Ablative Flash-Pyrolysis of Biomass Investigation of Upgrade Processes of Pyrolysis Liquids

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Fraunhofer Innovationcluster Bioenergy

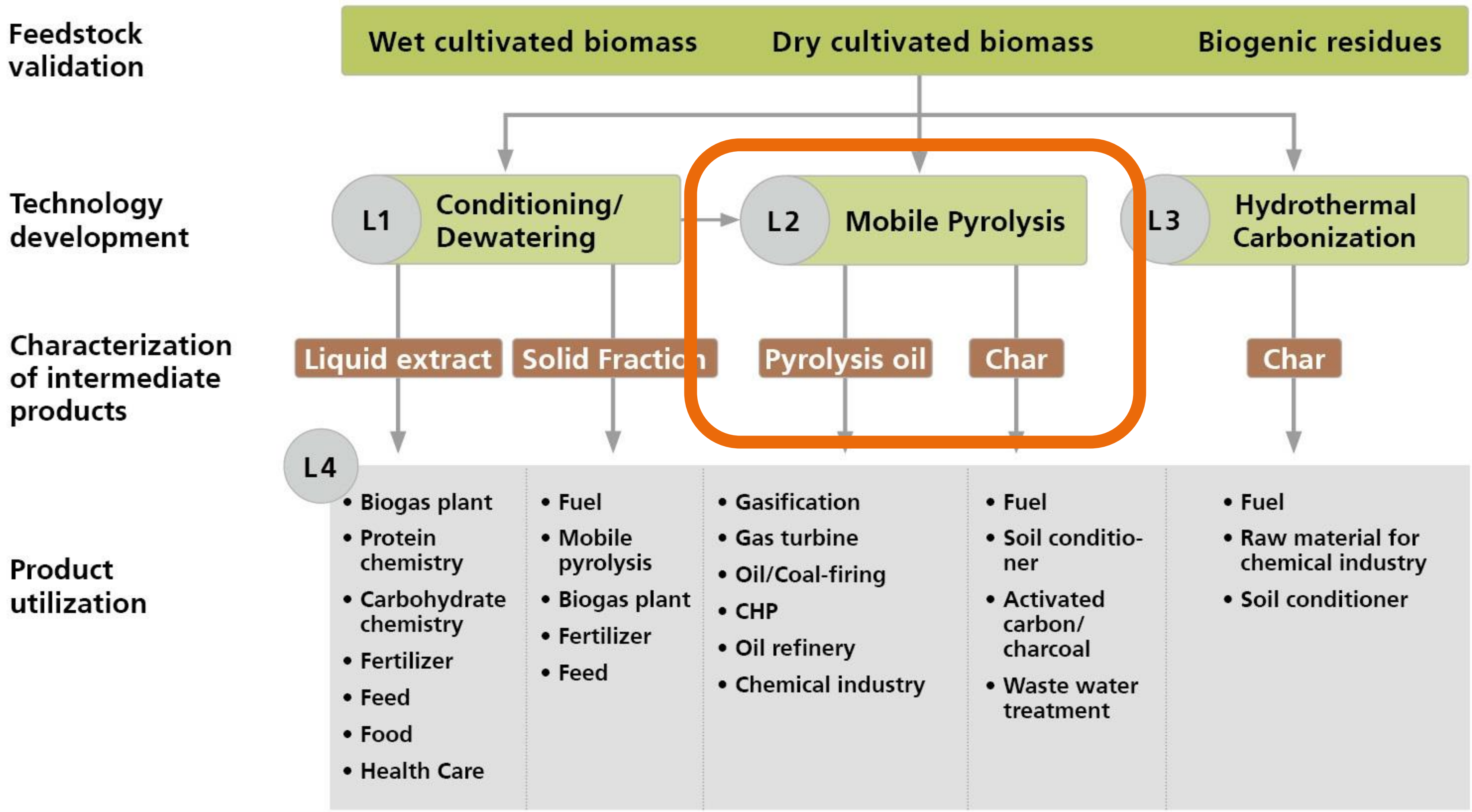
Innovationcluster »Bioenergy«

- Start 07/2012
- Project: 3.5 Years
- Project: 4 mio. €
- Current partners : 12 Companies, 2 Universities/ Research Institutes

Topics covered

- »Wet« biomass and waste streams as Carbon resource for material and energetic use
- Storable and transportable (economy!) intermediate products.
- Technologies for a mobile/decentral conversion

Project concept of the Innovationcluster Bioenergy -



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Why Ablative Flash Pyrolysis?

Specifications raised by industrial customer/partner:

Mobile onsite pyrolysis of **agricultural waste** e.g. straw, with **high throughput** (like threshers)!

- Slow pyrolysis not applicable due to high throughput requested
- Fast pyrolysis techniques as fluidised bed or rotating cone processes are not applicable due to the fact that fine particles are required for those processes and onsite grinding of straw is far to expensive.
- Ablative Flash Pyrolysis is the only applicable pyrolysis technology as it is suitable for untreated straw (onsite) and allows high throuput (4 t/h).

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Why mobile pyrolysis? Prozess chain straw – cost structure

	Cost ratio	Costs
Straw Harvest; Windrow stocking	26 % (Nutrient compensation)	**25,51 €/t**
Grabbing, (crushing), baling press	34 %	33,30 €/t
Transport 5 km	5 % (1 €/(t*km))	5 €/t
Storage (Field side/Hall, 6 months)	35 % (Hall)	35,00 €/t
Utilization/ disposition	100 % (Hall)	**98,81 €/t**

73 €/t = 75 % LOGISTIC COSTS

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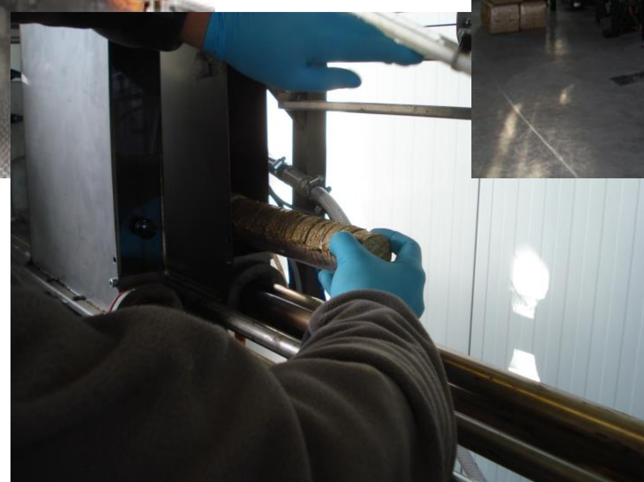
Ablative flash pyrolysis at Fraunhofer UMSICHT

10 kg/h wood or straw (briquette)

100 kg/h straw (chopped)



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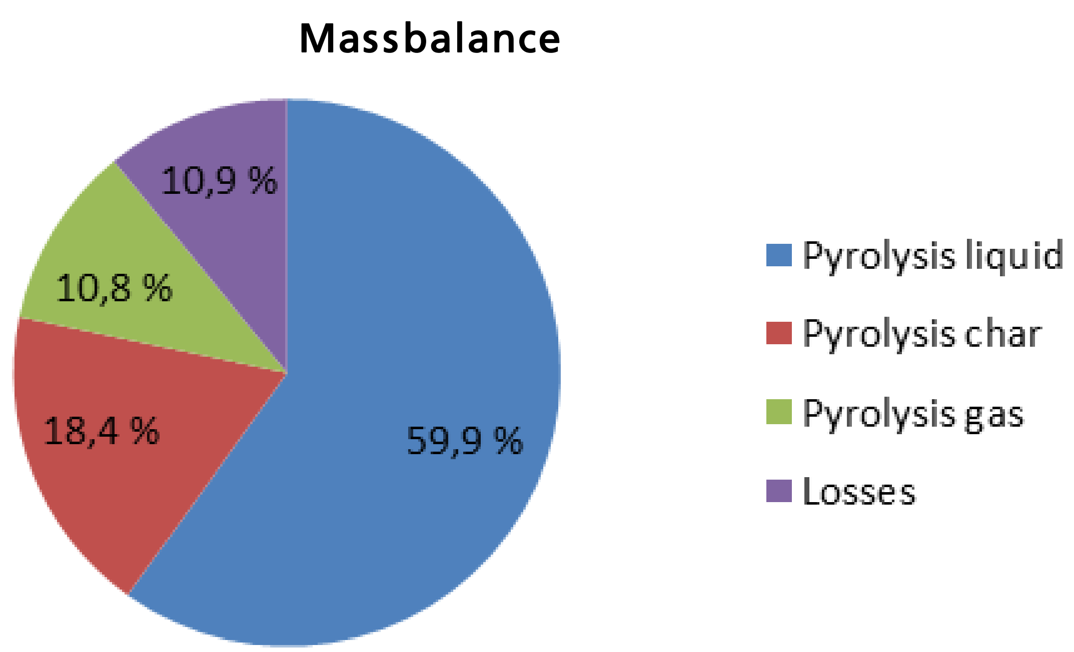
Experiments with wood / massbalance

Approximatly 200 kg of differend types of wood (sprunge, fir, beech) have been pyrolysed

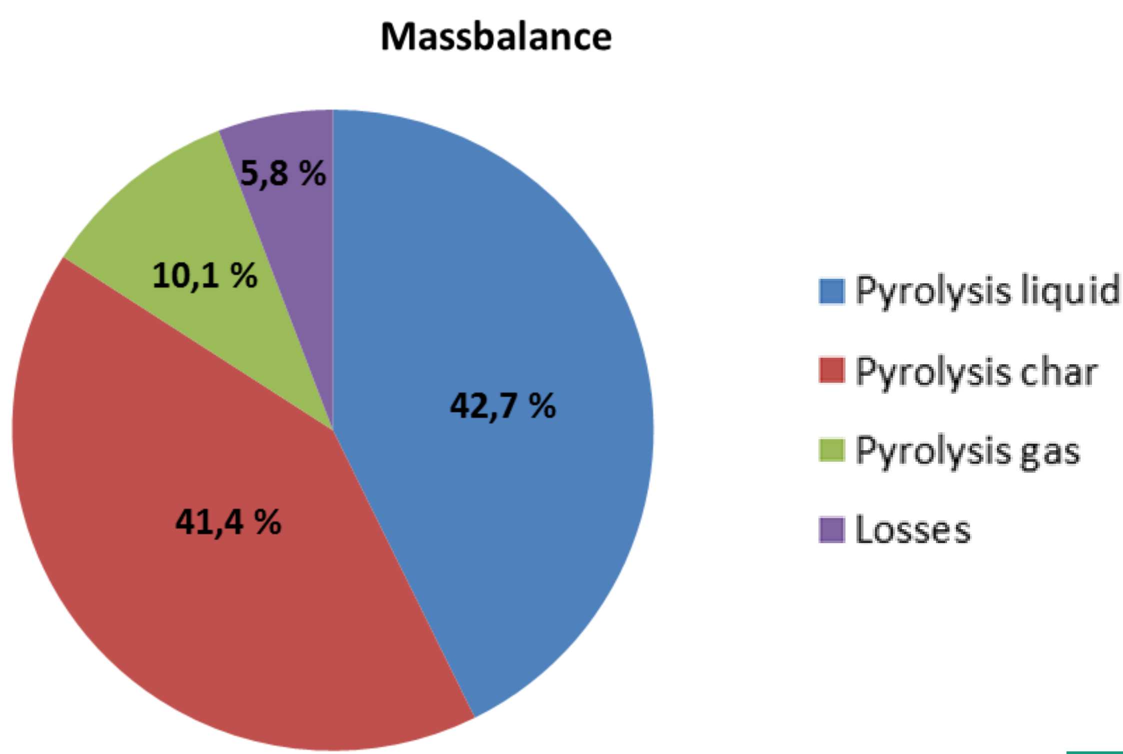
Massbalance has been worked out by pyrolysing 43,1 kg of beech wood at 550°C, contact pressure 60 bar, througput 3,1 kg/h, rotating plate 1 m/s



Experiments with straw / massbalance

Approximatly 100 kg of barley straw (pressed to briquetts of 48 mm diameter) have been pyrolysed

Massbalance has been worked out by pyrolysing 47,1 kg of barley straw at 490° C, contact pressure 50 bar, througput 6,5 kg/h, rotating plate 1 m/s



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Pyrolysis liquids – problematic components

Pyrolysis liquid consits out of up to 400 different components

like acids, sugars, phenols aldehydes ketones, oligomers, water

Problems (flash Pyrolysis):

- TAN (acetic acid), as there is no phase separation
- Viscosity (phenols, sugars), higher „Tar formation“
- Water content (up to 30%), as there is no phase separation
- Low heating value
- Aging (Polymerisation)

Upgrading – Esterification + Hydrogenation

„Development of a combined procedure for the upgrade of pyrolysis liquids with alcohols and hydrogen "

Founded by FNR, Germany (Fachagentur Nachwachsende Rohstoffe e.V.)

Co-Project: Fraunhofer UMSICHT (Oberhausen) & Thünen-Institut für Holzforschung (Hamburg)

Aims:

Hydrophobisation of liquids to induce phase separation

Increase of heating values

Increase of the pH value (lowering of TAN)

Decrease of the viscosity

Inhibition of aging – enhanced storage stability

= Applicable for CHP use / fuel

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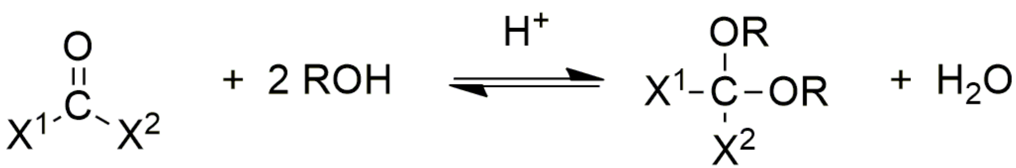
Upgrade pyrolysis liquids

Esterification/Acetal formation

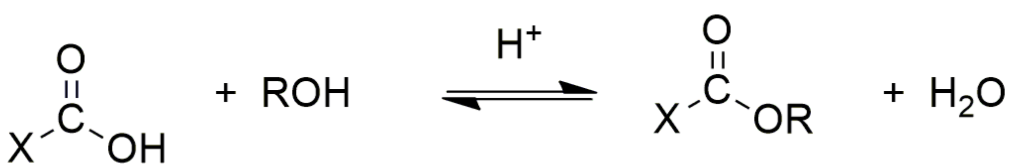
- Saturation of reactive/functional groups (Acids, Aldehydes, Ketones)
- Utilisation of higher alcohols (Butanol, Hexanol, etc.)

(better separation of water due to higher boiling point and hydrophoby)



Acetal formation

(Aldehydes, Ketones)



Esterification

(Acids)

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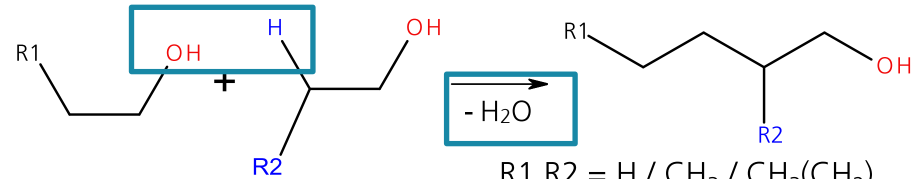
Production of linear and branched higher alcohols from methanol, ethanol, or butanol (US 2013/02 11146 Al , A. Kraft; A. Menne)

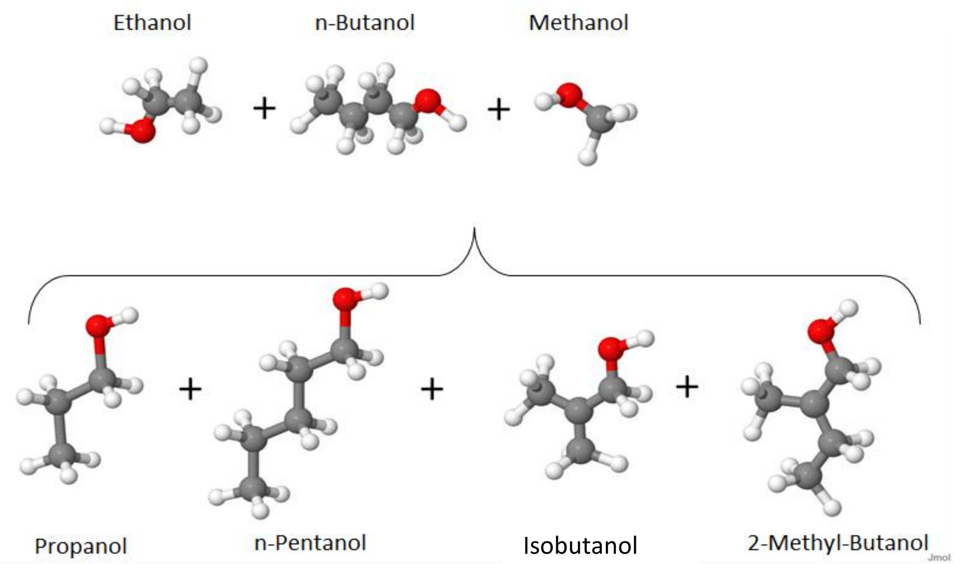
- The reactions of two mols alcohol forms a branched or linear higher alcohol under the elimination of water



R1,R2 = H / CH_3 / $CH_3(CH_2)_{n,\ n=1\text{-}3}$

- Side products are water, corresponding aldehydes, hydrogen, alkanes and alkenes

- Crossreactions (supported through Recycling of unconverted products or side products) forms higher alcohols with more than 6 carbon atoms



- Adding of Methanol leads to increased branching

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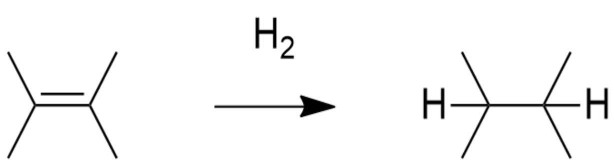
Further process

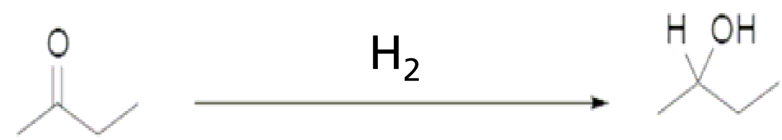
Thünen-Institut für Holzforschung, Hamburg (D. Meier)

Hydrogenation of esterified pyrolysis liquid (H_2 from char reforming)

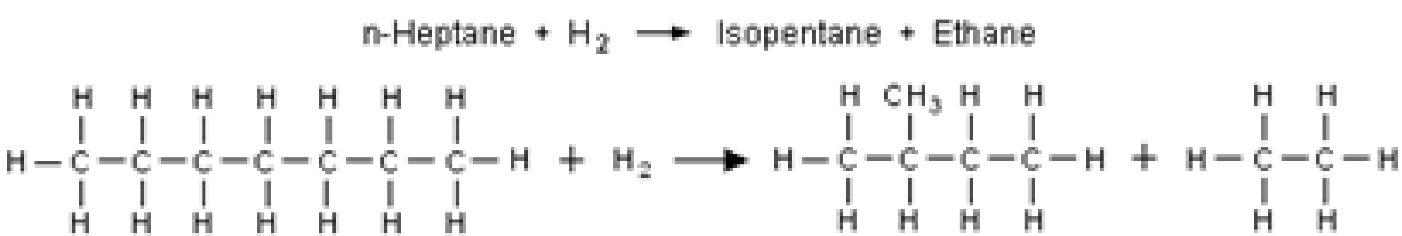
Two Options:

1. Hydrotreatment





→ Hydrocracking



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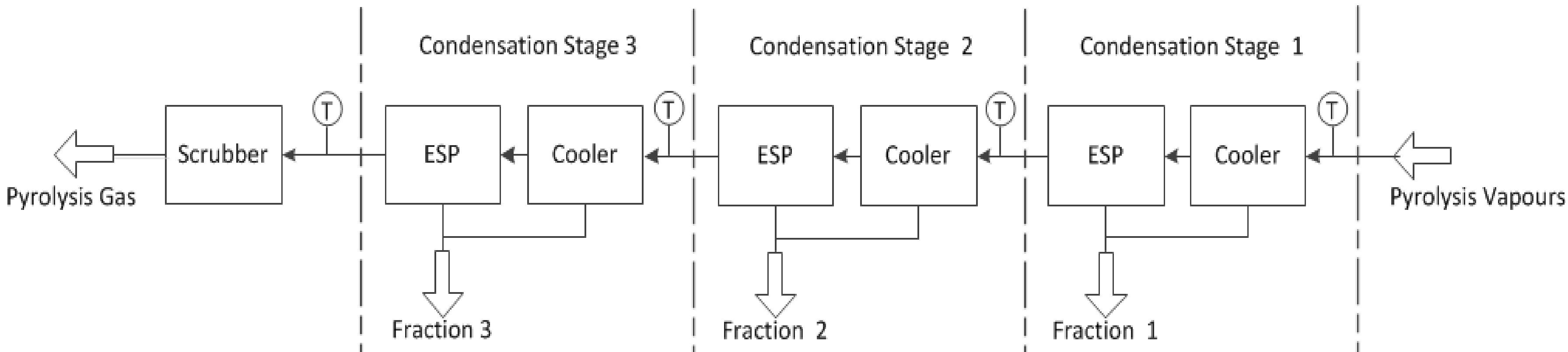
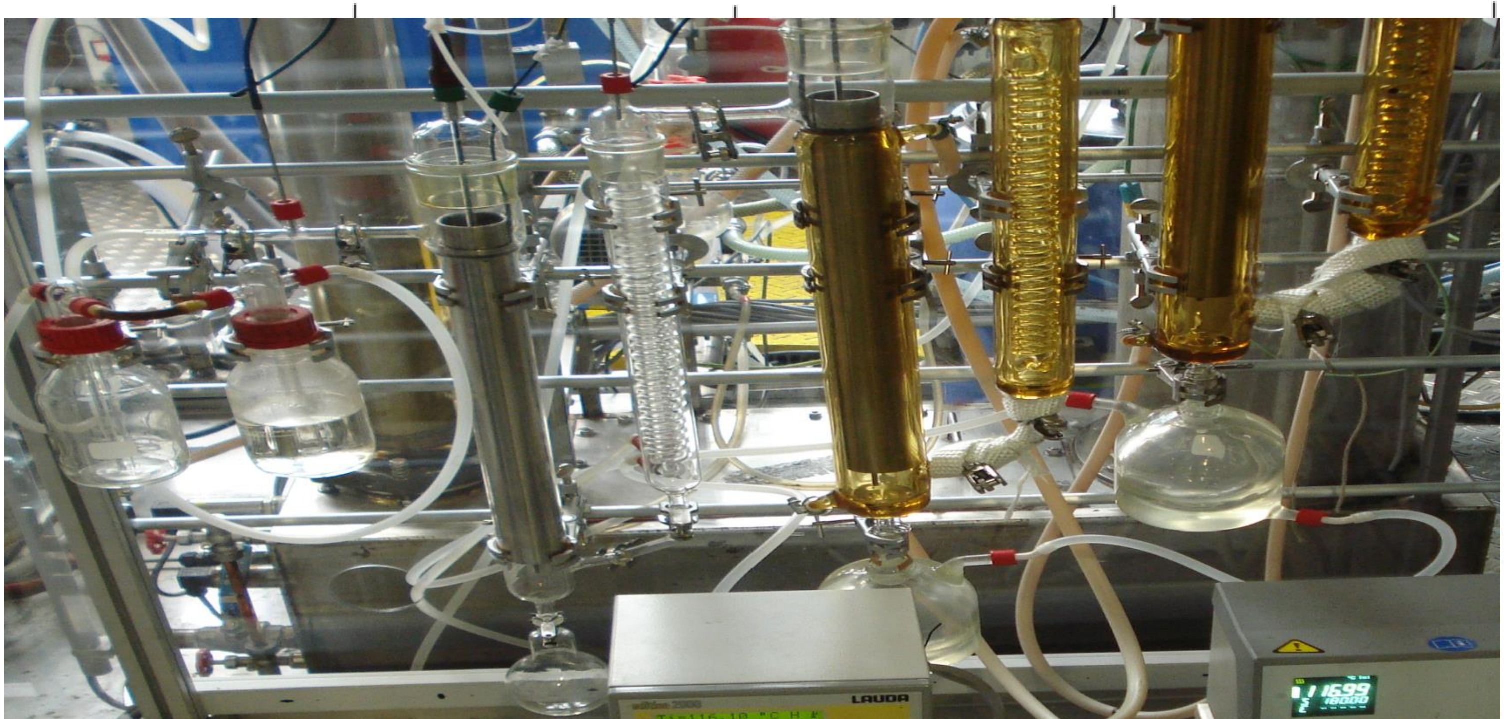
Fractional condensation of pyrolysis vapours

Even a simple, common condensation unit, consisting out of a cooler and an aerosol precipitator leads to two different fractions

	Mixture	Condenser	ESP
Mass	100 g	30,3 %	69,7 %
Water	32 %	59 %	41 %
Acids	3,5 %	34 %	66 %
Sugars	9,7 %	24 %	76 %

Fractional condensation of pyrolysis vapours





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Fractional condensation of pyrolysis vapours

Substance	Average Percentage	Boiling Point	Stage
Pyrolysislignin	**13,7 %**	**>>**	1. Condensation stage
Levogucosane	**4,0 %**	**384°C**	1. Condensation stage
Syringoles	**5,4 %**	**260-350°C**	1. Condensation stage
Guajacoles	**1,9 %**	**200-260°C**	2. Condensation Stage
Phenoles		182°C	2. Condensation Stage
Acetol	**3,5 %**	**147°C**	2. Condensation Stage
Glycolaldehyde	**4,0 %**	**131°C**	2. Condensation Stage
Acetic acid	**9,5 %**	**118°C**	3. Condensation Stage
Formic acid		101°C	3. Condensation Stage
Water	**24 %**	**100°C**	3. Condensation Stage
Propanal		49°C	3. Condensation Stage

First results for fractional condensation of pyrolysis vapours (beech)

	Reference	Fraction 1	Fraction2	Fraction3
Temperature	5 °C	125°C	90°C	5°C
Ratio	100%	38,4 %	11,1 %	50,5 %
Heating Value (LHV)	15,4 MJ/kg	23,6 MJ/kg	20,6 MJ/kg	9,2 MJ/kg
Water	28,7 %	3,7 %	5,7 %	51,0 %
C	39,6%	60,18 %	52,39 %	23,28 %
H	7,96 %	6,29 %	7,07 %	9,34 %
O	52,35%	33,39 %	40,45 %	67,38 %
Acids	10,4 %	1,1 %	8,5 %	16,9 %
Nonaromatic Aldehydes	3,47 %	0,39 %	9,22 %	0,33 %
Nonaromatic Ketones	5,5 %	0,9 %	9,7 %	6,3 %
Furans	2,6 %	1,8%	6,1 %	2,4 %
Pyrans	0,18 %	0,76%	1,4 %	0,1 %
Guaiacols	2,0 %	2,7 %	7,2 %	0,8 %
Syringols	5,5 %	12,3%	9,1 %	0,3 %
Sugars	5,94 %	17,5 %	5,2 %	0,02 %

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Conclusion:

- Ablative fast pyrolysis is working in lab and pilot scale
- Investigations for pyrolysis of wood and straw have been carried out in lab scale
- In pilot scale first test runs with straw have been undertaken
- Upgrade processes have to be carried out for optimisation of pyrolysis liquids
- First steps for esterification as well as for fractional condensation have been carried out

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Thank you for your attention

Förderhinweis

Der Fraunhofer Innovationscluster Bioenergy wird gefördert vom Ministerium für Innovation, Wissenschaft und Forschung des Landes Nordrhein-Westfalen (MIWF) mit Mitteln des Europäischen Fonds für regionale Entwicklung (EFRE) und durch die Fraunhofer Gesellschaft zur Förderung der angewandten Forschung e.V.

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	Beech wood	Straw organic Phase	Straw aqueous Phase
Ratio	100%	30 %	70 %
Heating Value (LHV)	15,4 MJ/kg	23,4 MJ/kg	8,3 MJ/kg
Water	28,7 %	15,9 %	59,6 %
C	39,6%	54,7 %	20,6%
H	7,96 %	7,9 %	9,6%
O	52,35%	36,6 %	69,6 %
Acids	10,4 %	4,3%	6,3 %
Nonaromatic Aldehydes	3,47 %	0,9 %	0,0 %
Nonaromatic Ketones	5,5 %	4,7 %	4,9 %
Furans	2,6 %	1,7%	1,5 %
Guaiacoles	2,0 %	4,5 %	0,5 %
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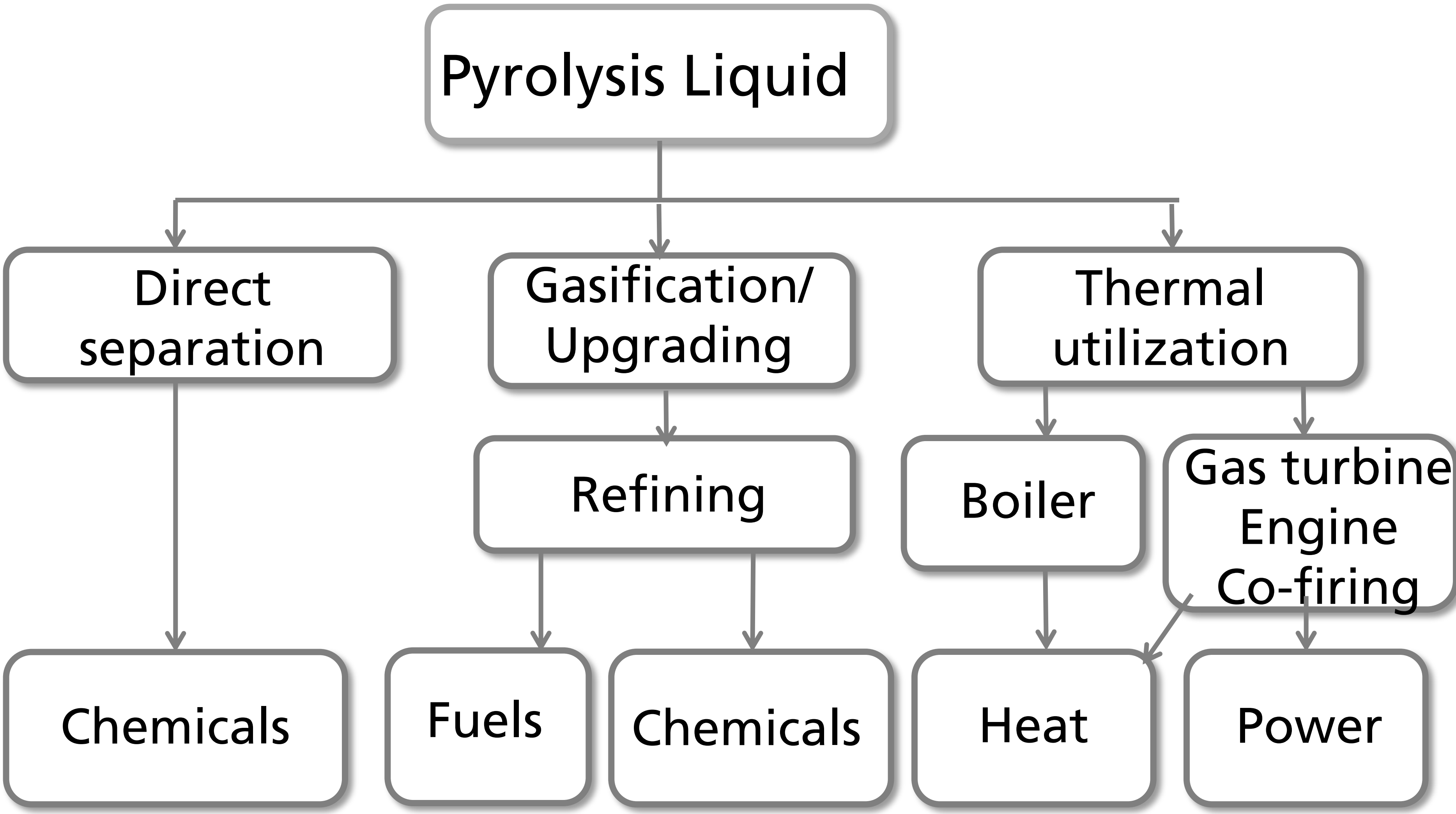
Sugars	5,94 %	0,9 %	1,8 %



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