskosten:	6,7 Mio €
Biomassejahreskosten:	2,34 Mio €/a
Katalysatorjahreskosten:	1,17 Mio €/a
Reststoffentsorgungsjahreskosten:	0,08 Mio €/a
Investitionsjahreskosten (10 J., 6%):	0,91 Mio €/a
Personaljahreskosten (3-Schichtbetrieb):	0,35 Mio €/a
Wartungsjahreskosten (6% d. Invest./a):	0,40 Mio €/a
Sonstige Betriebsjahreskosten:	0,25 Mio €/a
Gesamtjahreskosten:	5,5 Mio €/a
Produktherstellungskosten:	0,30 €/Liter

Figure 6-27: Biomass liquefaction: Process comparison [Willner05]

6.4.7 B/M PROCESS: MUEBORIT

Process developer:

Environmental Technology Stefan Bothur

Contact: Thomas Müller (mueborit@gmx.de), Stefan Bothur (umwelt.bothur@gmx.de), Hohe Strasse 15, 01561 Wildenhain, +49 3522 507749 or +49 351 2878942

Starting with conventional biomass gasification, the process developers have developed a patented catalyst-based digestion process for biomass. In collaboration with IFE Leipzig, investigations were conducted into digestion processes for dust gasification. Joint research on liquefaction is being carried out with HAWO ökologische Produktions-, Handels- & Logistik GmbH & Co. KG Hohenbucko. The process developers claim to have achieved a virtually complete conversion of wood into a liquid energy carrier.

Converting biomass into standard-compliant fuels involves considerable energy expenditure. The BM process does not aim for this; instead, it seeks to convert biomass into a liquid, combustible form in a simple way, thus making it usable as a substitute for heating oil or as a raw material for further syntheses for material applications.

This requires the conversion of lignin into soluble phenol derivatives (lignates), the reduction of the cellulose molecular size (peeling reaction, hydrolysis, etc.), and the breaking of the bonds between the components of the lignocellulose. One possible process is solvolysis (modification of the molecules through degradation reactions), whereby the water solubility of the biomass is increased by salt formation at the hydroxyl and carboxyl groups.

Lignocelluloses are completely dissolved in a potassium carbonate hydrate melt (approximately 30% water content) in a batch stirred tank reactor at approximately 5 bar overpressure (i.e., 6 bar abs.) and below 200°C. The process referred to here as "dissolution" encompasses a mixture of physical and chemical processes (molecular degradation, disproportionation reactions, salt formation at functional groups, etc.). The solution then contains predominantly organic salt ions (e.g., carboxylates, alkoxides). Organic compounds are then separated from the solution (density approximately 1.5 kg/m³) using a simple column (water as a carrier, separation via an overhead column). Further separation methods are under investigation.

The resulting product is a dark brown mixture of various compound classes. The calorific value of the product depends on the desired yield. The higher the yield, the higher the calorific value.

The more polar the compounds become, the more polar they are. Measurements at yields (in terms of energy) up to approximately 40% showed values of 35-37 MJ/kg. Residual materials are incinerated to recover process heat. The product's stability with regard to unwanted reactions during storage (polycondensation reactions, etc.) is also yield-dependent.

The residue remaining in the reactor still contains organic, polar substances that can be almost completely extracted. With acidification and the use of extraction agents, an energy yield of nearly 100% can be achieved. The process energy can be recovered and the potassium carbonate regenerated by burning the non-extractable portion.

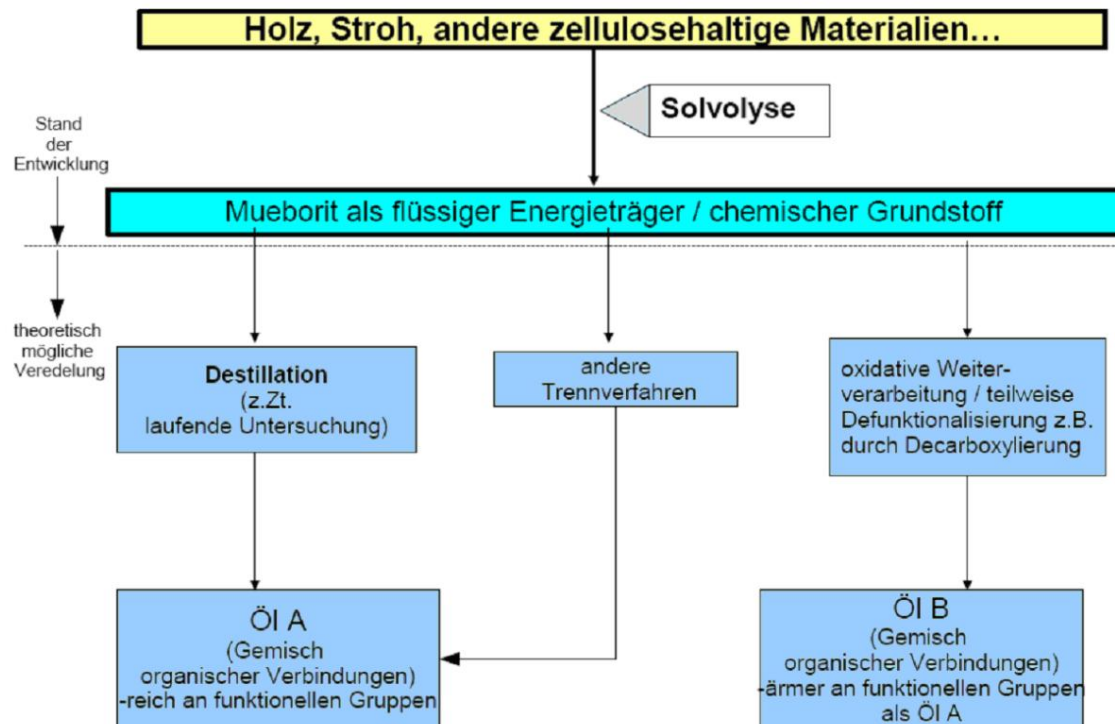


Figure 6-28: B/M process -- Solvolysis of lignocelluloses, [Müller06]

The developers see the advantages of their method in the following points:

- Process conditions (pressure, temperature, chemical aggressiveness) do not pose any special challenges
Requirements for material, design and installation location of the apparatus
- The process steps for the production and utilization of mueborite can be separated in time and place.
- According to current knowledge, possible plant sizes can be approximately 50-
Starting with 100 kW of thermal power.
- Theoretically, any lignocellulose-containing material can be used in the process.

Target users are self-producers of the input materials, either to cover their own energy needs or as a source of income from the sale of the products.

Next planned steps in process development:

- Construction of a practical training facility to determine process parameters
- Investigation of the physical and chemical properties of the product Mueborit with regard to its intended use.

6.4.8 LOW TEMPERATURE CONVERSION (LTC) OF ORGANIC RESIDUES

Process developer:

Gießen-Friedberg University of Applied Sciences

Contact: Prof. Dr. Ernst Stadlbauer, Wiesenstraße 14, 35390 Gießen, 0641/3092322

The so-called low-temperature conversion (LTC) of biomass is intended to

- aliphatic hydrocarbons (oil, C-5 to C-20),
- graphitic carbon with minerals,
- non-condensing gases (CO₂, KW C-1 to C-4) and
- Reaction water with dissolved salts

The process is carried out at atmospheric pressure, without oxygen, and at temperatures of 350 to 400°C in the presence of catalysts. It is called "Catalytic Defunctionalization of Organic Substances: CHNOS". The catalysts used are not specified.

Over the years, the initial sketches of the process (Figure 6-29) have evolved into a highly developed plant concept (Figure 6-31).

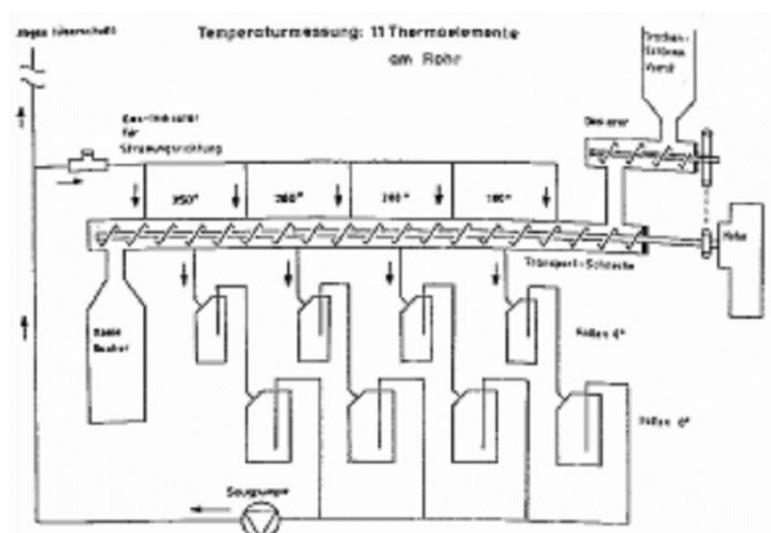


Figure 6-29: Schematic of an apparatus for the continuous low-temperature conversion (LTC) of sewage sludge, Prof. Bayer – Tübingen; from: E. Bayer, Kutubuddin, M. Korr. Abw., 29, 6, 1982

Based on the fundamental work done at the University of Tübingen since 1980, the following are Observe activities:

- 1990s: Trials in Canada and Australia (Bayer patent)
- Working in Germany (Steger / Aicher patent)
- From 1997: Construction of commercial facilities: Perth (ESI company), Rositz (Aicher company)
- From 2000: BMBF pilot plant: Rehau (Bayer, Südleider company / Leather Institute, ESI)
- From 2001: Laboratory trials with animal meal and sewage sludge (LET GI / Bayer Tübingen)
- 2003 - 2005: DBU pilot plant in Füssen (LET, W + F, RÜ, AZV Füssen)
- Since March 1, 2006: AiF project Fuels from animal fat and plastics
- In the application process: EU demonstration and experimental facility.

The following substances have been processed using this direct liquefaction method so far:

- Sewage sludge of various stabilization methods
- Animal and meat bone meal
- Rapeseed press cake, tar sands, bleaching earths
- Animal fat & used fats
- Plastics: PE, PP.

The NTK recycling concept is shown in Figure 6-30.

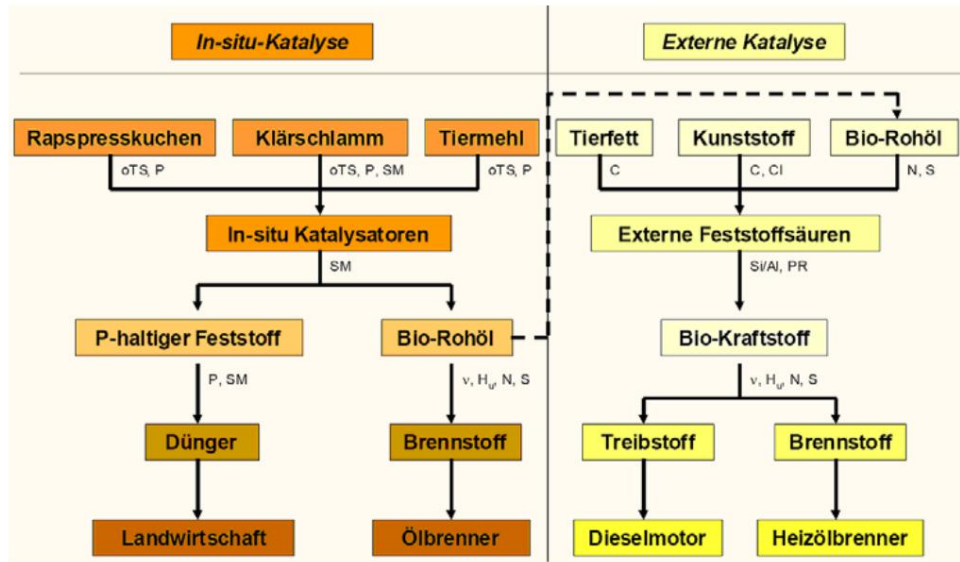


Figure 6-30: NTK utilization concept

Between March 2003 and October 2004, anaerobic and aerobic sewage sludge as microbial biomass, as well as animal meal, meat and bone meal and animal fat as animal biomass from animal carcass disposal, were subjected to low-temperature conversion (LTC) on a laboratory and pilot scale.

The reactor concept is based on the NTK model of a heterogeneously catalyzed reaction between the gaseous organic substances escaping from the biomass and the catalyst system, consisting of the solid carbonaceous residues.

This is a continuously mixed fixed-bed loop reactor with a spray condenser. The resulting condensate is collected in a buffer tank. The condensate then enters a three-phase centrifuge and is separated into reaction water, crude oil, and dust (see Figure 6-31).

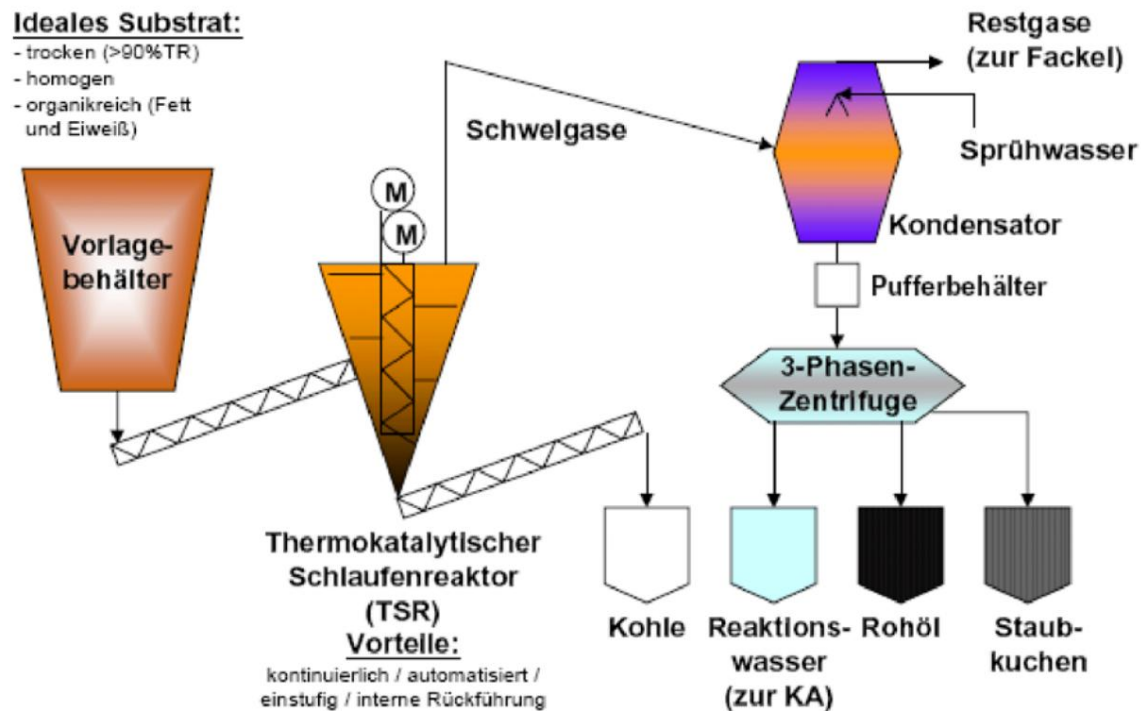


Figure 6-31: Process diagram of the condensation and separation system with tube condenser and Gravity separator [Stadlbauer06]

The oil yield from anaerobically stabilized sewage sludge is lower at 6-8% than from aerobic, unstabilized sewage sludge (15-30%). The oil yield is primarily determined by the fat and protein content of the biomass being processed.

Magnetic resonance spectroscopy (NMR) and infrared spectroscopy characterize the NTK crude oils obtained at 400°C under exclusion of oxygen as aliphatic hydrocarbons with an aromatic content of at most 5%, see Figure 6-32. Unreacted fatty acids are in the range of 2-5%, depending on the substrate.

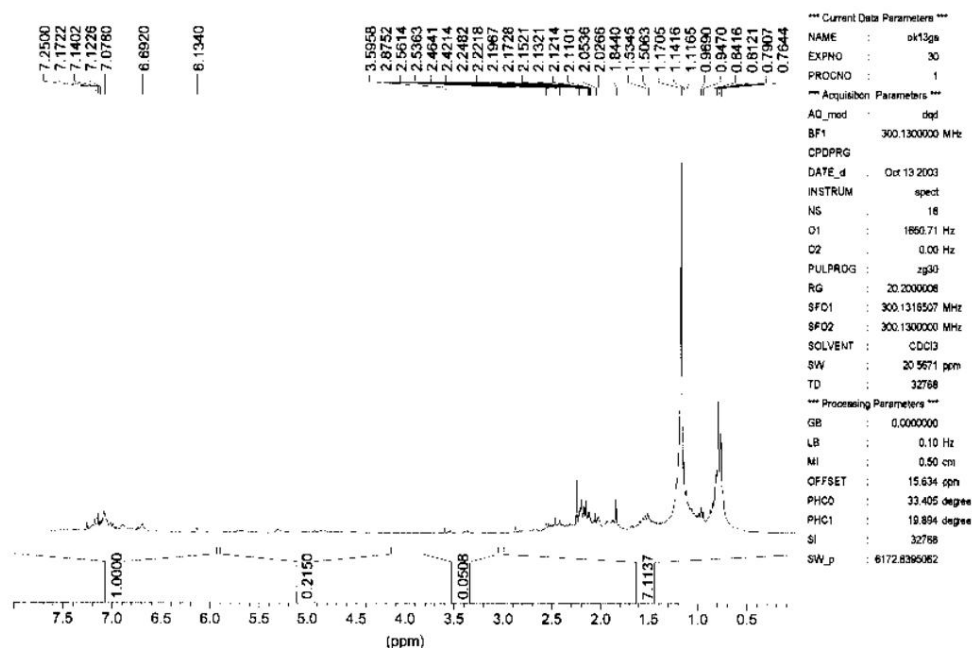


Figure 6-32: ^1H -NMR of NTK oil from sewage sludge/pilot plant; predominantly found Aliphatic compounds, few aromatics [Stadlbauer06]

In sewage sludge, heavy metals accumulate predominantly in the solid, carbonaceous residue at 400°C, depending on their volatility. In meat and bone meal, this residue contains approximately... Phosphate, at 27%, represents a source of biogenic fertilizers. According to E. Stadlbauer, the phosphate content was determined using ICP-MS and photometric methods. In meat and bone meal or animal meal, the heavy metal profile is predominantly influenced by the natural trace element content. The heavy metal issue is particularly relevant in sewage sludge. However, even here, solutions exist through halide volatilization.

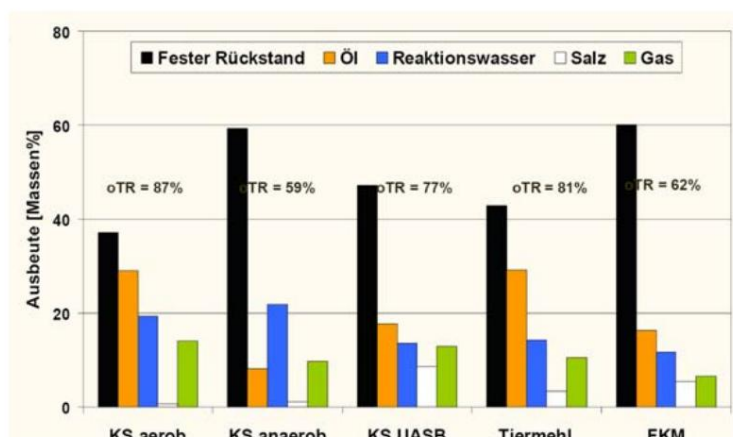


Figure 6-33: Mass balances of various sewage sludges (based on TR) at 400°C [Stadlbauer06]

Fester Rückstand aus Substrat	Analysenparameter								
	Ausbeute ¹	Asche	Schüttdichte	H _u	Energie ²	C	H	N	S
	[%]	[%]	[kg/m ³]	[MJ/kg]	[%]	[%]	[%]	[%]	[%]
Kom1ae	37,0	34,0	540	19,8	37,4	50,5	2,6	6,7	0,7
Kom2an	59,2	62,7	740	9,3	49,6	25,4	1,8	2,9	1,4
Kom3ae	53,4	64,2	440	10,4	42,1	26,1	1,4	3,9	0,4
Kom4an	67,9	91,2	671	1,7	15,8	7,0	0,4	1,3	1,1
Kom5ae	60,6	68,6	641	8,3	66,7	21,6	0,88	2,36	1,73
Kom6ae	61,3	64,5	587	10,0	46,1	24,9	1,62	3,8	0,62
Kom7an	n.b.	86,4	459	n.b.	n.b.	12,9	0,45	0,49	0,75
Ind1ae	81,8	87,1	553	n.b.	n.b.	9,4	1,0	0,9	0,4
Ind2ae	68,5	77,4	523	5,6	49,8	15,2	1,0	2,5	0,9
Ind2UASB	47,1	41,3	456	19,3	47,8	45,2	3,1	8,7	5,2
Ind3ae	24,0	48,5	464	15,0	21,5	38,5	2,8	7,2	2,3
TM1	n.b.	43,7	n.b.	n.b.	n.b.	35,9	2,1	6,1	<0,33
TM2	42,8	51,8	630	13,9	32,2	34,9	2,5	5,8	<0,33
FKM	60,1	67,2	680	8,2	33,7	22,8	1,9	4,4	<0,33
Ölschiefer	89,0	95,0	1143	n.b.	n.b.	3,34	0,23	<0,14	0,61
Mamona-Öl	12,4	n.b.	n.b.	n.b.	n.b.	79,8	12,9	n.n.	<0,33
Bleicherde	65,4	85,3	653	2,1	12,3	9,91	0,71	<0,14	0,43
Weizen	32,4	1,8	273	30,6	65,2	64,5	3,83	6,61	0,42
Raps	27,9	16,5	306	29,6	32,6	72,1	6,97	5,42	0,33
Raps mit Kat.	29,0	18,0	206	28,5	35,1	69,4	4,92	5,39	<0,33
Rapskuchen	34,7	16,1	345	27,2	47,6	64,5	3,83	6,61	0,42
Rapskuchen mit Kat.	40,4	16,3	331	26,5	54,0	65,2	4,49	6,61	0,38

¹ bezogen auf Substrat-Trockenmasse

² bezogen auf den Heizwert des Substrats

Figure 6-34: Analysis parameters of the solid residues from the conversion of various substrates [Stadlbauer06]

Figure 6-34 uses the following abbreviations: Kom: municipal sewage sludge, Ind: industrial sewage sludge, TM: animal meal, FKM: meat and bone meal, ae: aerobic, an: anaerobic and UASB: upflow anaerobic sludge blanket reactor.

The conversion of animal fat into aliphatic hydrocarbons (heating value > 40 MJ/kg) can be catalyzed at 400°C by dealuminized zeolites, while at 550°C predominantly alkyl aromatics are formed. The operator has filed a patent application for the production of liquid fuels from animal fat in this regard.

The analyses presented below show heating oil-like products (Figure 6-35 and Figure 6-36). The process developers do not claim to be able to produce fuels that meet standards.

The focus of development is moving towards the use of organic waste materials and plastics in a recycling process. The use of primary biomass is only of minor importance [Stadlbauer05].

	NTK-Öl aus KS (400°C)	NTK-Öl aus Tierfett (Wessalith, 400°C)
Ausbeute [%]	6,0	72,9
Heizwert [MJ/kg]	38,0	41,3
Dichte [kg/l]	0,9	0,8
Viskosität [mm ² /s]	5,9	2,3
C [%]	83,7	86,1
H [%]	14,6	13,8
N [%]	2,4	<0,14
S [%]	0,3	<0,34

Figure 6-35: Analysis results of NTK oils from sewage sludge and animal fat [Stadlbauer06]

Parameter	Heizöl EL	KS-Öl	Tierfettöl
Heizwert [MJ/kg]	42,0	38,0	41,3
O ₂ in %	5,5	2,7	5,6
T _{Gas} in °C	134	157,2	133
λ	1,34	1,15	1,37
CO ₂ [%]	11,0	13,4	11,3
NO _x [ppm]	68	432 ¹	98
SO ₂ [ppm]	30	-	0
Rußzahl in %	0,0	>3	0,4

Figure 6-36: Results from the combustion of NTK oils [Stadlbauer06]

6.4.9 OZMOENERGY (AUS)/ENVOSMART (NL)

The Australian company Ozmoenergy / Ozmotech Pty Ltd specializes in the liquefaction of plastic waste. The patented process is distributed worldwide from the Netherlands by Envosmart, also based in the Netherlands. This process is considered the origin of many commercially available and research-oriented systems for the liquefaction of plastics and waste oils.

According to the patent holder, the diesel oil / synthetic distillate (thermofuel) produced by liquefaction is suitable as fuel for the operation of combustion engines, generators and as an energy source for industrial combustion plants as well as fuel for CHP power plants.

Suitable materials include plastics made from: HDPE, LDPE, MDPE, PP, PE, and PS. Plastics made from: ABS, NY, PUR, and EVA (for which additives may be used) are moderately suitable. Not suitable are: PVC, PET, plastic-coated materials, and cellophane.

An overview of the semi-automatic process for liquefying plastics with a capacity of 10-40 t/d is shown in Figure 6-37.

The plastic waste enters the pyrolysis chamber via the dosing system. As the internal temperature rises, the plastic begins to melt, and pyrolysis commences. The gases produced during this process are passed through a patented catalyst converter and, during the catalytic decomposition process, are converted into light oil fractions. No information is provided regarding the type or function of this catalyst.

The cooling process in the condenser causes the oil to enter the recovery tank. A centrifuge cleans the oil, removing impurities such as water or small carbon particles. The clean oil then flows into the storage tanks, although a small portion is consumed as fuel within the system.



Figure 6-37: Process diagram OzmoEnergy, <http://www.ozmoenergy.de/technologie>, as of April 21, 2006

Table 6-4: Raw materials and reaction conditions for the Ozmoenergy process

Types of plastics	Reaction temperature [°C]	Recovered oil [l/kg] 0.94 1.15	By-product [%]
PE	420	0.95	1.68
PP	400		0.15
PS	350		5.82
Mixture of PE (70%), PP (15%) and PS (15%)	420	1.02	0.96
Flexible container bags (PP, PE)	390	0.96	2.20

(By-product: Materials remaining after combustion (dry coal, etc.), as a percentage of the plastics used; Foreign materials: Foreign substances, e.g., various paper waste – the permitted proportion of foreign materials is a maximum of 7%)

The recovery rate and the properties of the oil vary depending on the type of plastic and the decomposition temperature. Approximately 1 liter of oil can be recovered from 1 kg of plastic, provided it is polyethylene (PE), polypropylene (PP), or polystyrene (PS). The biggest difference compared to commercially available petrochemical products is that their combustion is cleaner and they do not contain any chemical elements that are not already present in the plastic waste.

were.

6.4.10 PLASTIC RECYCLING TECHNOLOGY (GOSSLER)

Process developer:

Gossler Envitec GmbH

Contact: Michael Gutknecht, Dr. Henryk Zmuda, Borsigstraße 4-6, 21462 Reinbeck, 040/72709250

Gossler Envitec developed three process variants for the production of synthetic fuels made from PE, PP, PET, PS, and mixed plastics. The thermocatalytic cracking reaction used takes place in the temperature range of 350–420°C at atmospheric pressure.

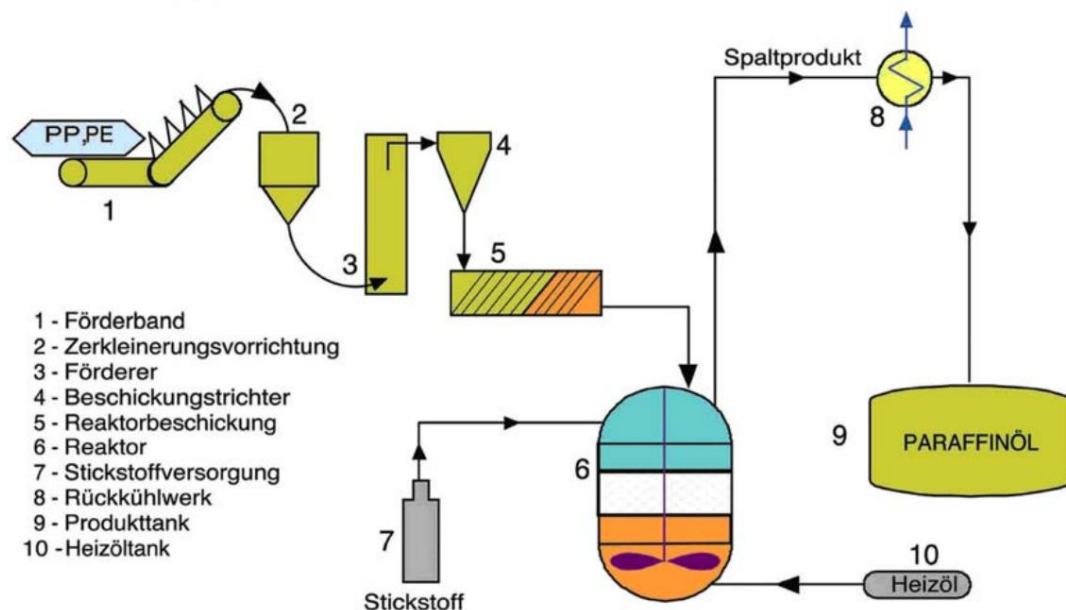


Figure 6-38: PE/PP catalytic cracking for the production of synthetic fuels [Gut06]

The PO waste to be recycled can contain residual amounts of PET without prior washing. Due to plant corrosion and the need for purity of the end products, PVC should only be present in very small quantities. According to the manufacturer, this method is particularly suitable for processing agricultural films and plastic containers contaminated with motor oil residue, as prior cleaning of the containers is unnecessary.

Based on this technology, a mobile pilot plant was recently built and inaugurated on June 23, 2005 [Gutknecht06].

6.4.11 CLYVIA CL500, DEPOLYMERIZATION PLANT Process

Developer:

Clyvia Technology GmbH,

Contact: Esther Stölzer, Friedrich-List-Allee 10, 41844 Wegberg-Wildenrath, 02432/893626

Development work began approximately ten years ago. Today, a pilot plant for the production of liquid hydrocarbons with heating oil-like properties through fractional depolymerization is available with a production capacity of 6 l/h in continuous operation.

The following are used

- Waste oils,
- Rinsing oils and
- Aliphatic plastics (crushed, 5-10 mm, max. 1 cm).

The process is carried out without a catalyst or the addition of hydrogen, but with the addition of hydrated lime and soda as additives. The heat of reaction is utilized in the process.

The waste oils, flushing oils, and plastics are preheated to 250 °C and treated with additives during this time. The main reaction is carried out at a maximum temperature of 420 °C and a vacuum of 200 to 300 mbar, after which the product is distilled off.

Wall coking in the reactor is to be counteracted by the small temperature difference between the reactor wall and the feedstock, as well as by a scraper operating in the reactor.

After any necessary desulfurization, the main products should be diesel or heating oil, with bitumen or fuel pellets as byproducts. In some cases, high pollutant levels may result in bituminous residues.

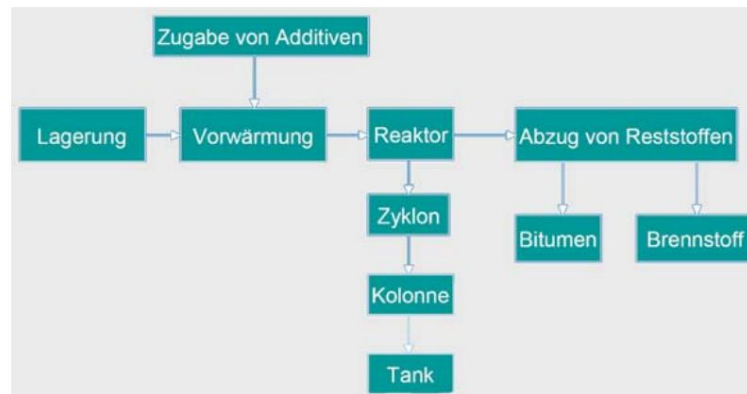


Figure 6-39: Block diagram Clyvia [Stölzer06]

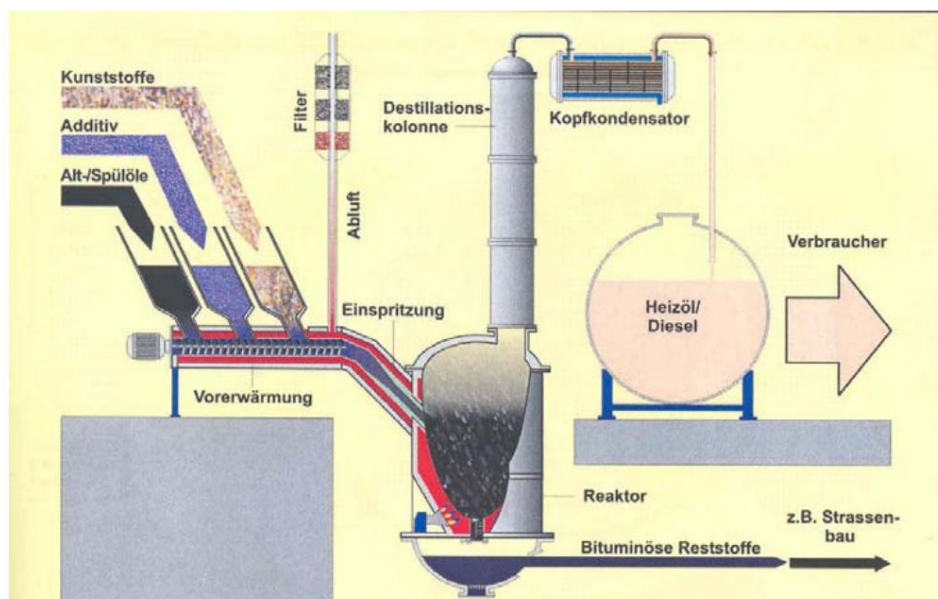


Figure 6-40: Process image Clyvia [Stölzer06a]

Clyvia Technology assumes that the depolymerization plants can be operated without a catalyst if waste oils, flushing oils and plastics are to be converted.

The small test facility also tested the Alphakat process, using 0.5% and 10% catalyst. Reaction time, temperature, and product quality were investigated, and the results were independent of the amount of catalyst added.

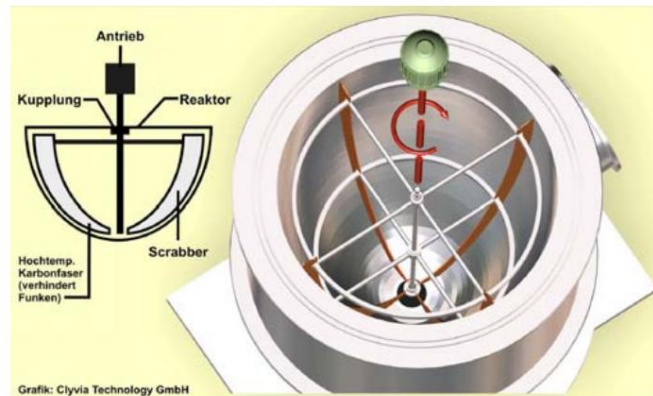


Figure 6-41: Scrabble system of the reactor, Clyvia Technology GmbH [Stölzer06a]

"Once the process temperature of 390 °C is reached, the cracked hydrocarbon fraction evaporates as diesel oil and is fractionated in the distillation column and condensed in the overhead condenser. This type of cracking differs fundamentally from conventional cracking processes such as pyrolysis. In particular, the process temperature is more than 300 °C lower, meaning very little carbon is produced. This carbon forms a black, tarry residue that must be removed from the reactor surface. The reactor surface is cleaned with a scraper (Figure 6-41). Maintaining a constant temperature ensures that only 4.5% of the product is gas, not 40%, which is used to heat the reactor..." [Clyvia05]

A Clyvia CL500 demonstration plant with a capacity of 600 l/h, a reactor volume of 1.5 m³, and a throughput of 10 t per day was recently commissioned. At the customer's request, the plant processes plastics in pellet form or as shredded wood chips, waste oils from the automotive industry, and heating oil tank cleaning residues (flushing oil). Initial tests of this plant with Australian crude oil produced a diesel-like product. Previous trials with green waste, wood chips, rubber, and bituminous materials were unsuccessful.

Recent investigations by the process developer in the Clyvia CL 500 test facility are examining whether bilge oil is suitable as a starting material for the production of heating oil by fractional depolymerization.

The fractions obtained during distillation, with a boiling range of approximately 205 °C to 375 °C, were analyzed at Aral Research in Bochum. As can be seen in Table 6-5, the quality of the bilge oil distillate, with regard to calorific value, cloud point, coke residue, water content, sulfur content, and ash, meets the requirements of DIN 51603-1 for light heating oil and the requirements for heating oil from refined oil according to DIN EN ISO 4259.

Table 6-5: Analysis of the product oil of a Clyvia CL500 system using bilge oil as feedstock [Stölzer06b]

Parameter	Einheit	IST-Werte laut Aral	DIN - Normen					
			51603-1 Heizöl EL leichtes Heizöl	51603-3 Heizöl S schweres Heizöl	51603-4 Heizöl ZT	Heizöl C	Reraffinate Heizöl R-LS	Reraffinate Heizöl R-TS
Dichte bei 15 °C	kg/m ³	850,8					ist vom Lieferer anzugeben	
Heizwert Ho	kJ/kg	45590						
Heizwert Hu	kJ/kg	42813			≥ 35000	≥ 35000	≥42000	≥42000
Flammpunkt	°C	49,0	> 55	> 80	≥ 55	≥ 85	> 61	> 61
Viskosität bei 20 °C bei 40 °C bei 70 °C bei 90 °C	mm ² /s	* > 4,057 *	< 6,00				≤ 15	≤ 30 ≤ 15
Cloudpoint	°C	-9	< 3					
CFPP	°C	-10	-10				ist vom Lieferer anzugeben	
Koksrückstand (vom 10 % Rückstand)	% (m/m)	< 0,10	< 0,3	> 17	≤ 16	≤ 25	≤ 0,5	≤ 10
Wassergehalt	mg/kg	59	< 200	5000	≤ 30000	≤ 5000	≤ 2000	≤ 2000
Schwefel	mg/kg	< 3,0	< 50	28000	≤ 10000	≤ 9000	≤ 5000	≤ 10000
Gesamt- verschmutzung	mg/kg	77	< 24					
Asche	% (m/m)	< 0,001	< 0,01	0.15	≤ 0,05	≤ 0,9	< 0,02	0.05
Cetanzahl (BASF)		53						
Gesamthalogen, angegeben als Chlor	mg/kg	< 5,0					≤300	≤ 300

6.5 SUMMARY - PROCEDURE OVERVIEW

The direct liquefaction processes under consideration draw on, among other things, process variants and experience from coal research as well as plastics and waste oil recycling. Comparing the processes is difficult because the data made available by the process developers is very incomplete. The process descriptions in the study are based on the available manufacturer specifications. Process developers express concerns regarding the release of process parameters such as pressure, temperature, feedstocks, and catalysts.

The lack of analytical results complicates the technical evaluation and the assessment of the process's economic viability. For both, information on the type and composition of the product oil and gases, as well as the residues, is necessary. This applies equally to analyses for characterizing the carrier oil and to mass, energy, and elemental balances.

Some process and plant developers suggest marketable products, but economic considerations are usually absent or incomprehensible. Raw material processing is necessary in all process variants, but this is not discussed further by the suppliers. In particular, the oxygen content and/or corrosiveness of the product oils is almost always significantly too high in relation to fuel standards.

The oils produced are partly used in boilers and diesel engines. Commercial use currently exists only for smoke flavorings obtained from pyrolysis oils. Other potential applications include flue gas cleaning using chemically modified oils and the production of adhesive resins for wood-based materials.

The direct use of the product oils in burners or engines requires quality standards that have not yet been met. Key reasons for this lie in the nature of the feedstock, the methods used for separating solids and condensing the liquid products, and the absence of hydrogen in some of the processes. If the product oils are used as an intermediate product for synthesis gas production, their quality is not a critical criterion.

7 RECOMMENDATIONS FOR ACTION

In Germany, there is a significant number of largely uncoordinated development projects in the field of processes for the so-called direct liquefaction of biomass into liquid hydrocarbons (primarily for mobile applications). The vast majority of these projects are characterized by a limited scientific understanding of the chemical and physical processes involved. Analysis of the investigated direct liquefaction processes, insofar as it was possible based on the data provided only reluctantly by the developers, suggests that the applicability of "one-pot" or "one-step" processes without the use of hydrogen is not promising.

While extremely simplified views of the underlying process may be tempting and promise a simple reaction pathway ("one-step process"), they completely overlook the fact that a chemical formula reveals nothing about the structure of, for example, the components of wood and thus fails to explain the actual reaction process. Chemical reactions of wood degradation products fall within the realm of organic chemistry. The functional groups present (alcohols, acids, esters, aldehydes, ketones, etc.) decisively shape the reaction process. The decomposition of the wood components (cellulose, hemicellulose, and lignin) leads to a complex mixture of organic molecules with a multitude of such reactive functional groups and a correspondingly high potential for repolymerization, forming undefined solid products. The action of hydrogen under increased pressure on such mixtures plays an indispensable key role in the eventual breakdown of these functional groups into water and possibly CO₂.

Such a two-stage process, involving the digestion of plant-based raw materials followed by the treatment with hydrogen to break down the always oxygen-containing functional groups, should—if the direct liquefaction approach is to be pursued seriously in the future—draw on the experience of, among others, the paper industry. This sector has a long technical tradition and a multitude of process variants for digesting plant-based raw materials. This, combined with a subsequent hydrogenation step, appears to be the only sensible approach that, with considerable investment in further process development, could lead to a technically promising method for producing liquid hydrocarbons from biomass.

This technical statement, however, requires careful economic analysis, with particular importance placed on realistically defining the system boundaries. When establishing extensive process chains, from the provision and processing of biomass through the actual process, including the procurement of all involved equipment and chemicals, to the final product processing into standard-compliant, marketable products, individual aspects can easily be overlooked in cost analyses. Raw material availability and costs, as well as hydrogen supply, require special attention in this regard.

In addition to biomass-based processes, methods relating to the reconversion of sorted plastics and, in some cases, other waste materials into liquid hydrocarbons are also presented in this context. These are, as expected, generally applicable.

However, it remains unclear to what extent these approaches are economically viable, taking into account all costs along the process chain from collection and sorting to largely pure fractions, through the actual conversion process with subsequent refinery processing to standard-compliant fuels and energy carriers.

Suggestions for further funding measures

- Organization of a comparison campaign between currently available processes (based on an IEA study from the 1980s – possibly also embedded here in the IEA Implementing Agreement “Bioenergy”) – prerequisite: same material (wood) for all and an accredited analysis laboratory for all participants; accompanying economic evaluation of all participating processes according to a uniform scheme.
- Currently no public funding is available for the construction or operation of demonstration plants – Reason: Upscaling processes that are not sufficiently understood is not advisable.
- In the field of applied basic research, promotion of work that clearly incorporates existing knowledge and specifically closes gaps; use of experience from coal liquefaction and the paper industry (for the digestion of wood).

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