

**Project: AQUEOUS THERMAL CONVERSION OF
BIOMASS TO HYDROCARBONS IN THE FLUID FUEL
RANGE - Hydrocarbons from biomass**

Tanja Barth

*Department of Chemistry, University of Bergen
Allégaten 41, N-5007 Bergen, Norway*

Geoff Abbott

*Department of Fossil Fuels and Environmental Geochemistry
(Postgraduate Institute) NRG: Drummond Building, The University, Newcastle
upon Tyne, NE1 7RU, U.K.*

Karsten Pedersen

*Department of Chemistry, Danish Technological Institute
Teknologiparken, DK-8000 Aarhus C*

Contract JOR3-CT97-0176

FINAL PUBLISHABLE REPORT

1. December 1997 – 31. November 2000

Research funded in part by
THE EUROPEAN COMMISSION
in the framework of the
Non Nuclear Energy Programme
Joule III

**AQUEOUS THERMAL CONVERSION OF BIOMASS TO
HYDROCARBONS IN THE FLUID FUEL RANGE -
Hydrocarbons from biomass**

3: Abstract (200-400 words)

Pyrolysis of biomass and organic wastes in the presence of water has been investigated to determine the efficiency of the conversion into petroleum compatible fluid fuels especially hydrocarbons. The work is primarily directed at understanding the chemical transformations that occur during the conversion. Model compounds for lignin and cutin have been investigated with detailed analysis to enable precise determination of reaction pathways and kinetics. The conversion of various biomass samples has been optimised using a pragmatic approach employing experimental designs on the pyrolysis conditions including the use of catalysts. Thermodynamic models and mass and energy balances have been established for some of the experimental conditions, and technological solutions have been evaluated and compared to alternative technologies for pyrolysis.

The results show that the aqueous pyrolysis can be a viable process for conversion of wet biomass into fluids. Good yields of light oils that are compatible with petroleum products are obtained from many raw materials, but the hydrocarbon content (in the strict chemical sense) is not necessarily high. The product profile is most dependent on the biomass type used, less on the pyrolysis conditions. Alternative products like phenols and acetic acid are produced more easily than hydrocarbons. Hydrogen is produced in good yields at relevant conditions, and is also a potentially very interesting product. The technique of pyrolysis in aqueous media is considered to have a potential for application in waste management and valorisation of biomass and organic wastes with high water contents.

Contents

3: Abstract	3
4: Partnership	5
5: Objectives	6
6. Technical description	6
6.1 State of the art before the project and structure of the work	6
6.2 Description of pyrolysis systems used in the project	7
6.3 Biomass types	7
6.4 Catalyst addition and evaluation of FT processes	8
6.5 Thermodynamic models and mass- and energy balance	8
6.6 Comparison with other pyrolysis techniques	9
7. Results and conclusion	9
7.1 Pyrolysis of biomass and waste materials	9
7.2 Pyrolysis of lignin and cutin models with detailed analysis	10
7.3 Thermodynamics, energy and mass balances	11
8. Exploitation plan and expected benefits	13
9. Illustration	15

4: Partnership

Co-ordinator: Tanja Barth

University of Bergen – UiB
Department of Chemistry
Allegaten 41
N-5007 Bergen
Norway

Partner: Geoff Abbott

Fossil Fuels and Environmental Geochemistry (Postgraduate Institute) - NRG
Drummond Building,
University of Newcastle-upon-Tyne,
Newcastle-upon-Tyne NE1 7RU,
U.K.

Partner: Karsten Pedersen

Danish Technological Institute - DTI
The Technology Park
DK-8000 Aarhus C
Denmark

Associate Partner to UiB

Den Norske Stats Oljeselskap – Statoil

5: Objectives

Principal objective:

To produce hydrocarbons in the petroleum range in high yield directly from solid biomass of various compositions using a one-step, aqueous, closed pyrolysis process.

Sub-goals:

- To increase the understanding of the chemistry of mixed biomass and pure biomass components in high-temperature aqueous reaction systems so that the critical factors for the reactivity of the biomass constituents and their transformation into hydrocarbons can be identified.
- To optimise the reaction conditions for maximum yields of liquid products from biomass carbon sources, to a level where at least 25 % of the initial carbon is converted to hydrocarbons and the produced oil- and gas phases contain at least 50 % hydrocarbon compounds.
- To compare the yields and compositions of the products from aqueous pyrolysis of biomass with results reported for flash pyrolysis processes.
- To determine the reactor conditions required for directing the reactions through a “one-pot” synthesis gas generation and Fischer-Tropsch type reaction sequence to give increased yields of hydrocarbons compared to pyrolysis based on cracking reactions only.

6. Technical description

6.1 State of the art before the project and structure of the work

A central factor for the establishing this project was the observation of very different ideas on state of the art for pyrolysis in petroleum geochemical research and in biomass thermal conversion. Petroleum geochemistry uses “slow” pyrolysis in closed reactors in the presence of minerals and variable amounts of water to simulate the natural processes of oil and gas generation and provide a hydrocarbon-rich crude oil as the main pyrolysis product. The most important aim is to produce a pyrolysate with a quality that resembles crude oil, which includes a high content of saturated hydrocarbons. The quantity is also important and is used to determine the quality of the source rocks or sediments that are pyrolysed. This field of pyrolysis is very active at present, with continuous improvement of the understanding of the basic processes involved.

The biomass community, on the other hand, has focussed on finding a technique that converts woody biomass into liquid products in a way that maximises the weight yield of pyrolysate relative to the woody starting material. The preferred method is fast or flash pyrolysis with a very short residence time at the pyrolysis temperature. The feedstock is dry wood chips, and the product bears no chemical resemblance to petroleum derived oils, but consists of fragments of the polymeric constituents of the wood with a very high content of oxygen. It is a stated objective to minimise the secondary conversion reactions to retain the high weight yield of product by keeping

the oxygenated, water soluble molecules from further reactions by rapid cooling of the product (quenching).

As a result of the very different process conditions, the chemical compositions of the liquid phases from the two pyrolysis techniques are very different, though the basic line of thought in using of temperature-driven depolymerisation of geo- and biopolymers to convert solid organic matter or biomass into fluids is basically the same. The potential for optimising pyrolysis with regard to product composition is therefore obviously present, but at the start of this project the influence of the reaction medium and catalytic effects, time-temperature-pressure parameters and initial biomass composition had not been systematically explored.

A major concern in the work performed here has been to investigate the chemical role of water as a reaction medium for clean and mixed biomasses. “Slow” pyrolysis in the presence of water has been explored both with a pragmatic approach using experimental design and in detailed molecular studies in small-scale experimental systems. The results from selected experiments have been used for calculation of energy and mass balances, and evaluations of feasibility of such processes in a larger scale. The experimental design studies have been quantitatively interpreted using multivariate response surface models to identify critical factors and predictive models. Very interesting thermodynamic models have been developed to describe the chemical stability of the products at different conditions of temperature, pressure and water content, and the positive effect of a water medium on hydrocarbon and hydrogen generation has been demonstrated. On the basis of very exact and detailed quantitative analysis of precursors and products, models for chemical mechanisms and reaction networks have been developed which explain the observations from pyrolysis of the model compounds and biomass samples. The spectrum of products from selected pyrolysis experiments from have been used to consider the feasibility and economy of such processes in a larger scale, and compare the product composition with results reported from fast pyrolysis of biomass.

6.2 Description of pyrolysis systems used in the project

Since the effect of water on pyrolysis reactions is a central question in this project, the pyrolysis systems used in the project are selected to tolerate addition of a considerable amount of water to initially damp or wet biomass. In part of the work, stainless steel reactors which have high pressure limits (60 Mpa at 350 °C) were used, and water was added in large excess to provide a strong driving force in the equilibria and at the same time be the reaction medium. The temperature control for the kinetic measurements required a large number of separate reactors with low mass and rapid heat transfer, and quartz tubes were used. The pressure tolerance of the sealed tubes defined a limit for the water content of the system. The two systems provide an opportunity to compare catalytic effects from the container surface, which is more probable for steel than quartz. Both systems are “slow”, with time scales in an hour range, and the effect of residence time has been a central area of investigation in both reactor systems.

6.3 Biomass types

Conventional pyrolysis research has recently focussed on clean woody materials. However, the analogy with natural petroleum generation processes suggests that

degraded mixed biomass types and biomass from micro-organisms and other non-vegetable origins may have higher potentials for production of fluid fuels by thermal conversion. A wide range of biomass types was thus addressed. One type of clean woody biomass (thermomechanical pulp from softwood) and one mixed biomass type (sewage sludge from a municipal plant) were investigated in detail, and a number of additional biomass types were tested in smaller experimental designs. The starting material was found to have a large influence on the product spectrum, as expected from the petroleum generation analogy.

The model compounds investigated in detail represent major constituents of woody and vegetable biomass (phenols and synthesised lignin model compounds) and of lipids present in both vegetable and animal biomass (palmitic and oleic acids). The reaction networks that have been determined are easily applied to the more complex biomass samples, and the degree of correspondence has been found to be very high.

6.4 Catalyst addition and evaluation of FT processes

Testing the hypothesis of a pathway for generating hydrocarbons by catalysed polymerisation of gas phase products has been a very challenging part of the work. Such processes would correspond to the Fischer-Tropsch type (FTT) conversion of synthesis gas (CO and H₂) to hydrocarbon mixtures, but would have to occur efficiently as part of the “one-pot” pyrolysis process. There is not much knowledge about potential catalysts for aqueous conditions, though some work has been done. For FTT processes, the catalysis is expected to occur by interactions between gas molecules on a metal surface (heterogeneous catalysis). The preparation of catalysts have thus of necessity been based on the gas-phase FTT literature, which may be only marginally relevant to the wet pyrolysis systems.

Homogenous (dissolved) catalysts also have a wide applicability in other parts of the reaction system, for example in the initial depolymerisation of biomass polymeric material. Using acid or basic conditions in the water also influences the product distribution. A number of different substances have been used in tests of catalytic effects, and the potential for directing the reactions towards selected product compositions has been found to be very high.

6.5 Thermodynamic models and mass- and energy balance

The presence of water during pyrolysis will influence the chemical driving forces in the system. This has been investigated by thermodynamical modelling, to see what effect water in different proportions has on the stability of representative compounds. Mass and energy balances based on specific experimental data have been made, using representative compounds in place of the more complex product fractions when necessary. This resulted in models that give good descriptions of the pyrolysis process based on established thermodynamically data, while still being applicable to the complex biomass conversion process.

6.6 Comparison with other pyrolysis techniques

The results from the aqueous pyrolysis process has compared to other pyrolysis techniques to provide a basis for evaluation which technology is best for a given raw material, in terms of product types and economic potential. The premise is that very wet raw material, which is unsuited for the more established flash pyrolysis process,

may be optimal in wet pyrolysis due to reduced preparation costs and more valuable products.

7. Results and conclusion

This work considers the conversion of biomass into fluid fuels by pyrolysis in the presence of water from a primarily chemical point of view. The chemical reactions that occur in have been studied on a detailed level using model compounds, and in a more pragmatic approach using natural biomass types and wastes. The thermodynamics and energy balance of such conversions are addressed, and finally the technical possibilities for such processes have been evaluated. The results thus go from the molecular level to plant size evaluations, and are relevant, interesting and potentially exploitable in many perspectives.

7.1 Pyrolysis of biomass and waste materials

The principal objective of producing hydrocarbons in the fluid fuel range in high yields using one-step aqueous pyrolysis has been achieved for bacterial sludges and some vegetable biomasses. The effects of temperature and other experimental factors have been investigated and predictive models have been developed.

The investigations show that biomass type is the most important variable for determining the conversion and product spectrum of biomass. Temperature, time and catalysts also influence the yields and compositions of the produced fluids.

The aim of converting “at least 25 % of the initial carbon into hydrocarbons”, and producing oil- and gas phases with at least 50 % hydrocarbon compounds has only been achieved for some specific biomass types. Improved catalyst systems are needed to generalise the results. The aim of finding conditions that promote “one-pot” FTT polymerisation of gas phase products into hydrocarbons has not been achieved, probably because the catalysts tested for this purpose are not efficient under the conditions used. Further work on catalyst development is thus of great interest.

The results from more than 200 pyrolysis experiments are collected in a catalogue of experimental designs and multivariate models for each biomass and catalyst type that have been investigated. The biomass types included in the catalogue are a clean woody biomass and waste from pupling, three kinds of sewage sludge, sludge from a beer brewery, residues from alginate production and *Miscanthus* (energy crop) biomass. The experimental conditions include temperature, duration, amount of water present, loading of biomass and addition of homogeneous and heterogeneous catalysts. Products include light and heavy oils, gas exploitable as fuel gas, exploitable aqueous products (especially acetic acid) and coke. The catalogue includes tables of yields and optimised models for prediction of yields as a function of experimental conditions.

The results can be summarised as follows:

- Biomass composition determines the initial reaction pathways and product spectrum in pyrolysis in aqueous conditions
- Excess water as reaction medium increases the fluid yields for most biomass types

- High carbohydrate biomass gives high coke yields in the absence of potassium and base
- Degraded biomass gives high fluid yields with no base added
- Microbial processes “improve” the biomass raw material, possibly by degrading the bio-polymers or by adding microbial biomass into the substrate
- Catalysts must be specifically tested for each biomass type in the range of pyrolysis conditions used here
- “In situ” FTT polymerisation of gas phase products to generate high yields of hydrocarbons was not achieved in the combinations of biomass type, experimental conditions and catalysts tested here.

7.2 Pyrolysis of lignin and cutin model compounds with detailed analysis

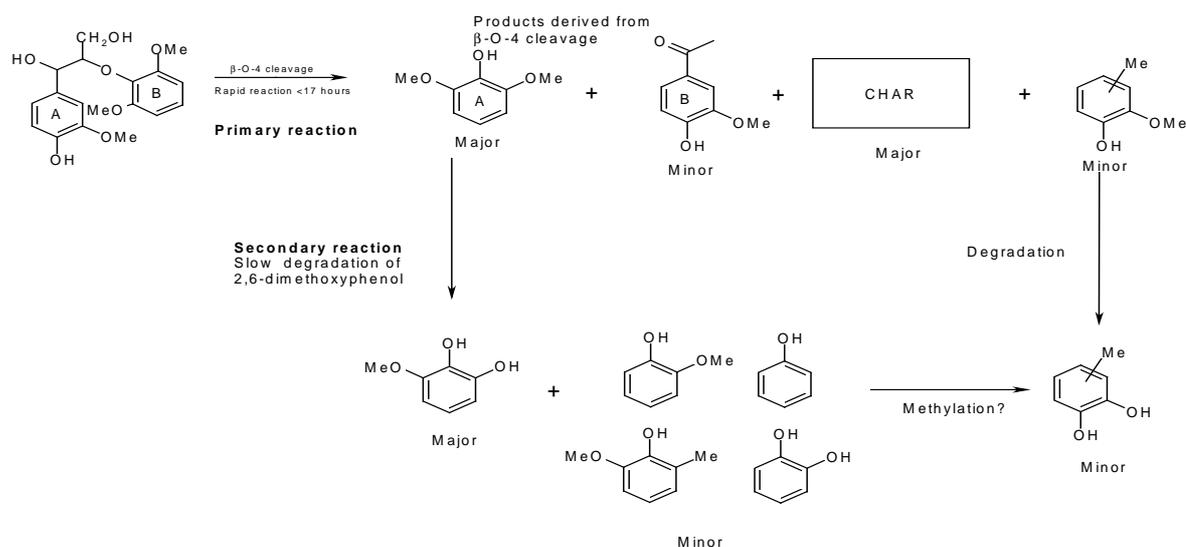
The reaction mechanisms of simple organic compounds, which can act as models for lignin and cutin in hot aqueous systems, have been investigated. The products formed from thermolysis of these compounds have been identified between 150 and 350 °C for time periods between 0 and 180 hours. Trace amounts of the aromatic hydrocarbon benzene were observed upon thermolysis of lignin monomers, however, the main liquid phase products are composed of methoxyphenols, phenols and catechols.

Pyrolysis product yields from the lignin monomeric units follow essentially first-order kinetics. Direct demethoxylation of methoxyphenols is not a major reaction pathway. In contrast the thermal demethoxylation of aromatic methoxy groups occurs via demethylation and dehydroxylation reactions. The influence of water and molecular oxygen were examined. Closed system microscale pyrolysis of 2-methoxyphenol in the presence of molecular oxygen yielded low amounts of phenol as well as benzoic acid and increased coke formation. This confirmed that pyrolysis should be conducted in the absence of oxygen.

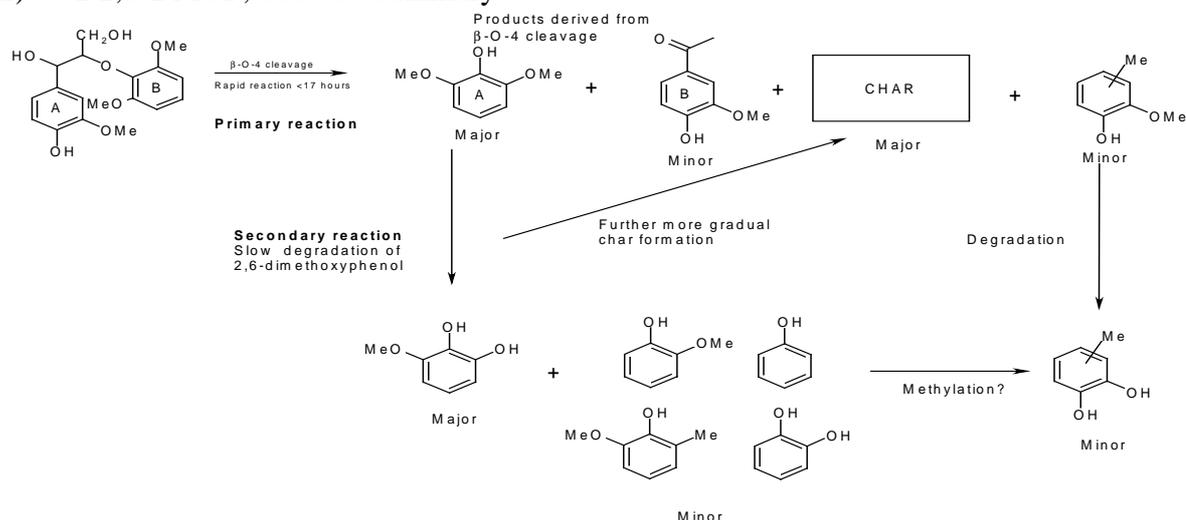
The primary reaction during thermolysis of lignin dimeric units and selected biomass types (namely thermomechanical pulp (TMP), beech wood and fungally decayed beech wood) was the homolysis of the beta-oxygen-4 link. Heating of both model dimers and TMP at temperatures equal to and greater than 270 °C yielded small amounts of water, this could arise from dehydroxylation of alkyl side chains or in the case of biomass from dehydroxylation of carbohydrates. The main secondary reactions during the thermolysis of model dimers and biomass were dehydroxylation as well as demethylation of aromatic methoxyl groups. In contrast thermolysis of lignin dimers did not yield polyaromatic moieties. Comparison of the liquid phase involatile reaction products for lignin monomers and dimers with biomass suggested that the methoxyphenol compounds are excellent analogues for lignin. Fungal degradation of biomass could be a useful pre-treatment step in that it can be used to control the pyrolysis product composition.

The reaction scheme for one of the model lignin dimers investigated in detail is illustrated below:

1) D2,6-DMOP, 270 °C - summary



2) D2,6-DMOP, 300 °C - summary



The mechanistical pathways that have been established for model compounds of lignin in woody biomass identify the critical step relative to hydrocarbon production as the conversion of simple, low molecular weight phenolic compounds into hydrocarbons by dehydroxylation. A similar limitation is seen for the fatty acid compounds investigated, where removal of the carboxylic acid function is the critical point. The knowledge of these limitations can be used to design improvements in the conversion process, e.g. better catalyst systems, to improve the yields of fluid fuels further. However, the identified main products from the direct conversion as used here are valuable and potentially exploitable as industrial chemicals, and can replace such chemicals now produced from petroleum.

7.3 Thermodynamics, energy and mass balance

Thermodynamic models support the experimental observations that the presence of excess water enhances increases the driving force for hydrocarbon production relative to carbon (coke). Hydrogen is also a promising product based on thermodynamic evaluations, and is also observed in good yields in the biomass pyrolysis. The energy

balance of the processes is moderately positive (temperature increase of 20-25 °C) or neutral. Thus, no basic limitations for the conversion of biomass into hydrocarbons exist in the thermodynamic aspects. The high yield of acetic acid that is observed in many experiments is not supported by the thermodynamic models. Additional work is needed to explain the acetic acid generation processes.

The energy and mass balance prepared on the basis of a set of experimental data for aqueous pyrolysis of clean woody biomass in water (weight ratio 1 g dry biomass to 9 g water) at 360 °C for 17 hours with sodium hydroxide added and is given in Table 1.

Table 1. Experiment K2-4

INPUT SPECIES	Temp.	Amount	Amount	Amount	Latent	Total
Formula	°C	Kmol	Kg	Nm3	Mcal	Mcal
C ₆ H ₁₂ O ₆ (DXTg)	360	5.551	1000	124.4	130.543	-1558.5
H ₂ O(g)	360	489.587	8820	10973.4	1369.684	-26927.4
OUTPUT SPECIES	Temp.	Amount	Amount	Amount	Latent	Total
Formula	°C	Kmol	Kg	Nm3	Mcal	Mcal
H ₂ O(g)	360	499.578	9000	11197.35	1397.637	-27477
H ₂ (g)	360	8.450	17.034	189.261	19.745	19.745
CO ₂ (g)	360	0.831	36.572	18.471	2.931	-75.225
CO(g)	360	0.002	0.056	0.045	0.005	-0.048
CH ₄ (g)	360	0.159	2.551	3.564	0.571	-2.274
C ₂ H ₄ (g)	360	0.013	0.365	0.291	0.062	0.225
C ₂ H ₆ (g)	360	0.06	1.804	1.345	0.354	-0.861
C ₃ H ₆ (PPYg)	360	0.015	0.648	0.345	0.110	0.185
C ₃ H ₈ (PPAg)	360	0.025	1.102	0.56	0.213	-0.408
C ₄ H ₁₀ (NBAG)	360	0.026	1.511	0.583	0.288	-0.496
C ₅ H ₁₂ (PENg)	360	0.009	0.649	0.202	0.123	-0.192
C ₆ H ₁₄ (HEXg)	360	0.143	12.31	3.202	2.326	-3.382
C ₆ H ₆ O ₃ (BTRg)	360	0.475	59.89	10.644	7.442	-43.168
C ₆ H ₆ O(PHEg)	360	1.151	108.31	25.795	13.907	-12.597
C ₂ H ₄ O ₂ (ACAg)	360	3.507	210.6	78.603	25.130	-339.346
Solid						
C ₂₀ H ₁₂ (PER)	360	0.065	16.4	0	1.484	3.946
		Kmol	Kg	Nm3	Mcal	Mcal
Total		19.372	-350.198	432.446	-27.899	555.108
BALANCE						
ELEMENT	Input	Output	Balance	Input	Output	Balance
	Kmol	Kmol	Kmol	Kg	Kg	kg
C	33.304	20.334	-12.971	400.017	244.227	-155.79
H	1045.782	1044.327	-1.455	1054.043	1052.577	-1.466
O	522.891	510.832	-12.059	8365.94	8172.998	-192.941

Element Balance Error: -38.95 % for C File: C:\HSC3\K24.BAL

The missing elements are oxygen (193 kg) and carbon (156kg), which is probably lacking carbon dioxide in the exit.

By adding carbon dioxide to the exit for balancing C and adjusting the O and H balance with steam and hydrogen, we obtain a temperature increase of about 20 °C.

The products from pyrolysis in an aqueous environment have been compared with the products from flash pyrolysis. The oil produced in the hydrous system is of better quality in the conventional petroleum sense, and the heating value is the double of the flash pyrolysis bio-oil. The economy of the hydrous process is better than the flash pyrolysis process for sludges as input materials. A general comparison of pyrolysis technologies is given in Table 2.

Table 2: Comparison of different pyrolysis technologies

Pressure	React. Time	Process	Yield (weight basis)	Primary product	Actor
Vacuum	1 s	Flash pyrolysis	70 %	C:57, H:6.3 O:36 H ₂ O:26, NWM	Univ. Laval, Univac
Atm.	1 s	Flash pyrolysis	70%	C:57, H:6.3 O:36 H ₂ O:26, NWM	RTI/Dynamotive, Ensyn
3Mpa	5m	Fischer Tropsch	30%	Synthetic oil	Sasol
2 Mpa	5 m	Thermo chemical liquefaction in recycle solvent	25%	O: Low Upgraded product	KTH, Stockholm
10 Mpa	5m	Meshano solvolytica liquefaction	40-60%		Univ of Sherbrooke, Ca
20 Mpa	30 m	Liquefaction in recycle oil with reducing gas	30%	O 1% NWM (refined product)	VTT, Veba oil
20 Mpa	30-90 m	Liquefaction in high pressure steam	25-35%	O:15 NWM	DTI, KTH,VTT, Risø
12-18 Mpa	10 m	Liquefaction in high pressure steam	50%	C:75, H:6.3 O:13 NWM	Shell Hydrothermal Upgrading Process
10-20 Mpa	360-1000m	Liquefaction in high pressure steam	28% HAc 20% HC	C:90, H: 7, O:2 NWM	UIB/UN/DTI

NWM : Not Water Miscible

Technical solutions for reactors and plants have been considered, and plants can be designed with an indicated good economy. If the residence time in the system can be reduced, the economy would improve. Again, catalysts could potentially improve the process and make the process even more economical.

8. Exploitation plan and expected benefits

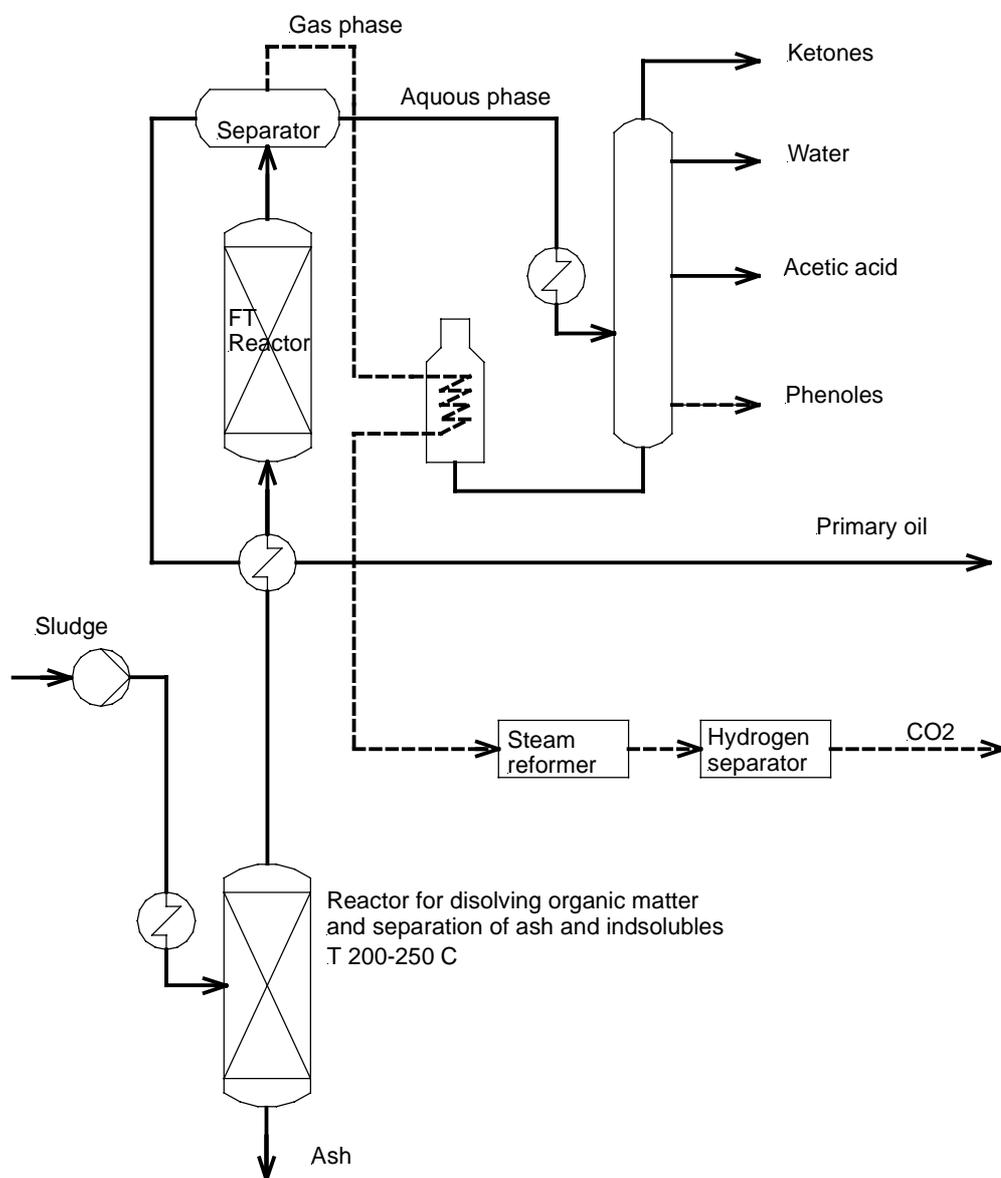
The main results of the project are the improved understanding of the kinetics and reaction pathways of lignin compounds during pyrolysis in the presence of water, the specific knowledge of the dependence of the conversion and product spectrum on the pyrolysis conditions for different biomass types during pyrolysis in aqueous media,

and the thermodynamic models for aqueous pyrolysis with energy and mass balances for two biomass types. These results will be exploited for further research and development in the following ways

- The kinetic schemes developed can be tested by other research workers and, if generally applicable, could be used in the exploitation of specific biomass or waste types.
- The catalogue with quantitative models describing the relationship for each combination of raw material and products can be used to select optimal combinations for further development of aqueous pyrolysis. The catalogue will be used as a basis for further basic and applied research, and potentially development of processes for valorisation and waste management for wet wastes.
- The thermodynamic and energy models will also be made available for use in further research and development of aqueous pyrolysis processes.

- 9. Illustration

Figure 1: A process scheme for aqueous pyrolysis of wet sludge.



Sludge or wet biomass is pumped, heated and fed the reactor, where the organic matter is dissolved. The reactor has an internal heat exchanger with tubes in which the sludge is heated downstream inside the tubes. The liquid becomes supercritical in the bottom where insoluble are separated by filtration and discharged. The liquid with dissolved organics is directed upward on the shell side of the tubes filled with catalyst.