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Expert opinion on
Catalytic pressureless oiling
(KDV procedure)
the company Alphakat

created by

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Authority for Economic Affairs and Labour

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Summary

On behalf of the Free and Hanseatic City of Hamburg, Authority for Economic Affairs and Labour, The KDV process ("Catalytic Pressureless Oiling") from the company Alphakat will be used.

GmbH is being reviewed. In particular, the question to be answered is whether the KDV-

The process can convert biogenic residues (biomass) into diesel fuel.

The basis for this work is the scientific experimental research on KDV-

Procedures at the Hamburg University of Applied Sciences (HAW)

Hamburg) in the years 2005 to 2008 under the direction of Prof. Dr.-Ing. Thomas

Willner and the self-presentation of the company Alphakat.

The KDV process is a direct liquefaction process that processes organic substances.

single-stage using a heavy oil phase as the reaction medium at

Temperatures between 300 and 400 °C below atmospheric pressure with support

by catalysts into liquid fuels and byproducts. After

Alphakat claims that the KDV process is capable of processing biogenic residues.

from the agricultural and forestry sector, such as straw and wood, and many others

to convert organic waste directly into diesel fuel.

experimental investigations at HAW Hamburg using straw as an example

However, biogenic model substances have shown that the product oils with

diesel-like composition not derived from biogenic input materials,

but from the mineral base oil, which is used to start the process

The start-up oil is introduced into the reactor. This start-up oil is not used during the process.

regenerates, so that the process comes to a standstill as soon as the starting oil

is used up. Furthermore, it was found that the fast-running

High-temperature pumps (called "turbines" or "chamber mixers" by Alphakat),

which are used as energy input systems, due to extreme thermal

and are very susceptible to mechanical stress. This is where Alphakat comes in, which

to demonstrate the long-term suitability of new pump developments. Finally, it was possible to

The zeolite catalyst used showed practically no effectiveness, and was also ineffective in the following cases.

The use of biomass leads to very rapid coking, it has been observed. This finding is

This was also confirmed by studies conducted by the Leibniz Institute for Catalysis e.V. A

Another problem is the continuous removal of solid residues and

spent catalyst from the system.

Alphakat's claim is to produce organic waste materials through direct, single-stage processes
thermochemical-catalytic conversion to produce diesel fuel

According to scientific findings, only pure hydrocarbons are involved, which

Moreover, they must be straight-chain and saturated. Therefore, they are limited.

The application area of the KDV process is essentially limited to waste oils and

Pure polyethylene. For fats and waxes, the KDV process is unsuitable due to the...

Suitable due to its limited oxygen content. While this does not produce diesel fuel that meets standards,

But if the fats and waxes are sufficiently long-chain and saturated, they can

Products are created that may be suitable as diesel additive components.

For thermodynamic and chemical reasons, the KDV process is unsuitable for

The following groups of substances are selected under the boundary conditions of the KDV process.

No n-alkanes can be formed in the diesel boiling range:

- Lignocelluloses (e.g., biomass such as energy crops, wood, straw, rapeseed,
Grass cutting plant products, corresponding agricultural products
Waste products, etc., as well as processed products such as paper, cardboard, pulp
etc.),
- protein-containing substances (e.g. B. Sewage sludge, animal meal and others
Animal waste products, food, etc.),
- unsaturated hydrocarbons (e.g., rubber, car tires, etc.),
- Plastics with branched, aromatic and/or foreign atomic structures
Molecules (e.g. polypropylene, polyester, polyamides, PVC, polystyrene, etc.),
- Oils containing foreign atoms (e.g., PCB- and PCT-containing transformer oils, etc.),
- Carbonized components (e.g. in charcoal, lignite, bituminous coal)
- as well as aromatic refinery residues, bitumens, asphaltenes and tars.

The latter substances also often contain elevated sulfur levels, which necessitate post-treatment of the oils.

They are fundamentally problematic.

also mixed waste fractions (e.g. shredder light fraction, hospital waste,

Household waste, etc.), as these contain large proportions of the aforementioned problematic substances, which
are included.

1. Mandate and basis for work

On behalf of the Free and Hanseatic City of Hamburg, Authority for Economic Affairs and Labour,
The Office for Economic Affairs, Port, and Technology, located at Alter Steinweg 4, D-20459 Hamburg, is the
The "Catalytic Pressureless Oiling" (KDV) process of the company
Alphakat Gesellschaft für Katalytische Aufbereitungstechnologien mbH in D-96155
Buttenheim (Alphakat) is to be examined. In particular, the question to be answered is whether
The KDV process is capable of processing biomass (e.g., biogenic residues from agriculture-
and forestry sector, but also from the household and commercial waste sector)
to convert into diesel fuel.

The basis for this work is the scientific experimental research on KDV-
Procedures at the Hamburg University of Applied Sciences (HAW)
Hamburg) in the years 2005 to 2008 under the direction of Prof. Dr.-Ing. Thomas
Willner and the self-presentation of the company Alphakat /1/.

2 Principle and characterization of the KDV procedure

The KDV procedure from Alphakat, as described on the company's homepage /1/

As described and shown in the flow diagram in Fig. 1, it belongs to the group of such

These are the direct liquefaction processes mentioned. This refers to processes which

high molecular weight organic substances such as waste oil, plastics or biomass in

comparatively low temperatures in the range between 250 and 500 °C

Cracking reactions (**cracking** = splitting of molecules, in the case of large molecular chains)

(also called **depolymerization**) in a single stage (directly) into liquid fuels, so

The aforementioned crude oils are converted. The KDV process operates under **atmospheric pressure**.

or slight negative pressure at temperatures usually **between 300 and 400 °C**.

Within **direct liquefaction**, the KDV process belongs to the group of oil-phase processes, in which the conversion reactions take place in a

Heavy oil sump phase is carried out. The heavy oil phase, which is performed during

The reaction temperature does not evaporate, and it serves as a liquid reaction medium for

the continuously supplied input materials. From this sludge phase

The product oil vapors evaporate along with other volatile components such as

gases, water and possibly numerous water-soluble compounds such as organic compounds

Acids, aldehydes, ketones, alcohols, etc. This principle is called...

Reactive distillation, i.e., the combination of reaction and distillation. The reactor

This is simultaneously the first distillation stage for the evaporation of the target products.

Target products are liquefied outside the reactor by **condensation** and

captured. In principle, further distillation stages, such as a

Rectification for fractionating the produced crude oils, analogous to petroleum refining.

consequences.

Further information on the principle and different variations of

Direct liquefaction of biomass as well as the basic functions of

The swamp phase and reactive distillation are described in volume 28 "Biocrudeoil" of the Gülzower

Expert discussions, published by the Agency for Renewable Resources

(FNR), can be found /2/.

In the KDV process, the process is started by using a **mineral oil-derived**

Base oil or start-up oil is presented as a heavy oil sump phase in the reactor and first, together with an added initial filling of catalyst powder, onto

The reaction temperature is preheated before the continuous supply of raw material.

begins. The heavy oil sump phase participates in the conversion reactions and

It is therefore consumed. Ideally, it is continuously replenished by

Intermediate products from the decomposition reactions of the raw materials are replaced. The question is, whether this actually succeeds or whether new heavy oil (base oil) is constantly being supplied from the outside.

The supply that needs to be provided is of central economic importance and also

Subject of this report. Furthermore, solids accumulate during the heavy oil phase.

Residues that must be separated continuously and reliably. This also presents a challenge.

This presents a significant procedural engineering challenge.

In the case of the KDV procedure, the implementation processes are facilitated by the use of

Solid catalysts, which are presented as **powders in the heavy oil reaction phase**

and are finely dispersed, supported. Catalysts basically have the task of...

to lower the activation energies of chemical reactions and thereby

To increase reaction rates, to lower reaction temperatures

and/or to direct reactions, ideally without being consumed in the process.

In the KDV process, ion-exchange active zeolites (crystalline alkali or

alkaline earth aluminosilicates) are used as catalysts, which also have the task of

have the ability to bind pollutants such as heavy metals and halogens (e.g., chlorine). In

In this case, the catalyst is consumed and must be regenerated. According to

Alphakat can be modified by adding lime or soda.

regenerate /1/.

A technical feature of the KDV process is the **mechanical**

Energy supply. This is achieved via fast-running high-temperature pumps (in

the legend of Fig. 1 calls it a **"high-performance chamber mixer"** and it is mentioned in the title of Fig. 1 (referred to as a **"turbine"**), which circulates the heavy oil sump phase.

drive. This is intended to reduce unwanted temperature gradients in the reactor system.

This avoids or achieves nearly homogeneous temperature fields.

Energy input pumps are subject to extreme thermal and mechanical stresses.

exposed, as the circulating swamp oil is under comparatively high conditions

To promote reaction temperatures, usually between 300 and 400 °C, and with abrasive solids such as catalyst powder and mineral residues from the raw materials are contaminated. Therefore, an important question is the service life of these materials. Energy input systems.

According to Alphakat, a chemical peculiarity of the KDV process lies in its design. in that, regardless of the input material , **diesel fuel** is available directly as a ready-made product. A product is created. Alphakat uses both "waste and" as suitable raw materials.

Residual materials such as

- Plastics of all kinds, including the PVC content,
- Rubber and car tires,
- Waste oils, waxes and greases of all kinds, including transformer and hydraulic oils,
- agricultural waste, animal waste products and spoiled food,
- Hospital waste, sterilized, dewatered and dried, as well as
- all refinery residues, bitumen, tars, etc.

as well as "biologically renewable raw materials" (biomass) such as

- Wood,
- Rapeseed and
- other plant products

specified /1/.

This statement completely contradicts experience with all other known

Direct liquefaction processes, in which **crude oils** are always produced that are in the

As a rule, there is no or only very limited similarity to conventional petroleum products.

especially fuels, unless one uses aliphatic waste oil or

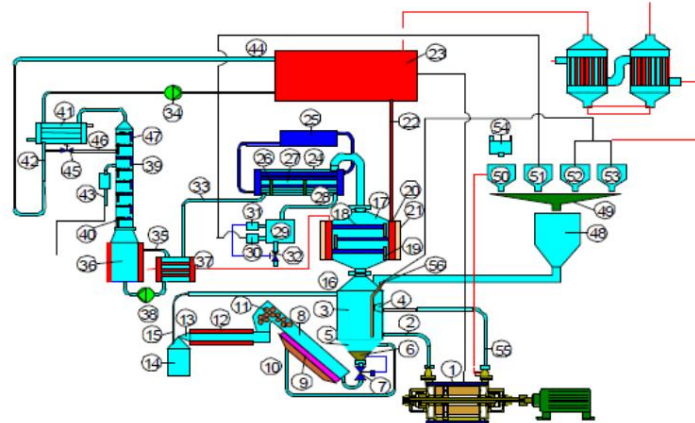
comparable substances are used as raw materials. The question is whether this special characteristic of the

The KDV process is actually feasible for all the numerous and chemically very

different types of residues mentioned by Alphakat, especially for biogenic

Residual materials (biomass) are the focus of this report.

Das weltweit erste Patent einer mit Turbine geheizten
Chemieanlage
Hier die Erzeugung von Diesel in dem KDV-Prozeß –
Anlage Kanada



- | | |
|--|--|
| 1. Hochleistungskammermischer | 0. pH – Messer |
| 2. Ansaugleitung des Hochleistungskammermischers | 31. Leitfähigkeitsmessung |
| 3. Separator | 32. Ablassventil |
| 4. Venturidüsen | 33. Rohrleitung Diesel |
| 5. Konischer Teil des Separators | 34. Vakuumpumpe |
| 6. Feste Rückstände (Schlamm) | 35. Wärmeträgerkreislauf |
| 7. Austragsklappe | 36. Umlaufverdampfer |
| 8. Pressschnecke | 37. Rohrleitung |
| 9. Filterwand | 38. Umlaufpumpe |
| 10. Produktdampfrückleitung | 39. Destillationsanlage |
| 11. Rückstandskuchen | 40. Glockenböden |
| 12. Heizschnecke | 41. Kondensator |
| 13. Düse | 42. Produktableitung Generator |
| 14. Heißproduktlagerbehälter | 43. Produktableitung Endprodukt |
| 15. Produktdampfrückleitung | 44. Leitung zum Stromerzeuger |
| 16. Mitteldestillate | 45. Refluxventil |
| 17. Dampfbehälter | 46. Produktrücklauf |
| 18. Destillationsboden | 47. Obere Kolonnenböden |
| 19. Rücklaufkanal | 48. Eingangsteil Rohstoff- und Reststoffzugabe |
| 20. Heizung | 49. Eingangstrichter |
| 21. Isolation | 50. Dosiereinrichtung für Katalysator |
| 22. Abgasleitung | 51. Dosiereinrichtung für Neutralisationsmittel |
| 23. Stromerzeuger | 52. Reststoffeintrag flüssig |
| 24. Kondensator | 53. Reststoffeintrag fest |
| 25. Kühlkreislauf | 54. Big- bag- Entleerungsvorrichtung |
| 26. Trennblech | 55. Temperaturmeßgerät nach Hochleistungskammermischer |
| 27. Überlauf | 56. Niveaumessmer |
| 28. Wasserableitung | |
| 29. Wasser- und pH – Behälter | |

Fig. 1: Flow diagram of the KDV process from Alphakat /1/

3 Target product: Diesel fuel

According to Alphakat, the KDV procedure is intended to be used independently of Diesel fuel is always produced as the input material /1/. A prerequisite for the Evaluating this claim requires knowledge of the properties of the target product.

Diesel fuel, also called diesel oil, is obtained during the distillation of crude oil in the form of light gas oil (middle distillate), specifically as a distillation cut approximately between 180 and 380 °C. The main components of diesel are linear, saturated hydrocarbons, so-called **n-alkanes**, whose carbon chain lengths (C number) are essentially determined by They have C-9 to C-23. Therefore, diesel molecules approximately have the chemical composition C-9 to C-23. Molecular form (CH₂)_n, so that **diesel molecules** appear in chemical reaction equations can be approximately represented by the short formula **CH₂**.

A typical medium-sized diesel molecule is, for example, n-cetane, as shown in Fig. 2. shown. The cetane number is then named, a characteristic of diesel fuel that is a measure of The ignition capability is important. The **cetane number** according to EN 590 must be at least 51. so that the diesel fuel has sufficient ignition capability. Both **linearity** and **Saturation** of hydrocarbons is necessary for a sufficiently high cetane number. Branched and unsaturated - especially aromatic - hydrocarbons worsen the cetane number.

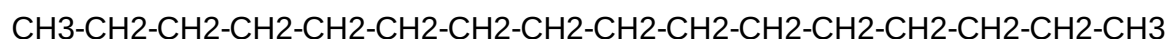


Fig. 2: Typical diesel molecule n-cetane = n-hexadecane = C₁₆H₃₄

A typical GC-MS analysis (gas chromatography-mass spectrometry analysis) The composition of a diesel fuel is shown in Fig. 3. The C numbers at the top of the The dominant peaks in Fig. 3 represent the homologous series of n-alkanes and specify the respective carbon chain length.

Important standard properties of diesel fuel according to EN 590 are listed in Table 1. compiled. The calorific value of diesel is approximately 42.5 MJ/kg.

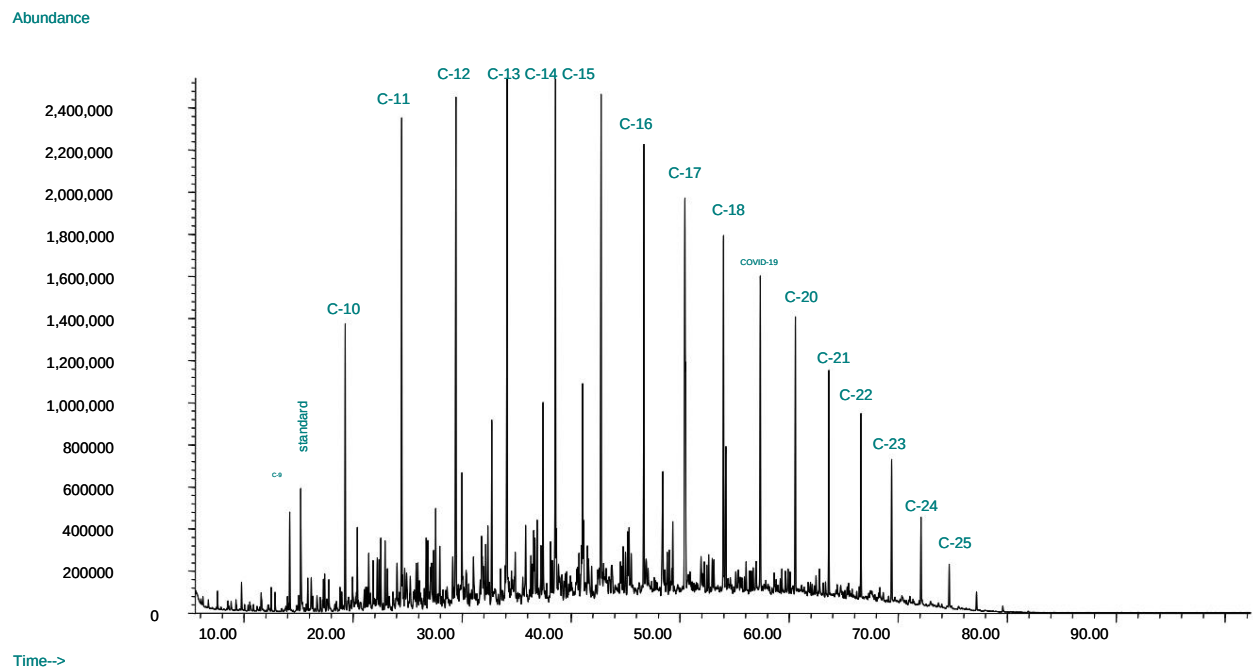


Fig. 3: GC-MS analysis of a commercially available diesel fuel
(C number at the peaks = carbon chain length of the corresponding n-alkane)

Table 1: Properties of diesel fuel according to EN 590
(PAH = polycyclic aromatic hydrocarbons)

parameter	min.	max.	Unit
Cetane number (standard)	51		
Density at 15 °C	820	845	kg/m³
kinematic viscosity at 40 °C	2.0	4.5	mm²/s
Flash point	55		°C
Coke residue		0.30	wt.%
Ash content		0.01	wt.%
water content		200	mg/kg
Sulfur content		10	mg/kg
PAH content		11	wt.%
Distillate content at 250 °C		65	Vol.%
Distillate content at 350 °C	85		Vol.%
Distillation temperature at 95% by volume		360	°C
Fatty acid methyl ester content		5	Vol.%

4 properties of biomass

According to Alphakat, the KDV method should make it possible to...

Single-stage thermochemical liquefaction also from biomass, which has practically no contains hydrocarbons, but consists predominantly of highly oxygenated and also consists of aromatic organic molecules, directly **n-alkanes** of

To produce diesel quality /1/. The discussion of whether this is possible, and the Interpretation of the experimental results with regard to this question can only be against the background of the composition and chemical properties of Biomass is used.

Solid plant biomass such as straw, wood, etc., belongs to the so-called Lignocelluloses. They consist essentially of cellulose, hemicelluloses and Lignin. Some typical compositions are summarized in Table 2.

The main component of straw and wood is cellulose, which makes up about half of the The dry matter is the main component. The remainder can usually be divided into approximately equal parts. Assign hemicelluloses and lignin.

Table 2: Composition of biomass in wt.% of dry matter /3/

	Cellulose	Hemicellulose	Lignin	Stärke/Zucker
Zuckerrübe	7	8	1	72
Weizenpflanze	18	12	8	38
Maispflanze	19	11	9	40
Weizenstroh	38	26	18	-
Corn stover	38	22	18	-
Miscanthus	47	20	25	-
Nadelholz	44	19	28	-
Pappelholz	50	17	18	-
Buche	42	23	20	-
Zeitungspapier	61	16	21	-

Cellulose

Cellulose belongs to the carbohydrates and is a long-chain, unbranched protein.

Polysaccharide. The degree of polymerization (the number of monomer units in a

The polymer molecule of cellulose in plant biomass ranges between 7,000 and

15,000 /4/. The gross molecular formula of cellulose is $[C_6H_{10}O_5]_n$. Cellulose

consists of sugar units, specifically β -glucose units as monomers, which

are $\beta(1,4)$ -glucosidically linked, as shown in Fig. 4. Due to the long

In unbranched molecular chains, cellulose serves as a tensile-strength structural substance of the

Plant fibers. The remaining free hydroxyl groups protrude from this band and

are able to form hydrogen bonds with neighboring chains. In the

In solid cellulose substance, these chains lie more or less parallel to each other.

They are stored and form crystalline areas.

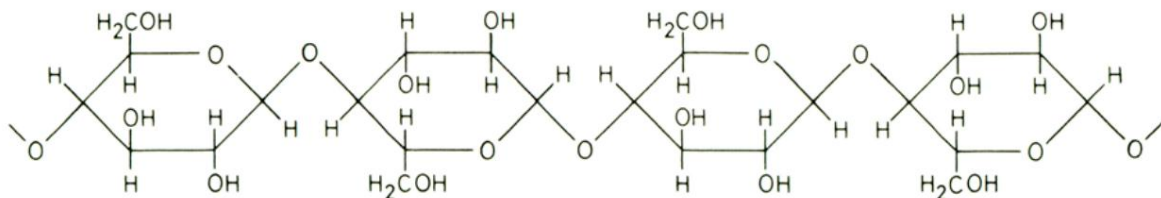


Fig. 4: Structural formula of cellulose /4/

The thermal stability of cellulose is moderate. In the case of thermal decomposition, the

between 250 and 300 °C and reaches its maximum at 350 °C /4/, break

regardless of whether catalysts are used or not, among other things the

CO bonds, especially the glucosidic links between the

Monomers (glucose units) /4/. Fig. 5 shows simplified possible

Reaction pathways of the thermal decomposition of cellulose. Almost

exclusively oxygen-containing compounds such as anhydrous sugars (e.g.

levoglucosan), furans as well as low molecular weight acids, alcohols, aldehydes, etc., all

Molecules that have no relation whatsoever to diesel molecules (see Section 2).

B.

Regarding the question of whether diesel molecules can form in this process, it remains to be seen whether diesel molecules can be formed.

It is important that carbon chain lengths (C chains) of a maximum of 6 C atoms

They arise through pure depolymerization (splitting of molecules) without superimposed

Polymerization (continuous linking of molecules to form longer chains) consists of

Therefore, there is no possibility of producing diesel molecules from cellulose between C-9 and C-23 (cf.

Section 2) to generate. Furthermore, even if superimposed polymerization occurs.

It would not take place without hydrogenation by high-pressure hydrogen.

It is possible to obtain saturated n- by eliminating the numerous OH groups (see Fig. 4).

to form alkanes, which are essential for diesel (see section 2).

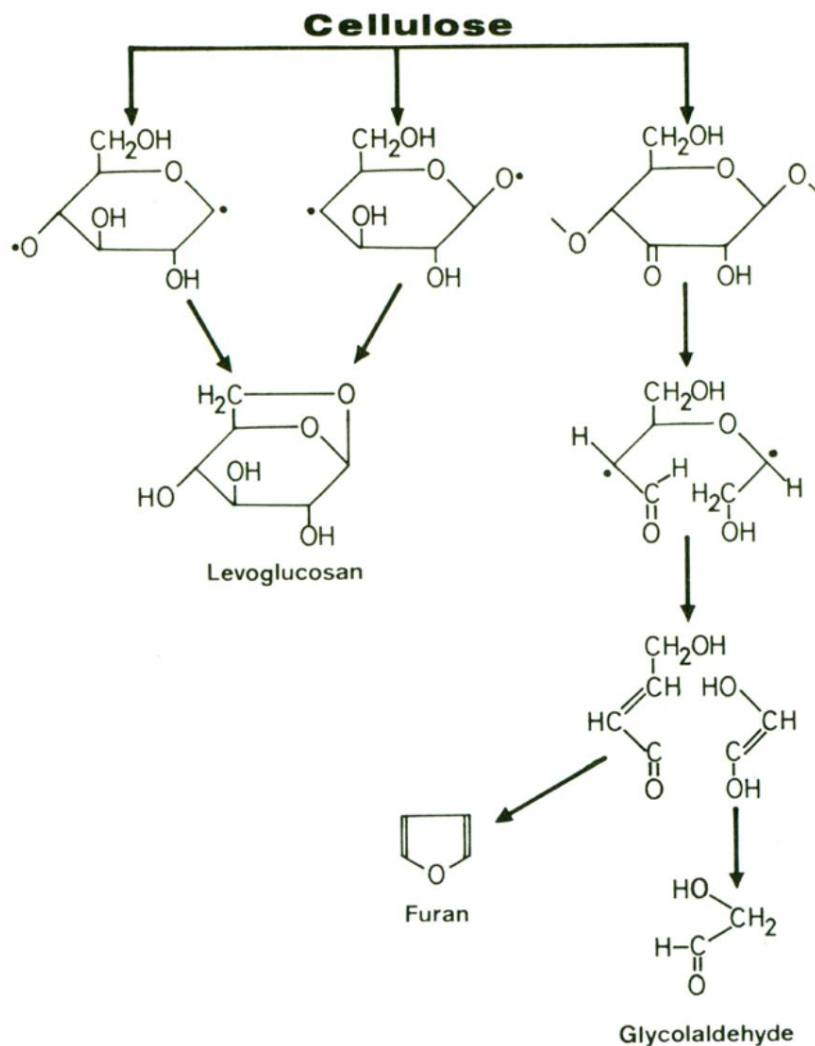


Fig. 5: Simplified reaction pathways of the thermal decomposition of cellulose /4/

Hemicelluloses (polyoses)

Hemicelluloses, or polyoses, like cellulose, are carbohydrates.

Unlike cellulose, hemicelluloses are spatially cross-linked and thus serve in

Plant material acts as a binding agent to absorb pressure loads. They consist of

made up of different sugar building blocks, predominantly pentoses.

The degree of polymerization of hemicelluloses is significantly lower than that of cellulose and

The value is usually given as between 50 and 200. Figure 6 shows an example of one.

Section of a hemicellulose molecule.

Among the three main components of lignocellulose, temperature stability is particularly important.

Hemicelluloses are least affected. Decomposition begins at around 220 °C [4]. In the case

thermal decomposition, in turn, is independent of whether catalysts are used.

Whether or not hemicelluloses will be produced applies to them due to their chemical similarity.

practically the same as for cellulose (see above). Thus, under the conditions of

The KDV process is therefore also not possible to produce diesel molecules from hemicelluloses.

generate.

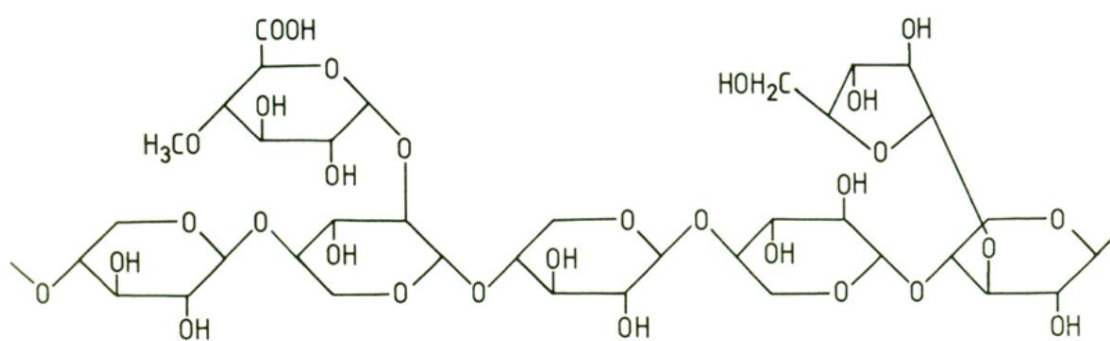


Fig. 6: Structural formula for hemicelluloses of softwood [4]

lignin

Lignin, originally meaning the actual "wood substance", plays a role as spatially cross-linked cement substance with particularly high strength, primarily for enormous pressure stability of woody stem or trunk substance in and It enables the incredible heights that trees can grow. Furthermore, it offers Its hydrophobic nature protects against water penetration.

Cell wall material. Lignin is not a carbohydrate like cellulose and Hemicelluloses, but is an aromatic polymer which is essentially composed of It is built up of phenylpropane units /4/. Fig. 7 gives a structural example.

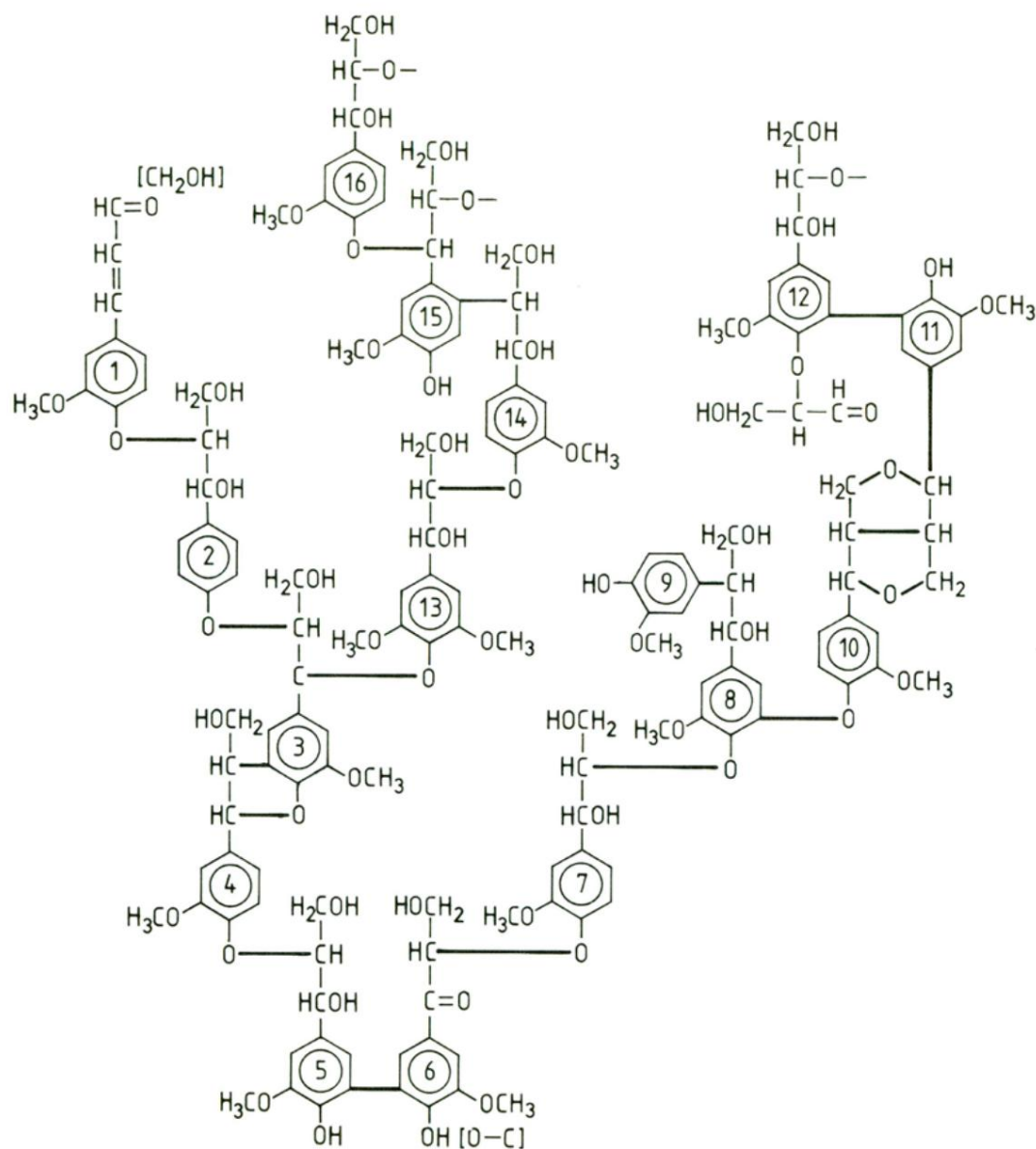


Fig. 7: Structural formula for spruce lignin according to Adler /4/

Lignin is relatively thermally stable. Compared to other lignocelluloses-

Components - hemicelluloses and cellulose - lignin decomposes under the influence

It is affected most slowly by heat. Thermal degradation does not even begin at 500 °C.

completed /4/. Essentially, during thermal decomposition the

Phenylpropane units (monomers) remain isolated. In particular, the

Aromatic nuclei (benzene rings) due to their particularly high thermal stability

obtained within the temperature range of the KDV process. Typical degradation products of the

Lignins are shown in Fig. 8. The use of [something] can also be based on this fundamental characteristic.

Catalysts won't change anything. Even if it were possible to remove the aromatic rings.

(benzene rings) would require a significant lack of hydrogen to break up the rings.

to produce saturated hydrocarbons (alkanes). Therefore, among the

Under the conditions of the KDV process, no diesel molecules are produced from lignin.

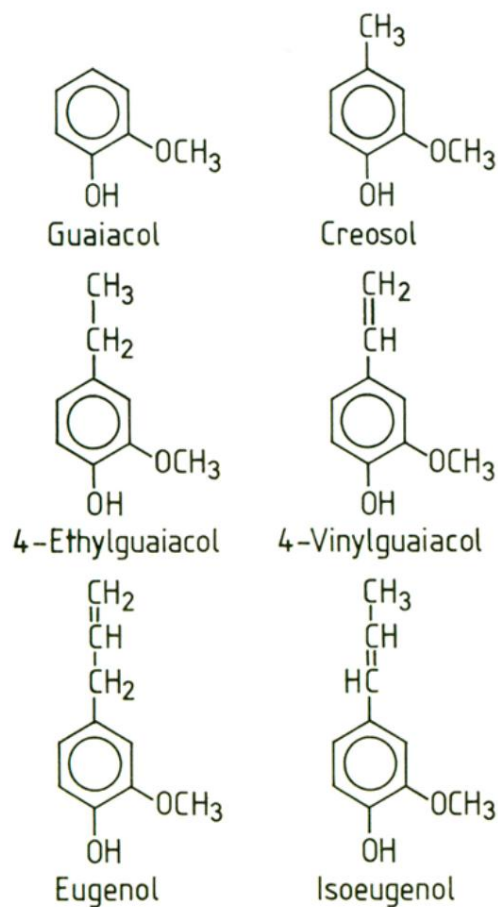


Fig. 8: Degradation products of the thermal decomposition of lignin /4/

Minor components

The minor components include the extractives. This term encompasses all low molecular weight hydrophobic compounds of wood, which can be compared with organic. They can be extracted with solvents, summarized. They consist essentially of Fats, waxes, resins, and tannins. Inorganic by-products are referred to as ash. The extractives play a role in the thermal decomposition of Biomass plays a subordinate role, as it is only present in small proportions in biomass. usually occur significantly below 10% /4/.

Pyrolysis of biomass

In all thermochemical decomposition processes, including catalytic ones, Pyrolytic reactions play an important role. Therefore, the study of pyrolysis Information about the basic decomposition behavior of organic materials. Pyrolysis is the term for the thermal degradation of chemical compounds. under exclusion of oxygen. In pure pyrolysis without additives or auxiliary substances, The reaction medium is an oxygen-free inert gas atmosphere that contains the volatiles. absorbs decomposition products. Pyrolysis produces solid, liquid, and gaseous products. Depending on the goal of the pyrolysis, attempts are made to maximize the yield of a to maximize these products.

The classic pyrolysis of wood produces, with slow heating and moderate temperatures, Temperatures up to about 450 °C; charcoal as the main product (wood carbonization).

Flash pyrolysis aims to process biomass through particularly rapid heating. to convert them directly into predominantly liquid products (pyrolysis or bio-oils) at temperatures between 450 and 500 °C. However, flash pyrolysis oils are not "oils". In the classical sense. They are even hydrophilic to a certain degree and therefore insoluble in normal oils. They typically contain about 25-30%. dissolved water. The calorific value of flash pyrolysis oils is extremely low, often even slightly lower than the calorific value of the biomass raw material. The status of Flash pyrolysis is described by Meier /5/.

High-temperature pyrolysis ultimately occurs at temperatures usually exceeding 800 °C. predominantly into gaseous decomposition products.

All pyrolysis processes are based on the thermal degradation of organic matter.

Polymers under oxygen exclusion. As described above, the following occur:

Main components of the biomass (cellulose, hemicelluloses and lignin) under

The effects of heat largely split it into low-molecular-weight fragments.

Countless different decomposition reactions occur as a result of the

different binding energies in the main components. In Fig. 9 the

Pyrolytic degradation of beech wood is depicted using thermogravimetry.

Decomposition of biomass begins at approximately 220°C and is initially essentially

the thermal decomposition of the hemicelluloses, above 250 °C followed by

of cellulose. The first decomposition products consist of

mainly water, carbon dioxide, carbon monoxide, methanol and

Acetic acid. The main phase of the reaction takes place in the temperature range of 330 to 400 °C.

pyrolytic degradation of lignin /6/.

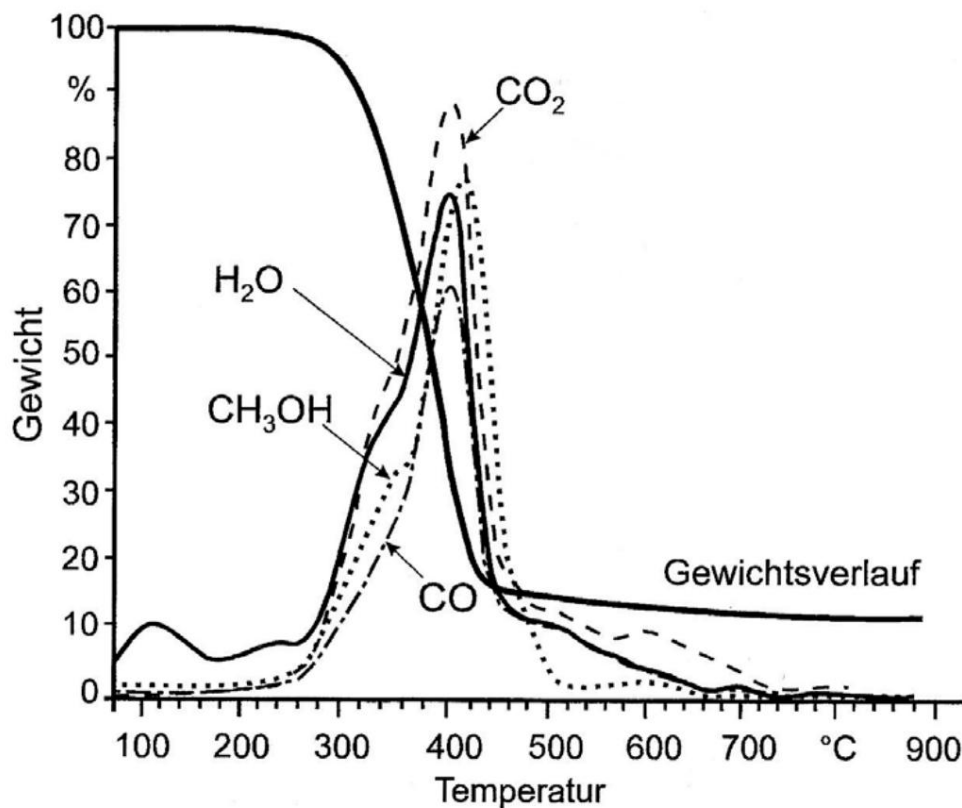


Fig. 9: Degradation of beech wood under the influence of temperature (heating rate 20 °C/min) /6/

5 properties of zeolitic catalysts

An important feature of Alphakat's KDV process is the use of zeolites.

of type A (see section 6.2) as catalysts, which are added in powder form to the heavy oil

The sump phase of the reactor system is stirred in. The following are some

The fundamental properties of such catalysts are summarized.

Zeolites are crystalline alkali or alkaline earth aluminosilicates. Their basic building blocks...

consist of SiO_4 and AlO_4 tetrahedra (silicon oxide and aluminum oxide)

Tetrahedra). By linking such tetrahedra via shared oxygen atoms

Secondary building blocks of the zeolites are formed, which develop into crystalline structures.

aluminosilicates, which have strictly regular pore systems with

Each possesses uniform pore sizes on the order of molecular diameters. Fig.

Figure 10 shows the structure of an A-zeolite, with each corner of a polygon containing a

silicon or aluminum atom represented, while at the center of each edge a

Oxygen atom sits [7].

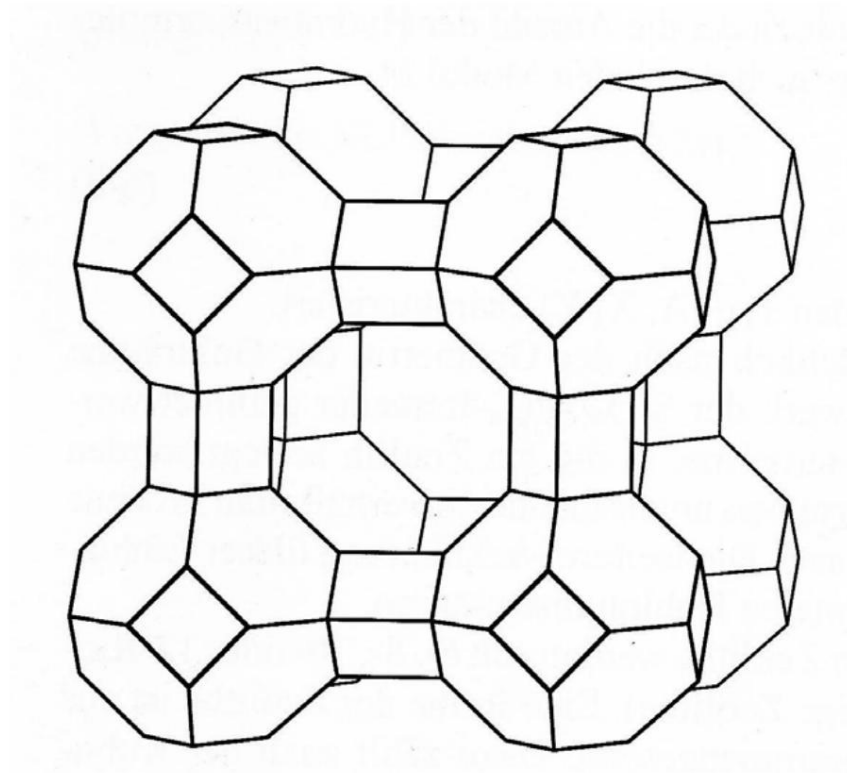
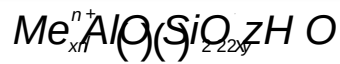


Fig. 10: Crystal structure of an A-zeolite [7]

Zeolites have the following general formula /7/:



In this formula, n corresponds to the valence of the metallic cation Me, usually Alkali metals such as sodium or potassium of valence 1, or alkaline earth metals such as Calcium or magnesium of valence 2. The molar ratio y/x or Si/Al- The relationship significantly determines the structure and properties of the Zeolites. An A-zeolite, for example, has a Si/Al ratio of 1 to 1.5. Because the uniform pore size in the range of molecular sizes and the defined Due to their porous structure, zeolites are often also referred to as molecular sieves.

The **zeolite A407 from Alphakat** (see section 6.2) is the Sodium form of an A-zeolite. According to the manufacturer Tricat/Südchemie in Bitterfeld describes this zeolite as a weakly active catalyst with a pore size of approximately 4×10^{-10} m (0.4 nm). Only small, unbranched particles can fit into such very small pores. Molecules inside.

Fig. 11 gives an overview of zeolites with different pore sizes in the Comparison with molecular sizes /8/. Figure 11 shows that in the alpha cat- Catalyst A407 with 0.4 nm pore size (= **Na-zeolite of type A = NaA "4A"** in Fig. 11) neither the raw material molecules nor the desired target molecules of Diesel fractions cannot pass through its pores. Therefore, this catalyst cannot pass through them. the conversion of raw material molecules nor the formation of diesel molecules support. Its ineffectiveness for catalysts is already quite high. A concentration of 10 wt.% in the reactor sump phase was achieved by the Leibniz Institute for Catalyst eV confirmed /9/.

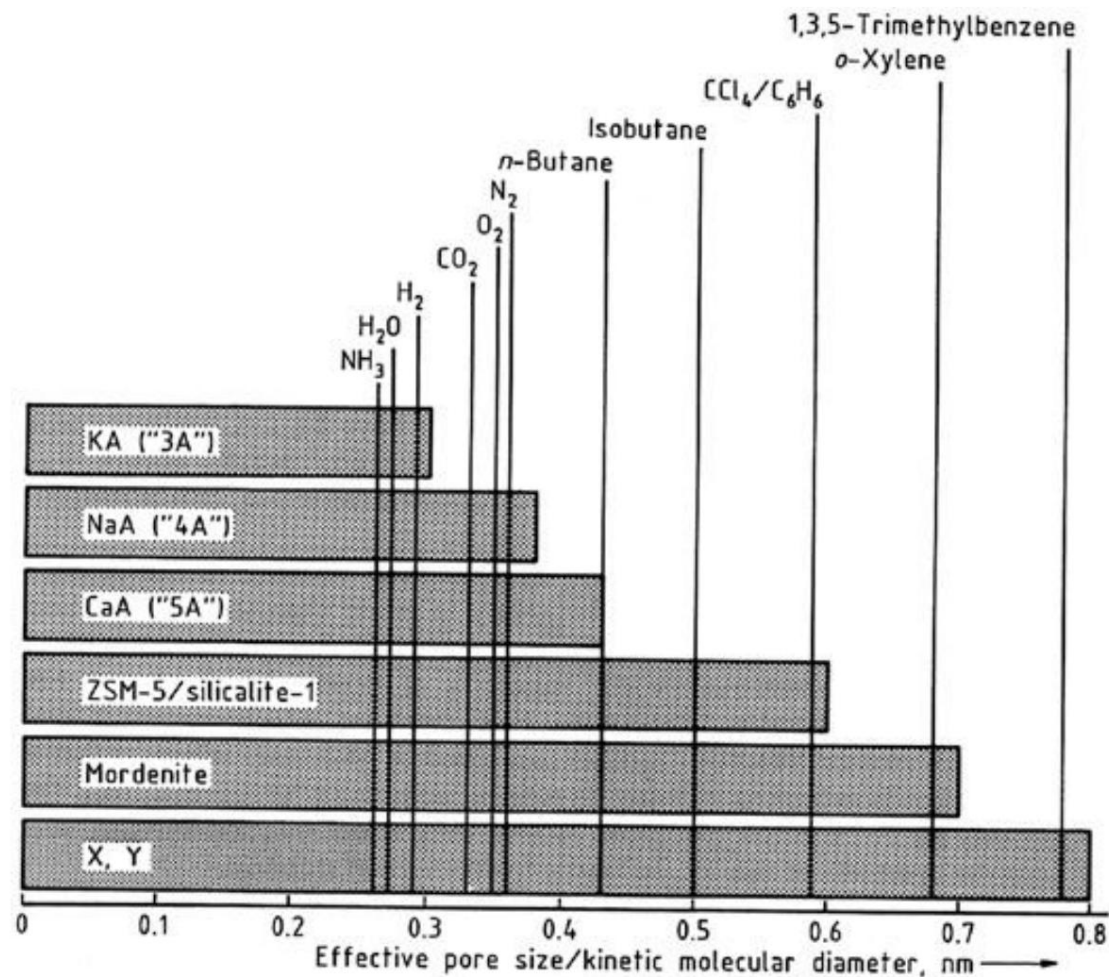


Fig. 11: Pore sizes of industrial zeolites compared to molecular sizes /8/

At HAW Hamburg, a weak effectiveness of the Alphakat catalyst was observed.

A407 only occurs in extremely high concentrations of over 25 wt.% in the

The reactor sump phase was detected. This observation confirms that this

Under the conditions of the KDV process, the catalyst does not behave as it normally would with zeolitic catalysts.

Catalysts are usually located on its large internal surface area (pore surface), but

It can only be effective via its comparatively small external surface area (particle surface area). Furthermore,

the catalyst loses effectiveness during the conversion of biomass or

comparable substances prone to carbonization as a result of coking of its

The surface very quickly loses its effectiveness completely (rapid deactivation).

6 Experimental investigations on the KDV procedure

Between 2005 and 2007, the KDV procedure was implemented at HAW Hamburg under

Management by Prof. Willner on behalf of Volkswagen AG in Wolfsburg and Lanor

Energy Systems Deutschland GmbH in Oer-Erkenschwick experimentally in

The pilot plant (raw material capacity 5 kg/h) was investigated.

The pilot plant scale was purchased by Alphakat and installed in the pilot plant of the HAW

Hamburg installed and operated. For the mechanical energy input, the following were used:

Pumps from Speck Pumpen Systemtechnik GmbH (Speck) in Roth near Nuremberg

deployed. This involved close collaboration with the company Speck, which in 2004 delivered the first Alphakat system.

has equipped a commercial data center in Mexico with pumps and therefore has access to the

who had the most practical experience in this area, cooperated. As a model raw material

At the pilot plant, cereal straw was predominantly used for biomass.

Specific scientific questions such as the stabilizability of

The swamp phase, the origin of the diesel-like product oil phase, and the

Reaction pathways of the biomass used and the heavy oil supplied as

The start-up phase was carried out in parallel and subsequently on a laboratory scale until 2008.

(Raw material capacity 1 kg/h) was investigated. The laboratory facility also served to carry out

comparative studies on different raw materials of biomass (e.g.

Cereal straw, miscanthus straw, rapeseed press cake, wood) via sewage sludge and

Animal meal to plastic-containing waste materials (e.g., shredder light fractions,

Hospital waste, DSD fractions, contaminated Plastic waste,

Pure plastic types). Furthermore, liquid input materials such as fats and oils, waste oils, vacuum residues

from petroleum refining and pyrolysis oils were also used.

tested.

The comparability of the results from the pilot plant and laboratory plant was examined in

Confirmed by comparative tests. This report focuses on the

Model studies on straw conversion, conducted on both apparatuses

were carried out.

6.1 Base oil used to start the KDV process

The process is initiated according to the KDV procedure via **submission**.

a mineral oil-based base oil, also known as starting oil, pre-oil or start-up oil

designated as the container into which a first filling of catalyst powder (see Section 6.2) is placed.

is mixed in (for experimental procedure see sections 6.3 and 6.4). For the

For this purpose, a temperature-resistant **circulating oil from BP of the type** was used in the investigations.

Energol CS 220 is used. Table 3 lists the properties of the base oil.

Table 3: Properties of the base oil: BP circulating oil type Energol CS 220

classification	paraffin-based
Density at 15 °C	888 kg/m ³
Viscosity at 40 °C	214 mm ² /s
Viscosity at 100 °C	18.3 mm ² /s
Boiling point	approx. 400 °C
Boiling	approx. 630 °C
Flash point	290 °C
Pourpoint	-12 °C
Water content	0.04%
Sulfur content	approximately 0.3%
Oxygen content	< 1%
Paraffin carbon content	60-61%
Naphthene C content	33-36%
Aromatic C content	4-6%
Iodine number	approximately 5
Oxid ash	< 0.01%

Manufacturer's specifications

6.2 KDV catalyst used

According to the KDV process, the process uses a mineral oil-based base oil.

(see Section 6.1), into which an initial filling of catalyst powder is mixed and

During the raw material supply, additional catalyst was consumed to compensate.

catalyst is supplied (for experimental procedure see sections 6.3 and 6.4),

started up. **An ion-exchange active aluminosilicate** was used as a **catalyst**.

Alphakat **type A407** from the manufacturer Tricat/Südchemie in Bitterfeld

used. Table 4 lists the properties of the catalyst. Figure 12 shows

a particle size distribution of the catalyst measured at HAW Hamburg,

which results in an average particle diameter of approximately 7 μm .

The water release behavior of the catalyst at increasing temperature is determined by

a thermogravimetric measurement shown in Fig. 13.

The stoichiometric composition of the, determined via elemental analysis

The catalyst leads to the following approximate zeolite formula:

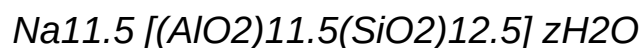


Table 4: Properties of the Alphakat A407 catalyst

Macroscopic form	white powder
Zeolite type ¹⁾	A
Zeolite form 1)	Na-form
Pore size 1)	0.4 nm
Mean particle diameter 2)	7 μm
Inner pore surface (BET) ²⁾	177 m ² /g
Water output up to 400 °C 2)	20% of the weight
2) pH value	10-11

¹⁾ Manufacturer's information Tricat/Südchemie in Bitterfeld 2)
Measurement HAW Hamburg

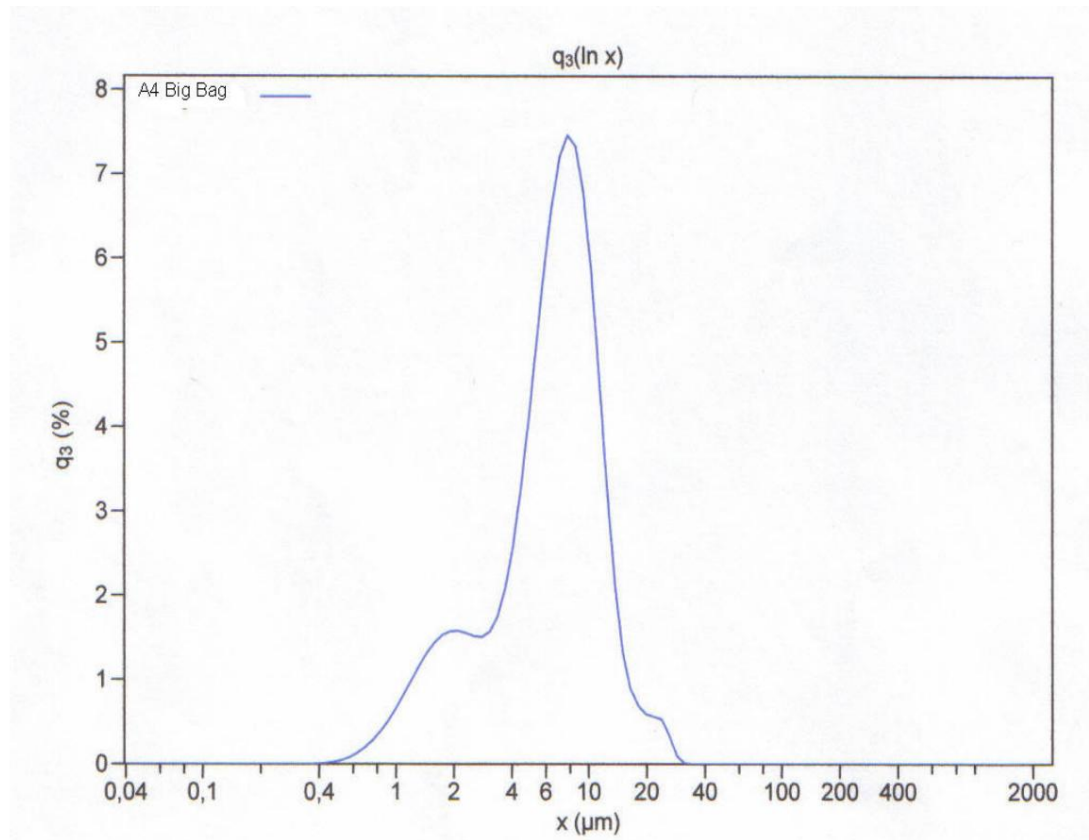


Fig. 12: Particle analysis of catalyst A407 (Study project M. Eichler, H. Kamm, S. Schippang, HAW Hamburg, June 2007)

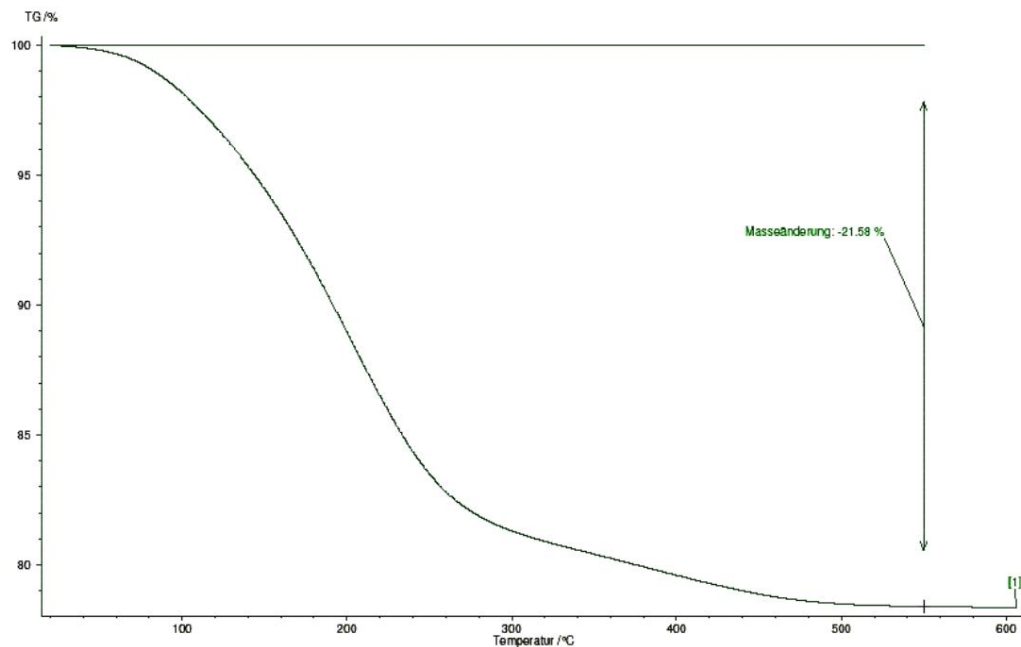


Fig. 13: Water release behavior of catalyst A407 as a function of temperature, measured via weight loss by thermogravimetry, heating rate 10 K/min under argon atmosphere (Master's thesis K. Oswald, HAW Hamburg, Dec. 2004, measurement TU Hamburg-Harburg)

6.3 KDV test apparatus on a 5 kg/h pilot plant scale

In 2005, a 5 kg/h pilot plant from Alphakat was purchased and installed in Technical center of the process engineering department of HAW Hamburg on campus Bergedorf installed. The capacity of 5 kg/h refers to the raw material input. The system operates at **atmospheric pressure** and is designed for semi-continuous operation. The operation is designed to be continuous with regard to raw material supply as well as gas and Condensate product removal, but discontinuously regarding the fixed Reaction residues that accumulate in the reactor during the experiment and only They can be drained and disposed of after the experiment is over. The operating temperature range is **between 300 and 400 °C**.

The flow diagram of the system is shown in Fig. 14. The stainless steel apparatus consists of the The core consists of a reactor with a volume of approximately 40 liters, through which the The heavy oil sump phase is continuously circulated as a reaction medium. This heavy oil circuit is operated by a high-temperature pumping system. maintain the heavy oil flow from the lower part of the reactor at It draws in atmospheric pressure and passes through a throttle valve into a cyclone separator. supplies the reactor, which is installed directly on top of it.

Other functions of the high-temperature pumping system include, on the one hand, the Homogenization of the heavy oil sump phase and, on the other hand, the energy input into the reactor system. Various pumps from the company Speck were used. The tests at the KDV technical facility of HAW Hamburg were conducted in direct The collaboration was carried out with Speck. The Speck company has already completed the first Commercial data center facility, which went into operation in Mexico in November 2004 was equipped with energy input pumps and thus had the longest experience in in this context.

The cyclone located directly above the reactor (see Fig. 14) has the function of... to allow the heavy oil sump phase to flow back into the reactor, thereby reducing the gas and to separate the vaporous reaction products and direct them upwards to the vertical to be passed on to the multi-stage distillation column installed above. At the top The gaseous and vaporous substances are extracted from the outlet of the distillation column.

The reaction products are fed to a condenser, where the vaporous products condense (liquefy) as oil and water phases, and are then collected in the subsequent condensate reservoirs. The fill level of the

The heavy oil sump in the reactor is monitored via a level indicator and a
Expansion vessel with viewing window checked.

The supply of shredded and dried raw material (biomass such as straw)
as well as the powdered catalyst, is continuously processed via a
Screw conveyor. The raw material is fed directly into the preheated
heavy oil sump phase is directed into the reactor. After the end of an experiment, the
Reactor sump contents with the solid residues enriched therein, including
The catalyst is drained from the bottom of the reactor into a sump collection container.
With this test setup according to Fig. 14, the essential characteristics of the KDV-
Process (see Fig. 1) such as a **heavy oil sump circuit with finely dispersed
Catalyst powder, a high-temperature pumping system for mechanical applications
Energy input** (referred to as "high-performance chamber mixer" in the legend of Fig. 1)
and referred to as "turbine" in the title of Fig. 1), a separation unit (in which
Pilot plant consisting of reactor and cyclone, called "separator" in Fig. 1
with additional solids separation) with the function of **reactive distillation**
(simultaneous reaction and first distillation stage to separate the product vapors)
as well as **product condensation** on a pilot plant scale and the
accessible to scientific investigation.

Fig. 15 shows the 5 kg/h test facility under construction in the technical center of HAW Hamburg.
still without insulation. Figure 16 shows the system in its operational state.

One **area of technical difficulty** remained the **high-temperature pumps** for
Energy input throughout the years of investigations at the
Pilot plant. All variants used by the Speck company were able to meet the requirements.
thermal and mechanical stresses (see Section 2) despite experience
Bacon in this area (see above) cannot be preserved for more than a few days. That was
While sufficient for test drives, it reveals a problem area for the technical
Implementation of the KDV procedure. This point therefore presents a particular challenge.
Challenge for the development of Alphakat's equipment.

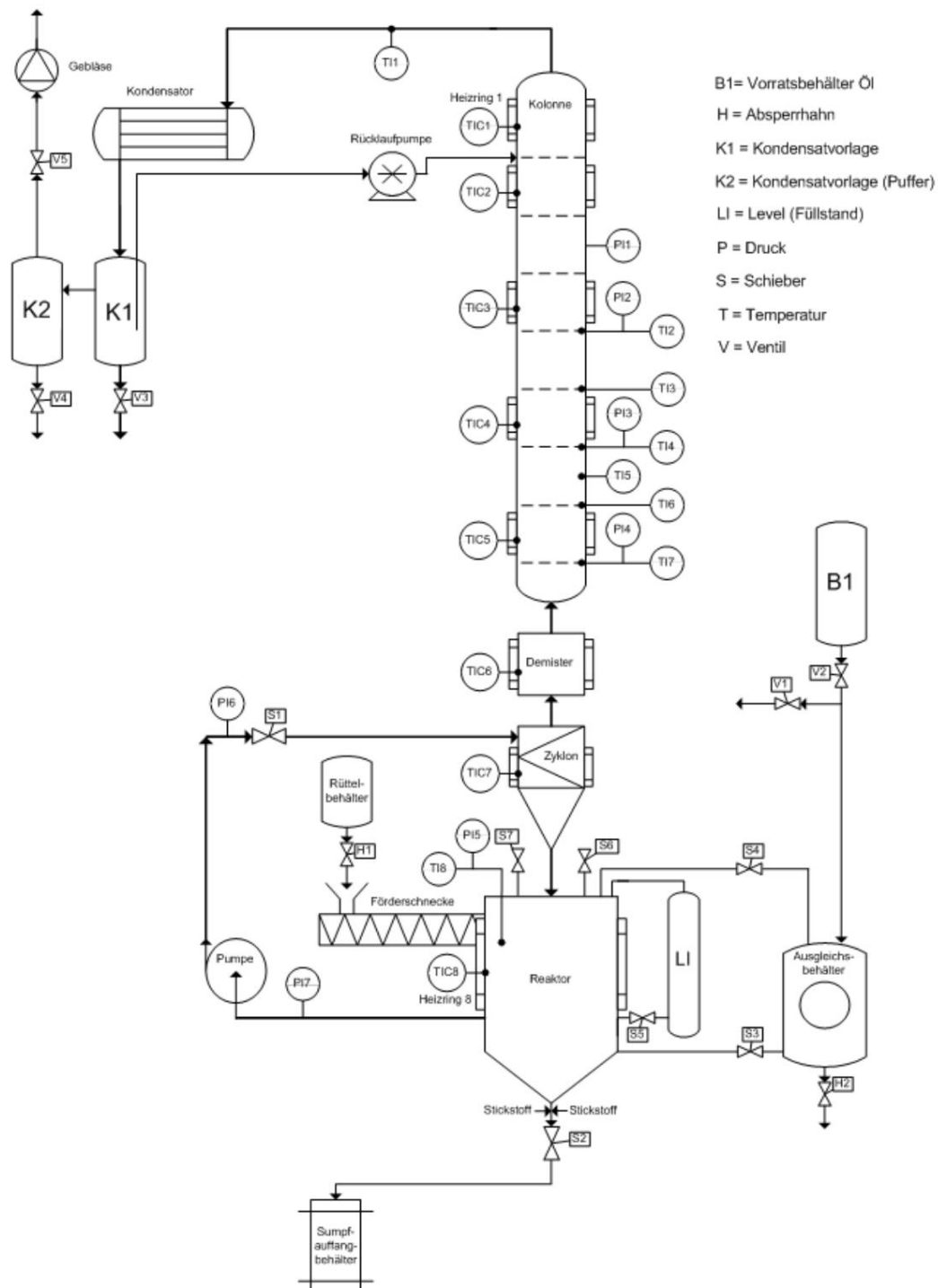


Fig. 14: Flow diagram of the semi-continuous 5 kg/h KDV pilot plant



Fig. 15: Semi-continuous 5 kg/h KDV pilot plant under construction

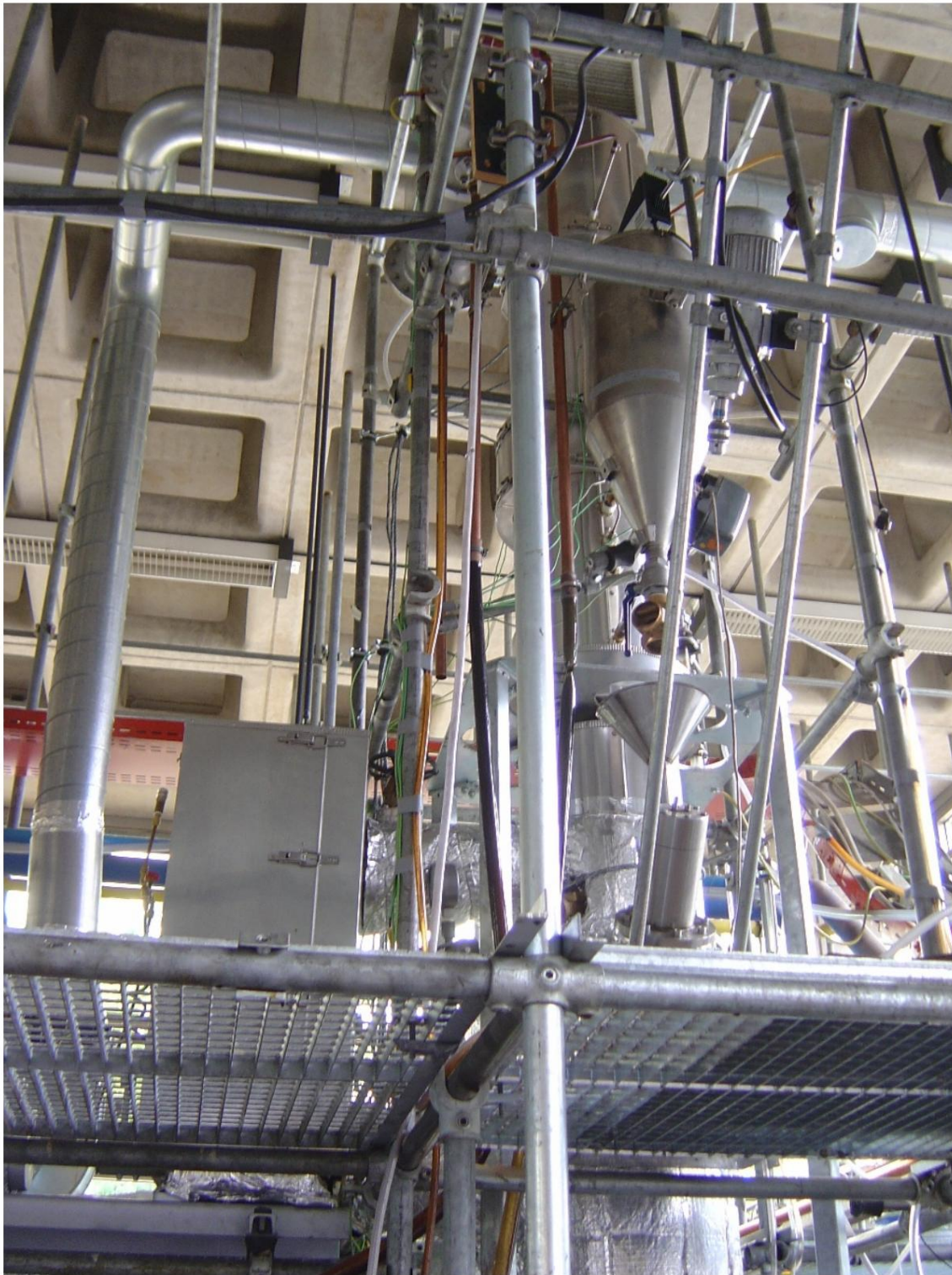


Fig. 16: Semi-continuous 5 kg/h KDV pilot plant in operating condition

The process in the pilot plant is started up according to the KDV-Method involving the submission of a mineral oil-derived base oil or starting oil, in which A first batch of catalyst powder has been mixed in. For the investigations For this purpose, a temperature-resistant circulating oil from BP, type Energol CS 220, was used. (see Section 6.1) and an ion-exchange active aluminosilicate as a catalyst. Alphakat type A407 (see section 6.2) from the manufacturer Tricat/Südchemie in Bitterfeld is used.

The supplied mixture of base oil and catalyst is first processed by means of the high-temperature circulating pump at a reaction temperature between 300 and Heated to 400 °C. Figure 17 shows the heating behavior of the system.

This takes place in an air-free, inert gas atmosphere (nitrogen). After reaching the The desired temperature is kept constant and the continuous supply...

on shredded and dried raw material (e.g. straw) together with a a certain proportion of fresh catalyst powder begins to be fed via the screw conveyor.

During this conveying period, the product condensates are collected. At the latest

If the enrichment of solids in the reactor sump phase requires it,

Raw material extraction has ceased and the experiment has ended. The reactor sump will be in

The sump collection container was drained.

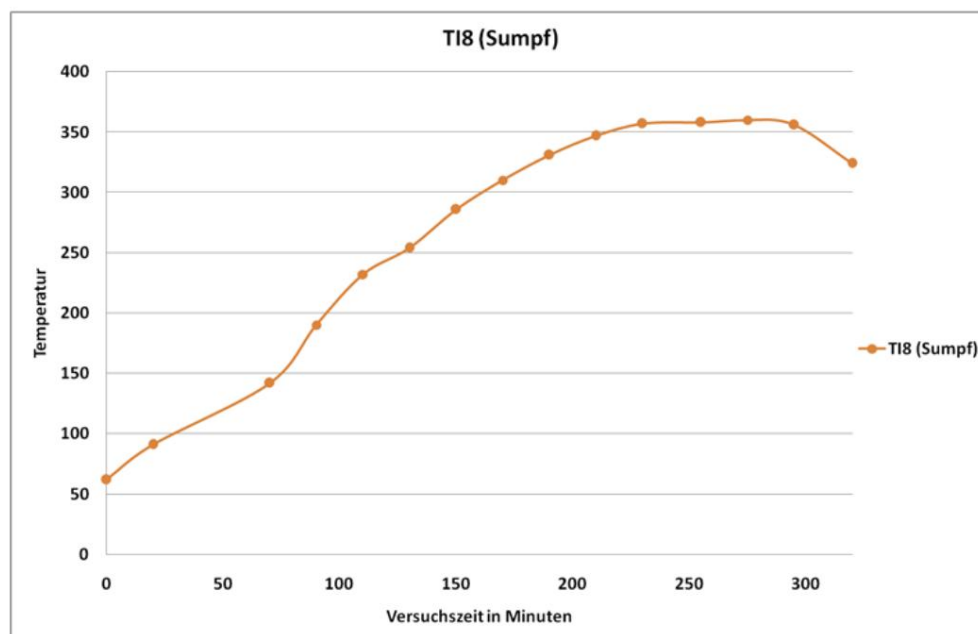


Fig. 17: Example of a heating curve for the 5 kg/h KDV pilot plant

6.4 Experimental setup on a 1 kg/h laboratory scale

Specific investigations into the KDV process were carried out on a 1 kg/h laboratory system. carried out (see section 6.5).

At the 1 kg/h laboratory system, all components except the mechanical energy input are... essential conditions of the KDV technical facility (**atmospheric pressure, Temperature 300 to 400 °C, continuous supply of raw material and catalyst, Heavy oil sump phase, type of base oil or starting oil, type of catalyst, Reactive distillation, continuous product removal and product condensation**) realized.

The basic principle of the laboratory setup is shown in Fig. 18. (In addition...)

Figure 19 shows a photograph of the apparatus. The design capacity is a raw material throughput of 1 kg/h.

The heavy oil sump phase is placed in an electrically heated laboratory facility.

A stirred reactor, with an inner diameter of 268 mm and a volume of approximately 10 liters, was used.

The lower part of the reactor contains the liquid or sump phase with the suspended catalyst, which in every attempt is mostly still before the

The heating phase is stirred in. After inerting and heating the reactor, the solid crushed raw material together with another catalyst component to

Compensation for catalyst consumption is continuously achieved via a screw conveyor directly into

The sump phase, preheated to reaction temperature, was run and at a

Stirred in at a speed of approximately 200 rpm. The rising product vapors escape.

The reactor is continuously cooled at the head outlet and is cooled via a water-cooled system.

Condenser. The condensate, e.g., from a heavier water phase and consisting of the lighter product oil phase above, is in a

The separating funnel collected the reaction gas, which was then separated using an electrostatic precipitator.

Aerosols were cleaned, flared, and removed. Solid residues and

Heavy oil components remain in the system, as in the 5 kg/h pilot plant (Section 6.3).

reactor sump and are drained into the sump after the experiment ends.

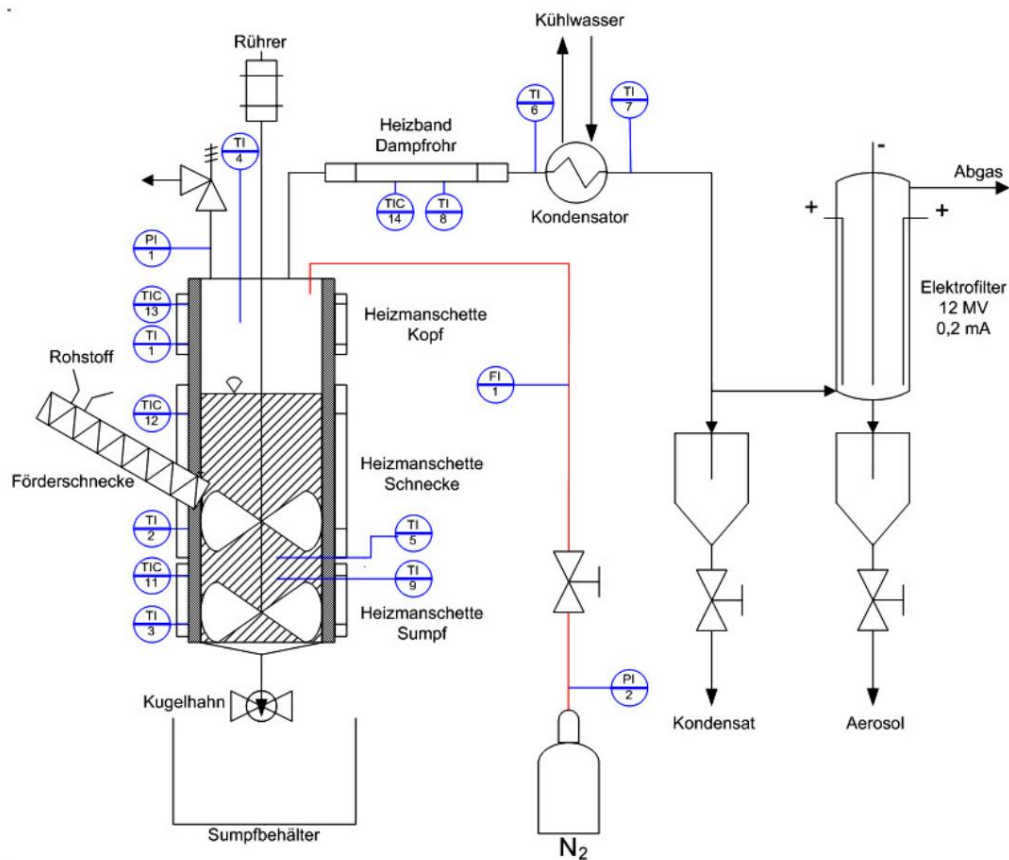


Fig. 18: Flow diagram of the semi-continuous 1 kg/h laboratory plant

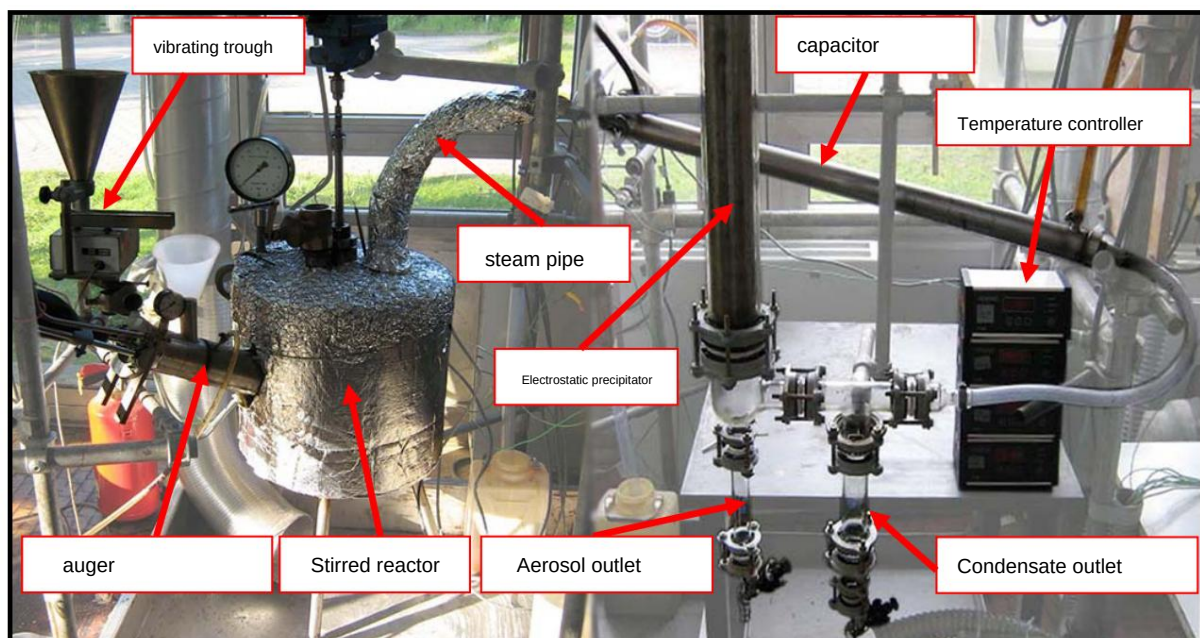


Fig. 19: Experimental setup of the semi-continuous 1 kg/h laboratory system

6.5 Experimental Results

The main investigations on the 5 kg/h pilot plant (see section 6.3) were tested using straw as a model substance for dry biomass residues (Lignocelluloses) performed. For the investigation of specific scientific Questions regarding the KDV process, such as the stabilizability of the swamp phase, origin the diesel-like product oil phase and reaction pathways of the biomass used and the submitted heavy oil as a starter sump phase were used in the technical center of the HAW Hamburg: Experiments on a semi-continuous laboratory system with a Raw material capacity of 1 kg/h was achieved.

The **comparability of the test results of KDV tests at 5 kg/h**

The pilot plant and the 1 kg/h laboratory plant were compared in comparative tests. both using the example of blind tests (base oil only, without raw material) and for Straw conversion **confirmed** (Section 6.5.1). This report mainly covers the Results of the laboratory experiments, which can be evaluated more precisely, are presented.

Operation under KDV conditions is described in sections 6.3 and 6.4. For the Investigations used a temperature-resistant circulating oil as the base or starting oil. from BP of the type Energol CS 220 (see section 6.1) and a zeolite as a catalyst. used by Alphakat type A407 (see section 6.2).

Preliminary tests on the 1 kg/h laboratory plant revealed that the catalyst A407 is very weakly active and has unusually high starting concentrations in the A reactor sump phase is required in order for any effect to be observed. Depending on the raw material used, the starting concentration of catalyst in the base oil should be at over 20 wt.% of the suspension. This was mostly done in test experiments for the purpose of To demonstrate an effect, even a starting concentration of 33 wt.% is required. The catalyst is placed in the reactor sump during the start-up phase of the process (heating phase).

The experimental results are described below. The **problems with The KDV high-temperature pumps** at the 5 kg/h pilot plant are described in section [number]. 6.3 shown.

6.5.1 KDV comparative tests on pilot plant and laboratory equipment

Comparability of KDV tests on the 5 kg/h pilot plant and 1 kg/h

The laboratory setup was confirmed using the example of straw conversion based on...

- Blind trials (base oil only, without straw addition),
- Tendency to coke buildup on the reactor walls,
- Temperature control,
- GC-MS analyses of the product oils and
- C14 analyses of the product oils.

These aspects will be discussed below.

In **blind tests**, the decomposition rate of pure base oil without

Raw material input was determined based on the condensate mass flow rate. Table 5 shows that the

Conversion rate of the base oil at both plants within the framework of the

Measurement accuracy (accurate to 1 decimal place on the pilot plant, accurate to 1 decimal place on the laboratory plant)

(to two decimal places) matches. This also indicates that the

Temperature control of the laboratory system, the pump energy input of the

The pilot plant is practically equivalent. This is confirmed by the complete

Prevention of coking on the reactor walls in both plants (su).

Table 5: Comparison of pilot plant and laboratory plant in the KDV blind test (base oil crackers only, without straw) at 370 °C (measurement HAW Hamburg)

	Technical plant	Laboratory equipment
Specific condensate mass flow rate in g/(min kg base oil)	0.3	0.33

An important feature of the KDV process is the **suppression of coking**.

the reaction walls due to optimal homogeneity of the temperature field by the

Pump energy input instead of a conventional one via temperature gradients

Controlled heat flow via heated walls or fixtures. Long-term trials

confirms the following despite the conventional energy input at the laboratory facility:

Complete comparability of pilot plant and laboratory facilities. This has been achieved.

through optimized stirrer action on the inner wall of the reactor

Laboratory facility. This also made it possible to use the laboratory facility for all previously driven

Raw materials with any tendency to coke on the reactor wall in the area of the

The swamp phase should always be completely avoided.

Temperature **control** is comparable in both systems. This is confirmed by same blank values for base oil conversion at the same sump temperature (see Tab. 5) as well as by the complete suppression of coking at the Reaction walls in both plants (so).

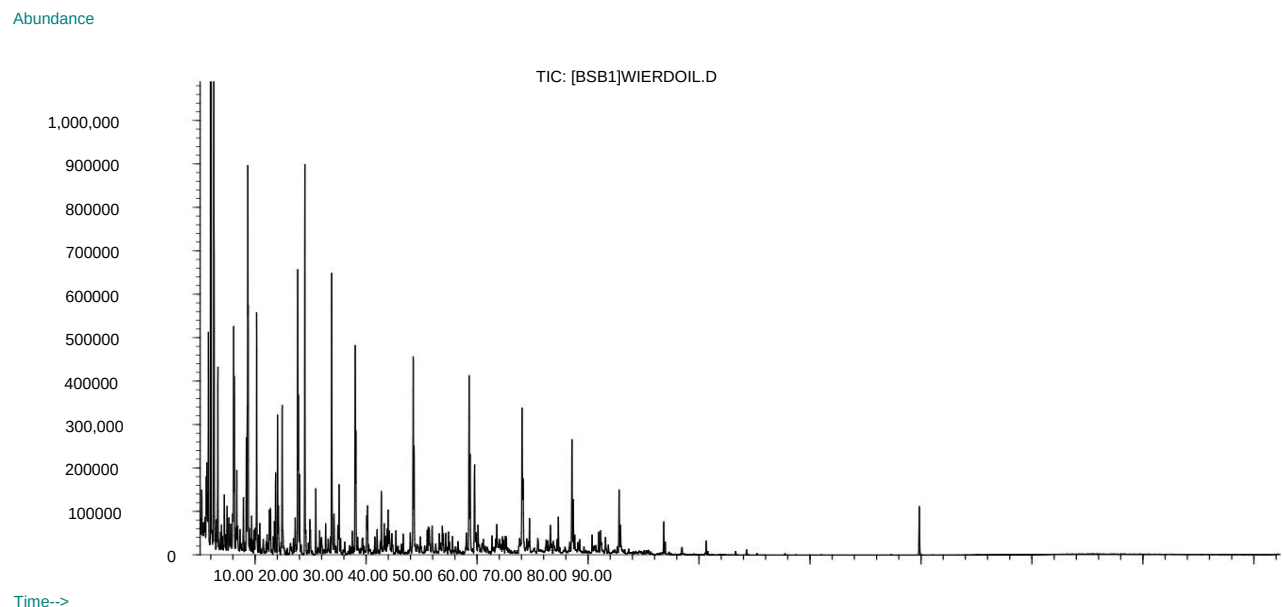


Fig. 20: GC-MS analysis of the product oil from a straw conversion experiment at the pilot plant at 370-380 °C (measurement BFH Hamburg - now vTI Hamburg)

Based on **GC-MS analyses** (gas chromatography-mass spectrometry-

Analyses of the product oils reveal whether the conversion reactions have progressed beyond the initial stages.

The same or different reaction pathways may occur. Figure 20 shows a typical GC-MS analysis for a straw trial at the pilot plant is shown.

Comparing this analysis with the corresponding ones for the laboratory setup (Fig. 22 and 23), a good match is observed. Both product oils are dominant.

the saturated linear hydrocarbons (n-alkanes) with a similar relative distribution.

Minor differences exist only in the upper limit of the chain length.

to recognize. At the pilot plant, the chain length range is slightly higher.

more limited (Fig. 20) than at the laboratory setup (Figs. 22 and 23). The cause

This is due to the internal return flow within the distillation column, which is located in the

The pilot plant is installed above the reactor and through which the product vapors are passed.

before their condensation (see Fig. 14), while in the laboratory system

The product vapors are condensed directly at the reactor outlet without return flow.

(cf. Fig. 18). As a result of the reflux in the distillation column of the

In the pilot plant, the longer-chain hydrocarbons are already partially processed in

The distillate condenses in the distillation column and therefore reaches the product condenser.

not after the column, or only to a lesser extent. However, this is not stated in the

This contradicts the comparability of the core KDV process in both plants. The fundamental similarity of the GC-MS analyses confirms that the

Conversion reactions in both plants proceed via the same reaction pathways.

Table 6: Comparison of pilot plant and laboratory plant based on the C14 analysis of the respective product oil from straw experiments with the derived quantitative determination of the biogenic carbon content (C content) in the product oil

Technical plant	Laboratory equipment
Biogenic C content in the product oil in % < 5% 1)	< 10 % 2)

¹⁾ Ingenia Consultants & Engineers, Eindhoven, NL, June 2007 2)
Shell, NL, Jan. 2007

Perhaps the most important comparability criterion in the case of

Biomass liquefaction tests **C14 analyses** (analysis of the radioactive C14 isotope =

Carbon-14 isotope) of product oils can be examined. C14 analyses allow the

Differentiation between biogenic (derived from biomass) and fossil carbon in the oil sample. Table 6 shows two

C14 analyses of typical product oils from

KDV straw tests on pilot plant and laboratory equipment were reported. In both cases

The biogenic carbon content in the product oil is very low (< 5 or < 10%).

This means that **the product oils contain diesel-like components (n-alkanes), as in**

The GC-MS analyses (see Figs. 3, 20, 22 and 23) are both

in both pilot plant and laboratory operations, practically exclusively from the

fossil base oil and not straw. This makes the theoretical...

Considerations confirm that the molecules of cellulose, hemicelluloses and

Under KDV conditions, no n-alkanes are formed in lignin in the diesel boiling range.

can (see section 4).

6.5.2 KDV tests with base oil without raw material (blind tests)

To determine the influence of the raw material (e.g., straw) on product formation, Comparative tests were conducted with pure starting oil without straw addition, so the aforementioned **blind tests**. Furthermore, to determine the basic effect of the catalyst to Testing included blind tests **with both catalyst ("catalytic" tests)** and also carried out **without a catalyst ("thermal" experiments)**.

Figure 21 shows the **product development** (condensate mass flow) as a measure of the rate of conversion of the base oil, which in comparative

Blind tests with and without catalyst **showed no effect of the catalyst on the**

The conversion of pure base oil without raw materials is demonstrable, although the Catalyst concentration in the catalytic tests was extremely high at 33 wt.% in the sump.

The setting was high. The curves in Fig. 21 show the reaction kinetics.

Model calculation for a first-order reaction, which shows very good agreement with the measured values.

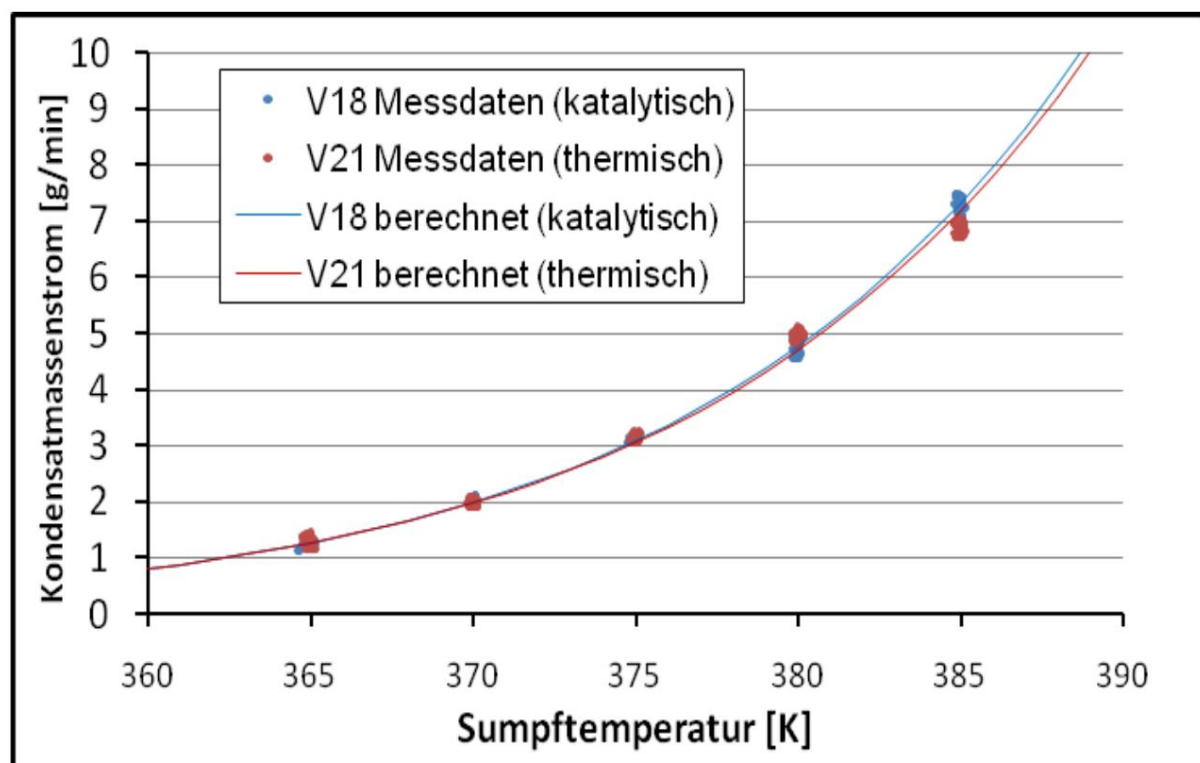


Fig. 21: Comparison of product development in thermal (without catalyst) and catalytic (with 33% catalyst A407 lutro) blind tests for a starting quantity of 6 kg base oil, laboratory setup (Master's thesis A. Lüken, HAW Hamburg, April 2008)

lutro = air-dried, Correction: The swamp temperature is given in °C.

The **ineffectiveness of the catalyst in pure base oil conversion**

(Blind trials) is also through comparative measurements of

Activation energies for catalytic and thermal base oil conversion (see

Table 7) and by comparing the **product oil composition** based on

GC-MS analyses are clearly shown in Figures 22 and 23. Table 7 shows virtually identical results.

Activation energies for the thermal and catalytic reactions. This is a

clear indication that the catalyst is having its effect, which is particularly evident in a

A reduction in activation energy would prevent it from unfolding.

Accordingly, Figures 22 and 23 also show no significant differences in

Component spectrum of the product oils. This result confirms the theoretical considerations that the pores of

A407 are too narrow for the substances to be treated.

Hydrocarbon molecules of the base oil are and therefore not suitable for a

The pore surface area required for catalytic effectiveness is available (Section 5).

Table 7: Comparison of activation energies for thermal and catalytic base oil conversion in the temperature range 360 to 400 °C; catalytic condition: 33 wt.% A407 in the sump, laboratory setup (Master's thesis Th. Thomé, HAW Hamburg, Feb. 2006)

	catalytic	thermal
Activation energy in kJ/mol	294.8	299.9

Nevertheless, we find that in pure base oil cracking, regardless of the

Catalyst use results in very good product oil quality with regard to the production of

Diesel fuel. This finding can be seen in Figures 22 and 23 in comparison with the

Derive the diesel analysis (Fig. 3). The product oil analysis in Figs. 22 and 23 shows in the

Chain length range between C-9 and C-23, the desired n-alkanes, which are suitable for a

Good diesel quality is important. Additionally, the product oil contains a short-chain

Fraction below chain length C-10. This short-chain fraction corresponds to the

Boiling range of a gasoline fraction. However, this gasoline boiling fraction would be

This results in poor gasoline quality, since **n-alkanes**, although **having good cetane numbers** (for diesel)

but this results in **poor octane ratings** (for gasoline).

This finding for base oil can be attributed to the application of the KDV method to

Waste oils are transferred. Therefore, it can be expected that the KDV procedure will be used for waste oils.

Even without the use of the KDV catalyst, satisfactory diesel components can be produced.

can.

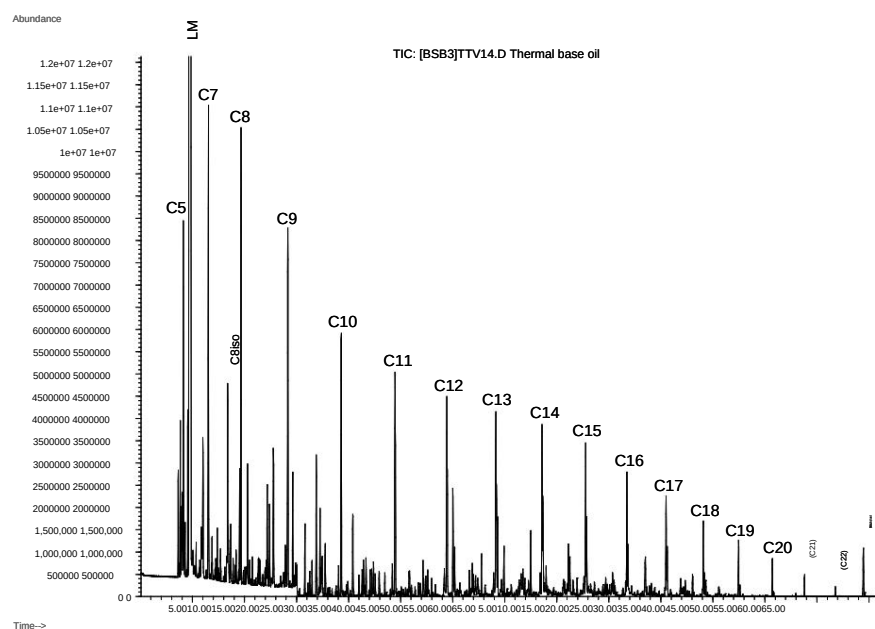


Fig. 22: GC-MS analysis of the product oil from thermal base oil cracking (blind test), mean reaction temperature 380 °C. (Diploma thesis Th. Thomé, HAW Hamburg, March 2005; measurement BFH Hamburg - now vTI Hamburg)
(C number at the peaks = carbon chain length of the corresponding n-alkane; see Fig. 3)

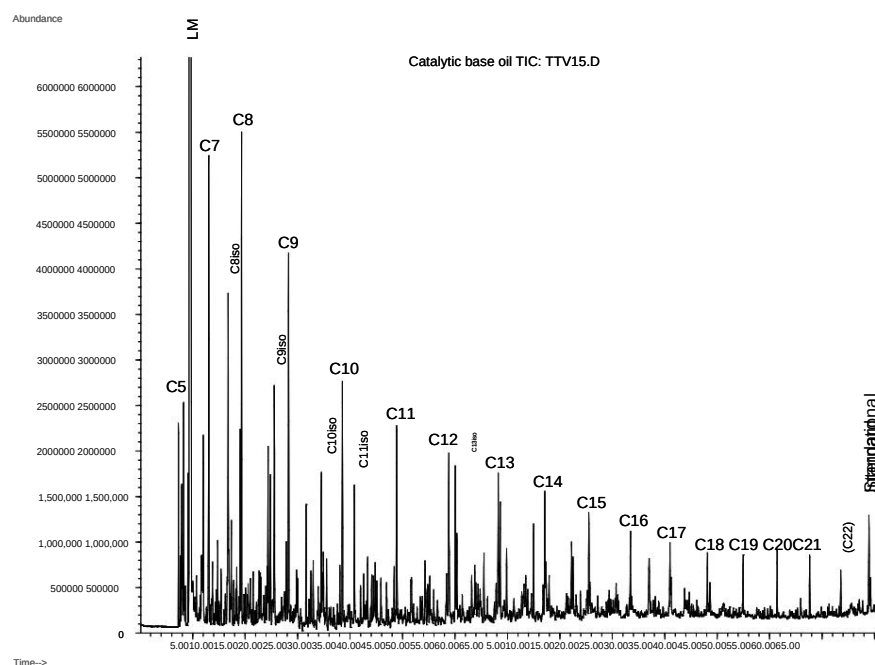


Fig. 23: GC-MS analysis of the product oil of the catalytic base oil cracking (blind test), mean reaction temperature 380 °C, 33 wt.% A407 in the sump.
(Diploma thesis Th. Thomé, HAW Hamburg, March 2005; Measurement BFH Hamburg - today vTI Hamburg)
(C number at the peaks = carbon chain length of the corresponding n-alkane; see Fig. 3)

6.5.3 KDV trials with straw

Most of the test runs for the KDV process were conducted on the 5 kg/h pilot plant.

(Section 6.3) were driven with cereal straw. As described in Section 6.5

Special investigations were conducted, particularly to improve the

Understanding the chemical processes (e.g., the origin of diesel-like substances)

Product proportions, the catalyst function and the influence of raw materials) as well as the balance sheets were carried out on the 1 kg/h laboratory system.

Table 8 shows the raw material properties of the straw used. The processing of the raw material, in particular the comminution to a particle size of less than 5 mm, was carried out at HAW Hamburg.

Table 8: Composition of cereal straw (Master's thesis A. Lüken, HAW Hamburg, April 2008)

Moisture content relative to weight (lutro)	12.4%
organic content with respect to weight (lutro)	84.6%
inorganic content with respect to weight (lutro)	3.0%
(lower) calorific value Hu	15.9 MJ/kg

(lutro = air-dried)

When evaluating and interpreting the straw trials, it must be taken into account that...

The collected **product condensate contains up to four different liquid phases**

can separate from each other, which are in order of increasing density of

Arrange them from top to bottom. Figure 24 shows the corresponding appearance.

the measuring cylinders for collecting the straw condensate, which occurs during a KDV-

The test run is generated, as shown. For clarification of terms, the following are shown in Fig. 24:

The names for the individual phases, as used below, are inserted. From top to bottom, these are the light oil phase (dark brown, thin), the medium oil phase (blackish brown, thin), the aqueous phase (reddish brown to beige, thin), and the heavy oil phase (blackish brown, thin).

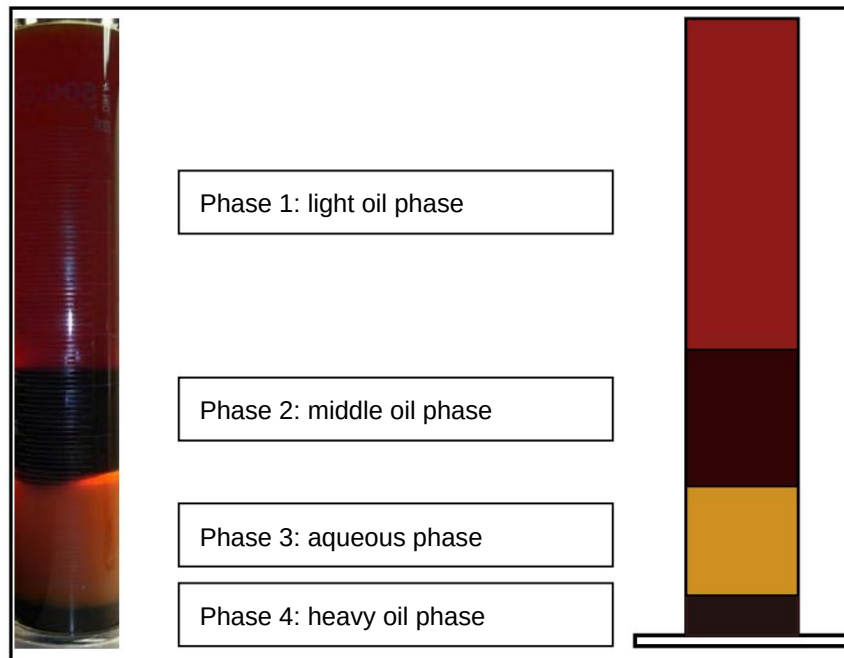


Fig. 24: Designation of the condensate phases of a collected fraction (= one filled measuring cylinder corresponding to a test time of 20-30 min at the laboratory facility) from a straw experiment (Master's thesis A. Lüken, HAW Hamburg, April 2008)

As can be seen in sections 6.3 and 6.4, a KDV trial goes through the following trial phases:

- 1.) **Heating phase without raw material input:** In the catalytic experiment, the submitted base oil-catalyst mixture (suspension of the sump phase) or, in the thermal comparison test, only base oil without catalyst. the desired reaction temperature (370 °C in the case of straw) heated up.
- 2.) **Reaction phase with raw material supply:** With constant temperature The reaction temperature is determined by the raw material (straw) in the catalytic case. together with some catalyst to compensate for the used catalyst, continuously pumped into the sump phase of the reactor, and it is Condensate is continuously collected as a liquid product.
- 3.) **Cooling phase without raw material input:** At the end of an experiment, e.g. when the upper limit of the solids concentration is increased by the accumulation of solids Once the residue level in the reactor is reached, the raw material supply is stopped, after After a certain follow-up time the energy supply is switched off and during During cooling, the reactor sump phase was drained from the reactor.

For a typical **catalytic straw experiment** with A407 at the laboratory facility, the

Experimental procedure based on the condensate fractions that accumulate during the experiment in

The fractions collected in graduated cylinders are shown in Fig. 25. Each "fraction" means

including a filled measuring cylinder, which in Fig. 25 represents a test time of approximately 26 min.

This corresponds to the water phase during the heating phase, which originates from the area in the sump.

presented catalyst. During the raw material supply, including the

During the after-phase, the aqueous phase is formed from the raw material straw. Simultaneously, a heavy oil phase (phase 4) occurs during the raw material input, while a medium oil phase (phase 2) is barely detectable.

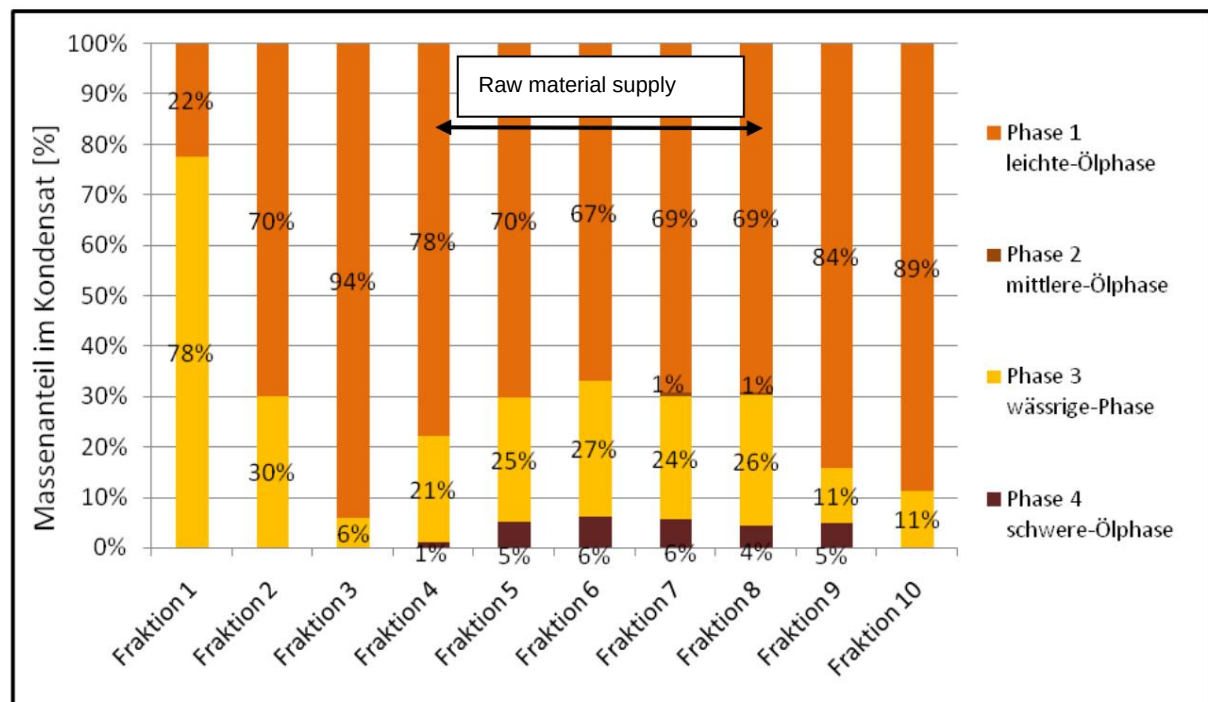


Fig. 25: Condensate fractions collected in a catalytic 1 kg/h straw experiment, laboratory system, 370 °C, 33 wt. % A407 (lutro) in the sump (Master's thesis A. Lüken, HAW Hamburg, April 2008) *air-dried*

Figure 26 and Table 9 show the GC-MS analysis of the heavy oil phase.

Analysis reveals typical biomass decomposition products, particularly lignin-derived phenol derivatives. This clearly indicates that the oil phase originates from the biomass (straw).

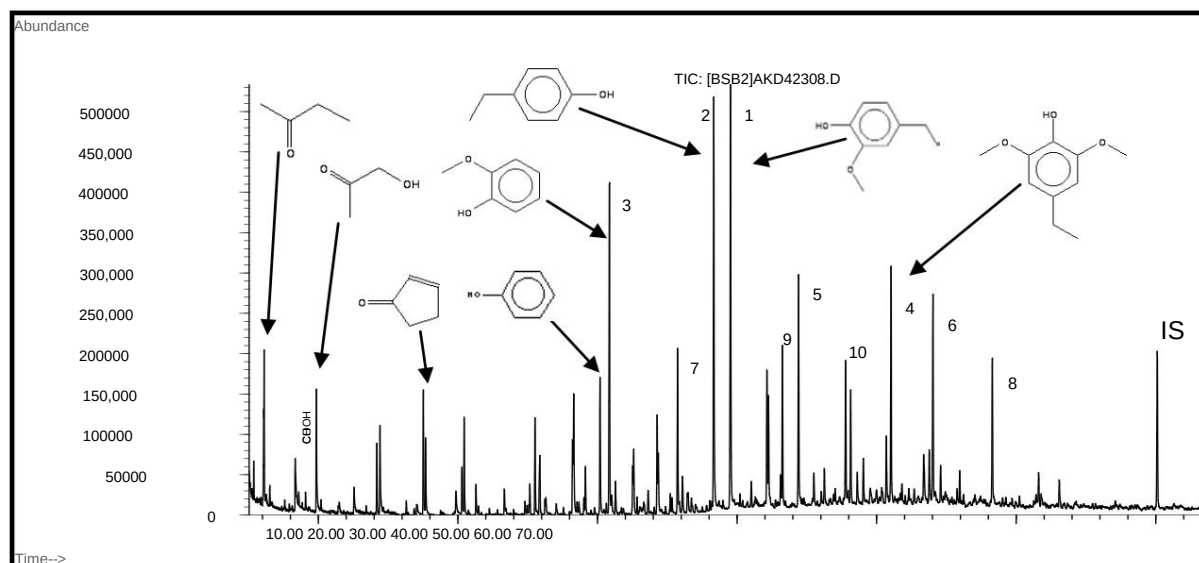


Fig. 26: GC-MS analysis of the heavy oil phase of fraction 8 from Fig. 25; catalytic 1 kg/h straw test, laboratory setup, 370 °C, 33 wt.% A407 (lutro) in the sump (Master's thesis A. Lüken, HAW Hamburg, April 2008; measurement BFH Hamburg - now vTI Hamburg); *lutro* = air-dried

Table 9: Peak identification for GC-MS analysis from Fig. 26

No.	RT	name	Sum formula	structure
1	39,542	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	
2	38,334	Phenol, 4-ethyl-	C ₈ H ₁₀ O	
3	30,861	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	
4	51,042	Phenol, 4-ethyl-2,6-dimethoxy	C ₁₀ H ₁₄ O ₃	
5	44,408	Phenol, 2,6-dimethoxy-	C ₈ H ₁₀ O ₃	
6	54,040	ni		
7	35,750	Phenol, 2-methoxy-4-methyl-	C ₈ H ₁₀ O ₂	
8	58,291	4-(1-Propenyl)-Syringol	C ₁₁ H ₁₄ O ₃	
9	43,256	Phenol, 2-methoxy-4-propyl-	C ₁₀ H ₁₄ O ₂	
10	47,786	Iso-eugenol	C ₁₀ H ₁₂ O ₂	

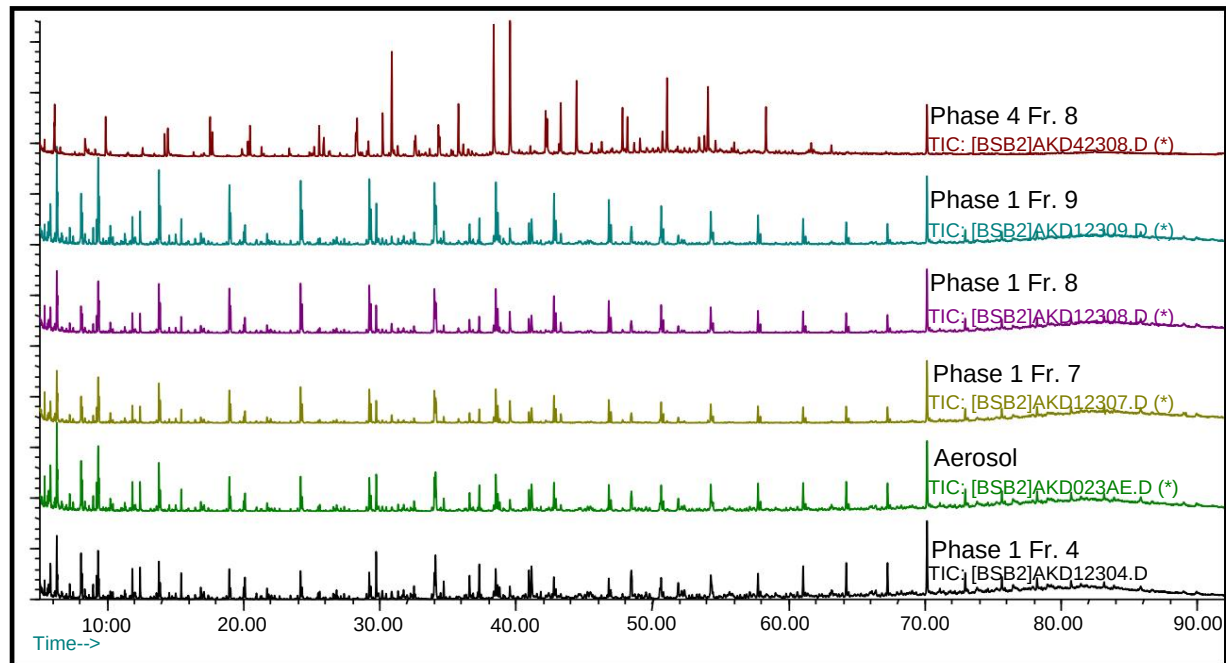


Fig. 27: GC-MS analysis comparison for different condensate phases from Fig. 25; catalytic 1 kg/h straw experiment, laboratory setup, 370 °C, 33 wt.% A407 (lutro) in the sump (Master's thesis A. Lücken, HAW Hamburg, April 2008; measurement BFH Hamburg - now vTI Hamburg); *lutro* = air-dried

Finally, Figure 27 provides a comparison of the GC-MS analyses for different Product condensate phases of the catalytic straw experiment of Fig. 25. For the light oil phase (phase 1), consisting predominantly of n-alkanes, during the No change, and therefore no raw material influence, is discernible over the entire raw material supply period. Furthermore, no similarity can be observed between Phase 1 and the biogenic Phase 4. Rather, the agreement between the light oil phase (Phase 1) and product oils from blind tests, which involved only base oil without raw material (see Figures 22 and 23), indicates that the n-alkane-containing light oil phase

(Phase 1) clearly originates from fossil base oil. This finding confirms the C14 analysis (see section 6.5.1).

For comparison, Fig. 28 shows a typical **thermal straw test** (without cat.)

As shown in the case of the catalytic straw experiment (Fig. 25), a

The fraction again lasts approximately 26 minutes. During the heating phase there is

This time, unlike in Fig. 25, there is no water phase, as there is no catalyst this time.

is used as a water source. During the raw material supply, including the

In the after-phase, an aqueous phase is formed from the raw material straw, along with a medium oil phase

(phase 2) and a heavy oil phase (phase 4). The formation of the medium oil phase in the thermal straw experiment

(Fig. 28) differs significantly from the catalytic straw experiment (Fig. 25). **A closer examination of this**

Differences based on comparative studies of solid residues

in the swamp shows that this by no means indicates a catalytic activity of the A407

This has been proven. Rather, the A407 prevents the release of the middle oil phase (phase 2) simply by adhering to and binding it.

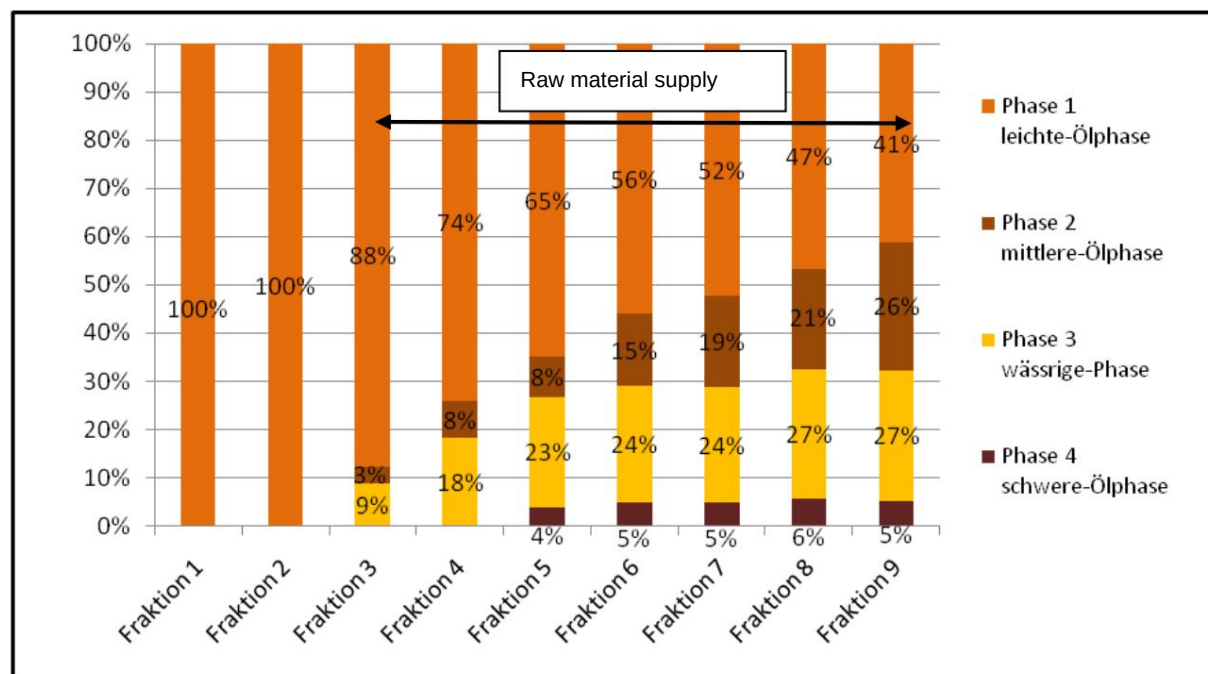


Fig. 28: Condensate fractions collected in a thermal 1 kg/h straw experiment, laboratory setup, 370 °C, no catalyst (Master's thesis A. Lüken, HAW Hamburg, April 2008)

Figures 29 and 30, along with Tables 10 and 11, show the GC-MS analysis of the heavy oil phase (phase 4) and the medium oil phase (phase 2), respectively. The analyses show that both oil phases contain virtually the same typical biomass decomposition products as in the catalytic straw experiment (Figure 26, with Table 9). Therefore, both oil phases (phases 2 and 4) clearly originate from the biomass (straw).

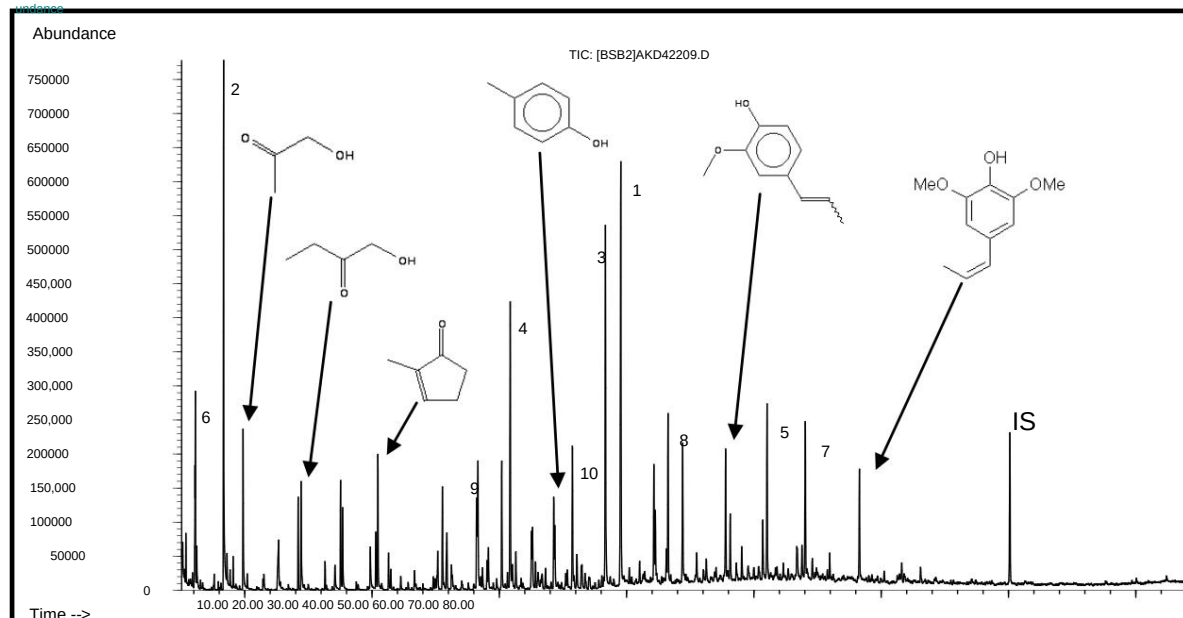


Fig. 29: GC-MS analysis of the heavy oil phase (phase 4) of fraction 9 from Fig. 28; thermal 1 kg/h straw experiment, laboratory setup, 370 °C, no catalyst (Master's thesis A. Lüken, HAW Hamburg, April 2008; measurement BFH Hamburg - now vTI Hamburg)

Table 10: Peak identification for GC-MS analysis from Fig. 29

No.	RT	name	Sum formula	structure
1	39,541	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	
2	8,342	Acetic acid	C ₂ H ₄ O ₂	
3	38,333	Phenol, 4-ethyl-	C ₈ H ₁₀ O	
4	30,860	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	
5	51,030	Phenol, 4-ethyl-2,6-dimethoxy	C ₁₀ H ₁₄ O ₃	
6	6,129	2-Butanone	C ₄ H ₈ O	
7	54,039	ni		
8	43,255	Phenol, 2-methoxy-4-propyl-	C ₁₀ H ₁₄ O ₂	
9	28,321	2-Cyclopentene-1-one, 2-hydroxy-3-methyl-	C ₆ H ₈ O ₂	
10	35,749	Phenol, 2-methoxy-4-methyl-	C ₈ H ₁₀ O ₂	

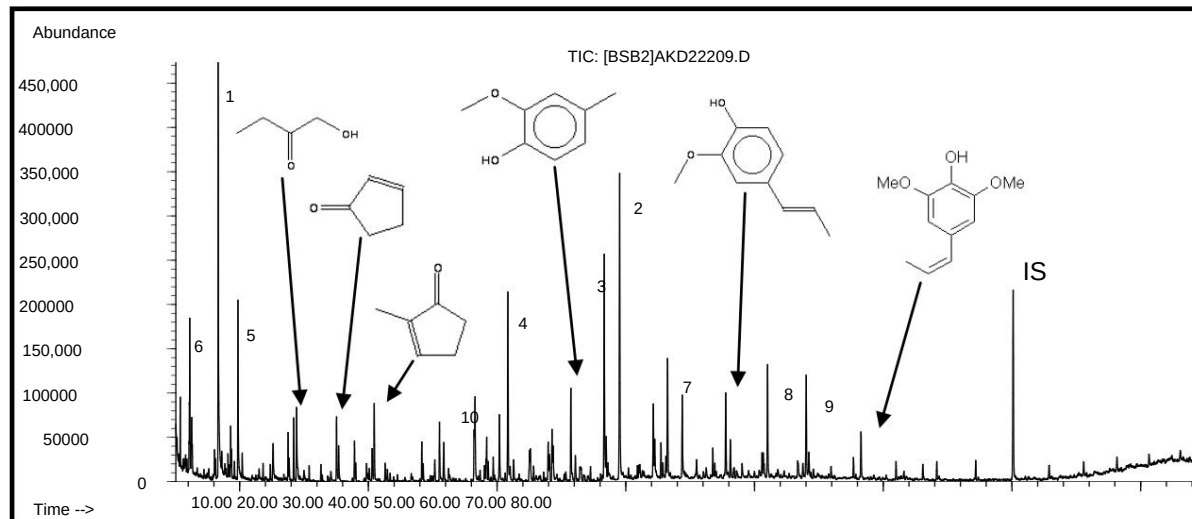


Fig. 30: GC-MS analysis of the middle oil phase (phase 2) of fraction 9 from Fig. 28; thermal 1 kg/h straw experiment, laboratory setup, 370 °C, no catalyst (Master's thesis A. Lüken, HAW Hamburg, April 2008; measurement BFH Hamburg - now vTI Hamburg)

Table 11: Peak identification for GC-MS analysis from Fig. 30

No.	RT	name	Sum formula	structure
1	8,337	Acetic acid	C ₂ H ₄ O ₂	
2	39,531	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	
3	38,323	Phenol, 4-ethyl-	C ₈ H ₁₀ O	
4	30,851	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	
5	9,871	(Acetol) 2-Propanone, 1-hydroxy-	C ₃ H ₆ O ₂	
6	6,135	2-Butanone	C ₄ H ₈ O	
7	43,257	Phenol, 2-methoxy-4-propyl-	C ₁₀ H ₁₄ O ₂	
8	51,020	Phenol, 4-ethyl-2,6-dimethoxy	C ₁₀ H ₁₄ O ₃	
9	54,029	ni		
10	28,289	2-Cyclopentene-1-one, 2-hydroxy-3-methyl-	C ₆ H ₈ O ₂	

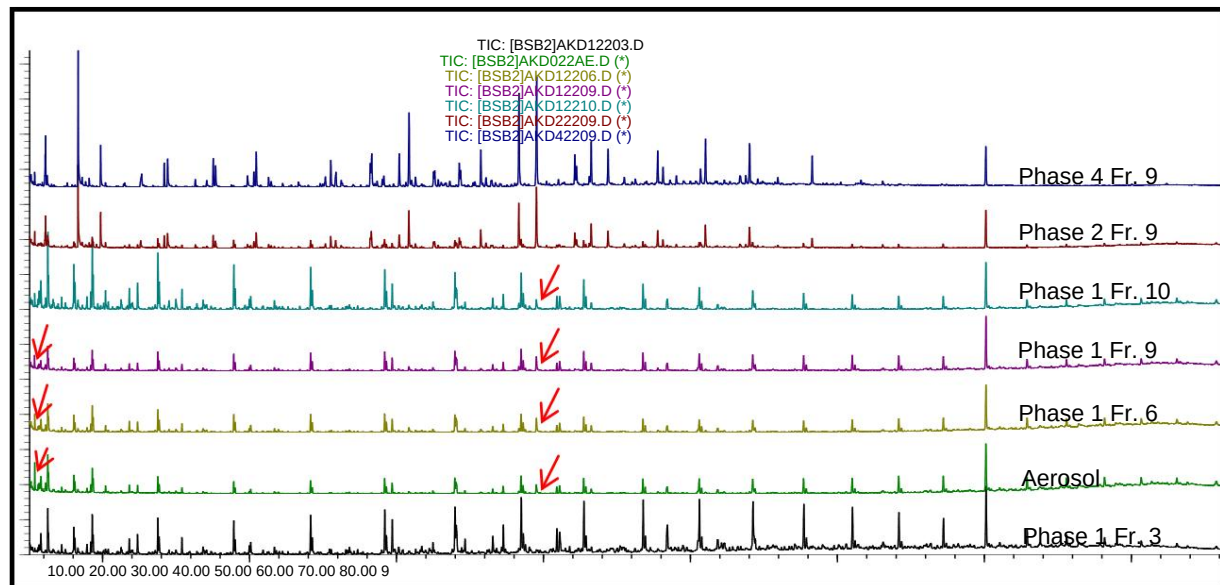


Fig. 31: GC-MS analysis comparison for different condensate phases from Fig. 28; thermal 1 kg/h straw experiment, laboratory setup, 370 °C, no catalyst (Master's thesis A. Lüken, HAW Hamburg, April 2008; measurement BFH Hamburg - now vTI Hamburg)

Finally, Figure 31 provides a comparison of the GC-MS analyses for different Product condensate phases of the thermal straw experiment from Fig. 28. Fig. 31 confirms the similarity of biogenic oil phases 2 and 4, while the light phase 1 (including the aerosol captured in the electrostatic precipitator; see Fig. 18) again the is attributable to cracking products of fossil base oil (e.g., an important component is missing). (Biogenic key component in phase 1 at the location marked by a red arrow). Thus, the C14 analysis regarding the light oil phase (Phase 1) also confirmed for the thermal straw experiment (see section 6.5.1).

An enlarged view of the GC-MS analysis for the light oil phase (phase 1)

The thermal straw test in Fig. 32 with Table 12 confirms this in comparison with

Figures 22 and 23 show that biogenic components are only soluble in the light oil phase in isolated cases and in low concentrations.

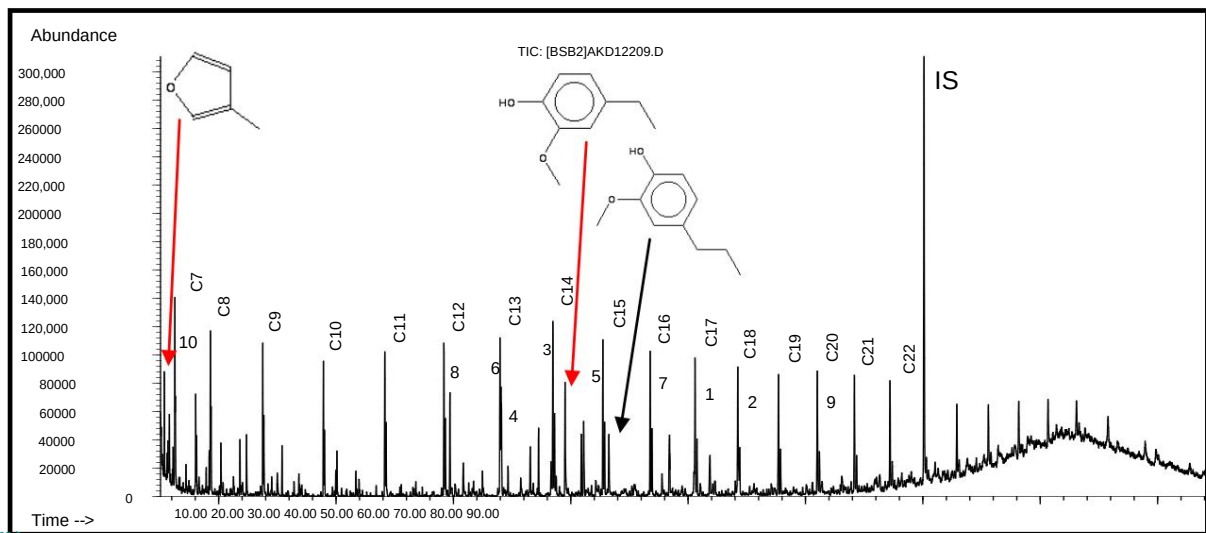


Fig. 32: GC-MS analysis of the light oil phase (phase 1) of fraction 9 from Fig. 28; thermal 1 kg/h straw experiment, laboratory setup, 370 °C, no catalyst (Master's thesis A. Lüken, HAW Hamburg, April 2008; measurement BFH Hamburg - now vTI Hamburg)

Table 12: Peak identification for GC-MS analysis from Fig. 32

No.	RT	name	Sum formula	structure
1	50,606	Heptadecane	C17H36	n-Alkan
2	54,242	Octadecane	C18H38	n-Alkan
3	38,491	Tetradecane	C14H30	n-Alkan
4	34,061	Cycloundecane, 1,1,2-trimethyl-	C14H28	cycloalkane
5	42,742	Pentadecane	C15H32	n-Alkan
6	33,982	Tridecane	C13H28	n-Alkan
7	46,780	Hexadecane	C16H34	n-Alkan
8	29,206	Dodecanese	C12H26	n-Alkan
9	61,021	Eicosane	C20H42	n-Alkan
10	6,268	Heptane	C7H16	n-Alkan

6.5.4 Outlook on other raw materials

In addition to biomass, numerous other [other] products have been used in recent years.

Organic raw materials such as mixed plastic-containing waste (e.g., shredder-lightweight fraction, disinfected hospital waste, DSD fractions), pure plastic types (e.g.

Polyethylene, polypropylene, polystyrene, PVC), sewage sludge and many other residues examined.

It turned out that under KDV conditions, diesel-like

Hydrocarbons only from paraffinic raw materials with sufficient saturated and sufficiently long n-alkanes can be produced. These include paraffin-based

Base oils, waste oils, and polyethylene. In the case of fats and vegetable oils.

(Triglycerides) were not used in pure form in diesel components, but at least in elevated levels were found in crude oil.

In all other cases, **crude oils are initially produced**, which require further processing, as they bear little or no resemblance to natural oils, depending on the raw material.

diesel components or other conventional fuels.

In general, it was observed that heteroatoms such as oxygen, nitrogen,

Sulfur, chlorine or other halogens in the raw material are always also present in the produced crude oil.

halogens occur. In the case of halogens, there is a chance that they can be masked by basic additives. to significantly reduce, but not completely eliminate. They occur in the raw material.

aromatic compounds are present, so the aromatic rings (benzene rings) always remain also found in the produced crude oil. Only their separation from larger components...

Molecular networks or polymer chains can be observed.

Remarkably, it was not possible to establish a definitive result for any of the raw materials examined so far.

The catalytic activity or effectiveness of the KDV catalyst A407 has been demonstrated. This finding is consistent with theoretical considerations.

to the extremely small pore size of A407 and with test results of the

Leibniz Institute for Catalysis eV /9/. In the case of the processing of waste oils and

Polyethylene could benefit from this finding for the application of the KDV process.

This has a positive effect, as the catalyst appears unnecessary and the operating costs are reduced.

The process could therefore be reduced.

7 Discussion of the results of the KDV procedure

The experimental investigations on the KDV procedure at HAW Hamburg in

Within the framework of numerous diploma and master's theses as well as study projects over the years

From 2005 to 2008, both on a pilot plant and laboratory scale, the example

the conversion of straw as a model substance for biomass (lignocelluloses) the following

The findings reveal:

- The KDV catalyst A407 shows no catalytic effect.
- The diesel-like components in the light oil phase (phase 1) of the
The product oils are derived exclusively from fossil base oil and not from
the biomass.
- The KDV catalyst prevents the release of a large portion of the biomass-derived product oil (middle oil
phase or phase 2) by adhering to and binding it. This adsorption of oils or tars to the catalyst surface
allows for rapid deactivation of the

catalyst expected. Furthermore, rapid coking of the

Catalyst detected. A resulting deactivation could be observed.

However, this cannot be proven under KDV conditions, as the catalyst is visible from the front.

no catalytic efficacy was observed in blind trials with pure

The use of base oil without biomass input could be confirmed.

The question is whether the fossil fuel start-up phase in biomass use will gradually be replaced by a

The replacement of new, biogenic swamp-phase heavy oil is closely linked to the

Question: which reaction pathways does the biomass follow besides the base oil, and which

Products are generated in the process. Detailed investigations are conducted using solid and liquid samples.

and gaseous reaction products show that the biomass is essentially

Carbonized. The product distribution for the biomass is approximately as follows:

35% solid residue, 30% aqueous phase, 20% biogenic crude oil , 15% gas

The biogenic crude oil contains no n-alkanes in the diesel boiling range and is therefore unsuitable as a diesel
component. It also lacks similarities to other conventional fuels.

or fuels do not exist.

In parallel, the fossil base oil is converted into the light, diesel-like product oil phase.
converted.

Once the base oil is used up, the KDV process comes to a standstill, as
It does not form any new, biogenic swamp-phase heavy oil, at least according to current knowledge.
Insufficient knowledge. But even if a biogenic
If a swamp phase were to form instead of the fossil base oil, this would be beneficial for the KDV-
The Alphakat process is not helpful, as the lack of base oil then leads to...
would no longer form n-alkanes in the diesel boiling range and thus the claim
Alphakat converts biomass directly into diesel fuel using the KDV process.
Being able to convert it would remain impossible.

Studies under KDV conditions on other raw material classes have
This shows that diesel components only work when saturated and sufficiently long
n-Alkanes can be produced as raw materials. This is therefore only relevant for a few.
Suitable raw materials include waste oils and polyethylene. Also suitable for fats and vegetable oils (triglycerides).
Is there a chance that diesel fuel additive components will be used under KDV conditions?
can be produced. Standard-compliant diesel fuel is produced from it in particular.
due to the oxygen content of approximately 11% in the triglyceride according to current knowledge
Knowledge cannot arise.

Therefore, the KDV procedure claims to directly supply diesel fuel.
produce, unsuitable for all other classes of organic substances such as the
the above-mentioned lignocelluloses (biomass), protein-containing substances
(sewage sludge, animal meal, food, etc.), unsaturated hydrocarbons (e.g.
rubber products, etc.), aromatic hydrocarbons (e.g. asphaltene, etc.),
All types of plastic except polyethylene and many other materials. Also mixed materials.
Waste (e.g., shredder light fraction, hospital waste, DSD fractions, household waste)
etc.) are therefore problematic, as they always contain contaminants that are not in
Diesel fuel can be converted.

Sources:

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