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Stabilization step within hydrotreatment of fast pyrolysis bio-oil

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Stabilization Step within Hydrotreatment of Fast Pyrolysis Bio-Oil

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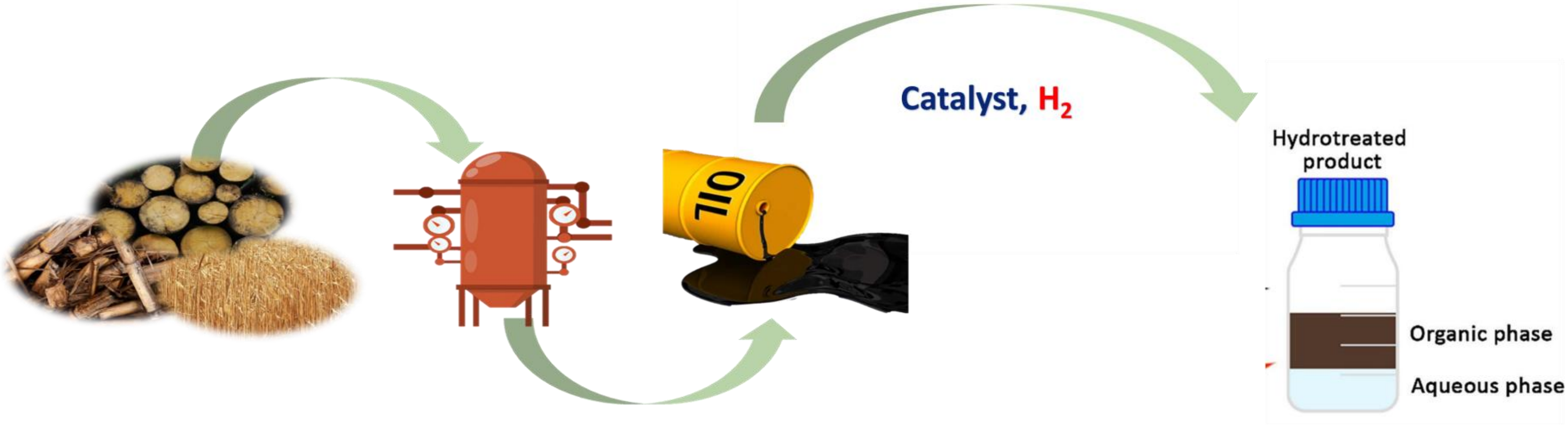
EUBCE
32nd European Biomass Conference & Exhibition

Utilizing Fast Pyrolysis Bio-Oil for Maritime Transportation

Fast pyrolysis bio-oil (FPBO) offers one of the viable alternatives for Marine fuels

- Lower-quality fuels such as bunker oil and marine diesel
- FPBO upgrading may be needed to meet marine fuel requirements
- Chemical/physical reactions, such as hydrotreatment, are being explored to upgrade bio-oil for meeting marine fuel requirements.

Upgrading – Hydrotreatment Process

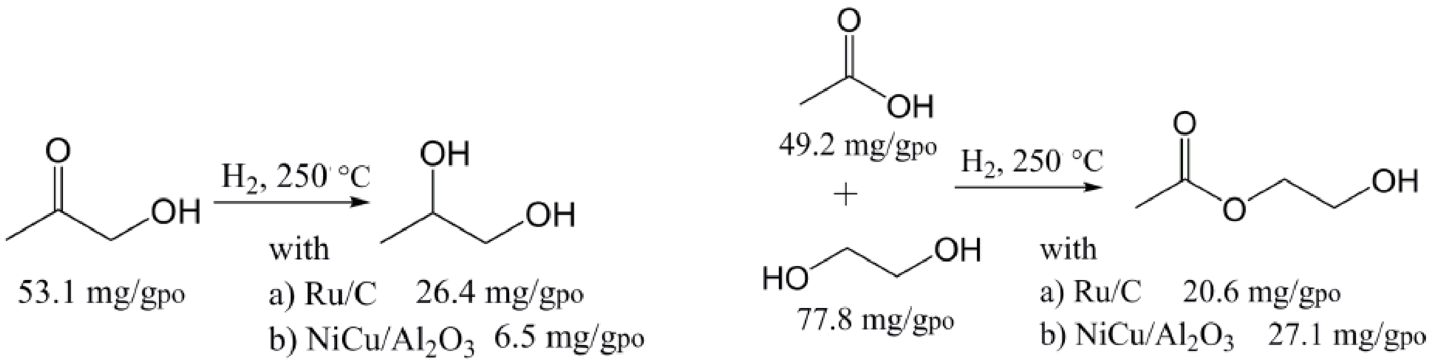


- Reaction of FPBO with hydrogen in the presence of catalyst
- Promotes deoxygenation and hydrogenation reactions

Upgrading – Hydrotreatment Process

Bio-Oil Stabilization (150 °C - 250°C)

- Convert carboxylic acids, aldehydes, and ketones into alcohols
  - Side reactions: crosslinking and polymerization
- Water formed induces the separation of some coke precursor molecules to the aqueous phase



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Deep Hydrotreatment

- **Advantages of Stabilized Oil**: The initial stabilization removes the most reactive compounds, reducing the risk of catalyst deactivation and reactor fouling during the subsequent deep hydrotreatment step.
- **Hydrogenation and Deoxygenation**: Increasing hydrogen content while decreasing oxygen content

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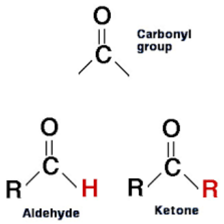
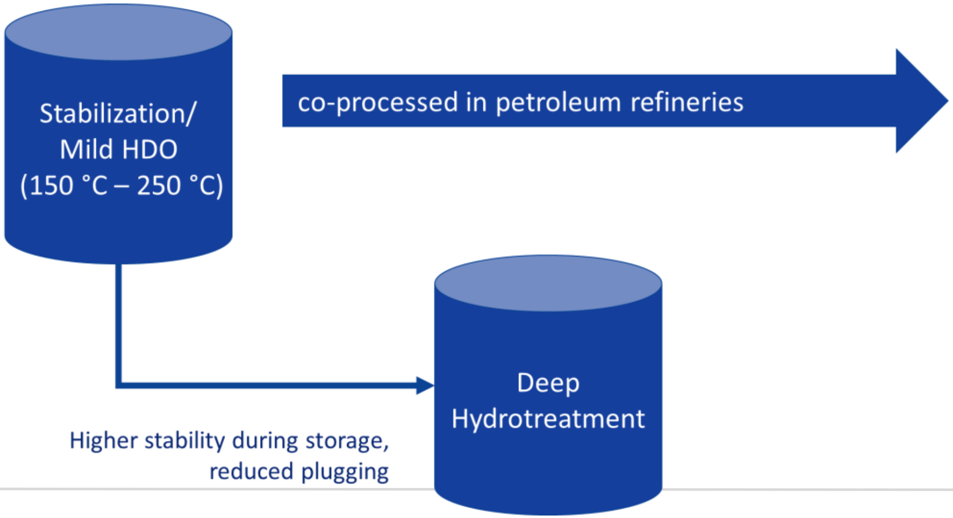
- **Hydrogenation and Deoxygenation**: Increasing hydrogen content while decreasing oxygen content

Two-Step HDO Process

Bench, pilot, or industry scales: Continuous stability of reaction systems

- Suppression of Catalyst deactivation
- Clogging of Lines
- Polymerization





Process – Dual Batch

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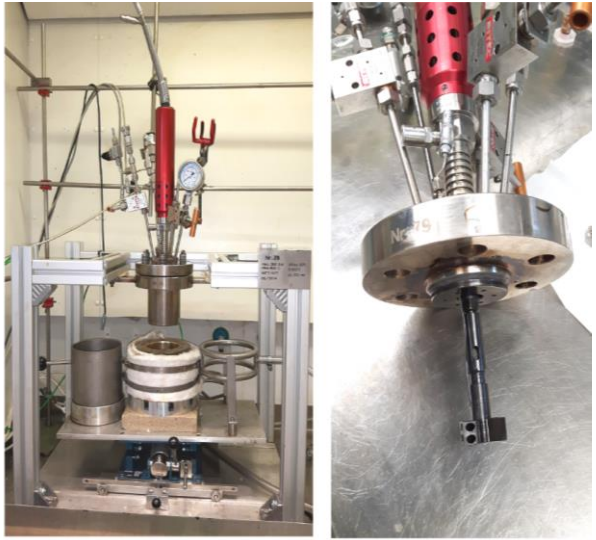
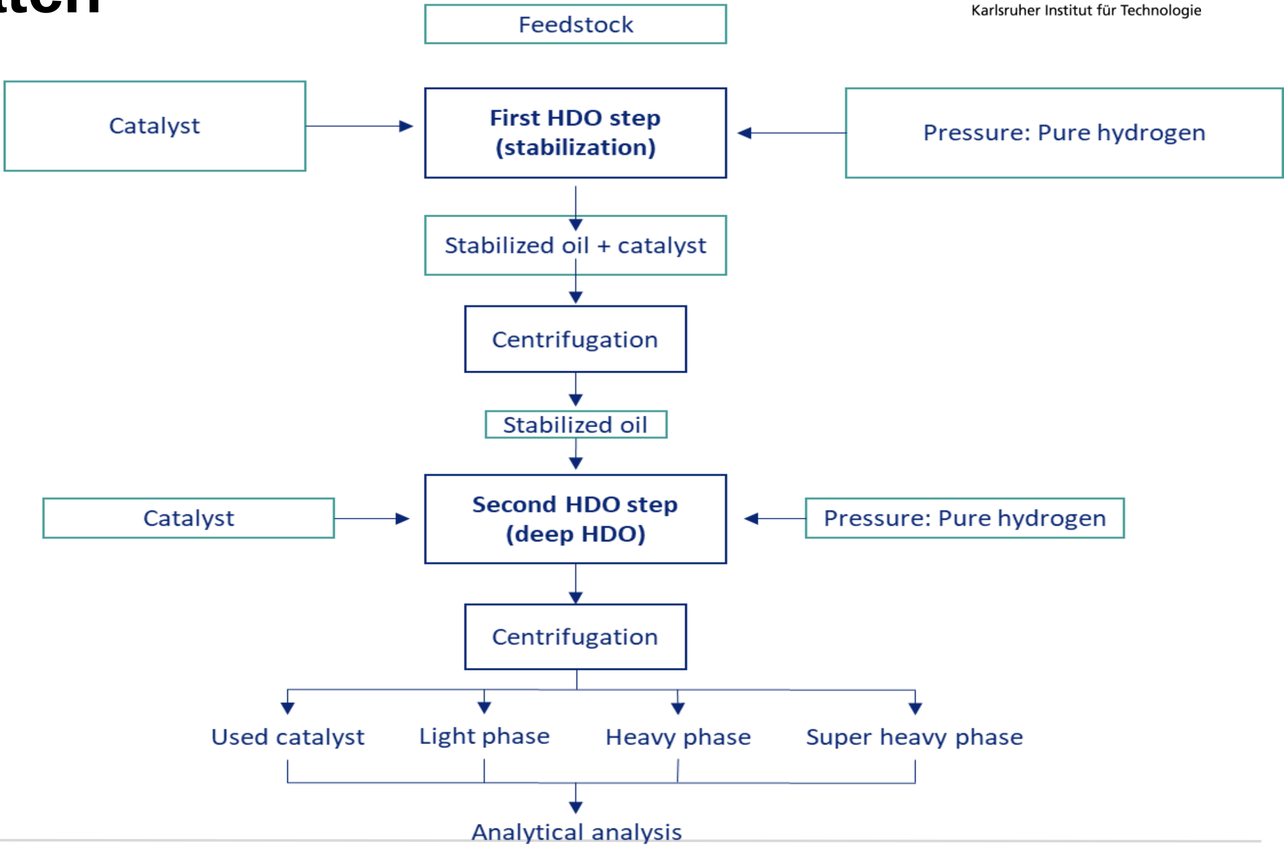


Autoclave used for the dual-batch experiments at KIT..



Catalytic Hydrotreatment

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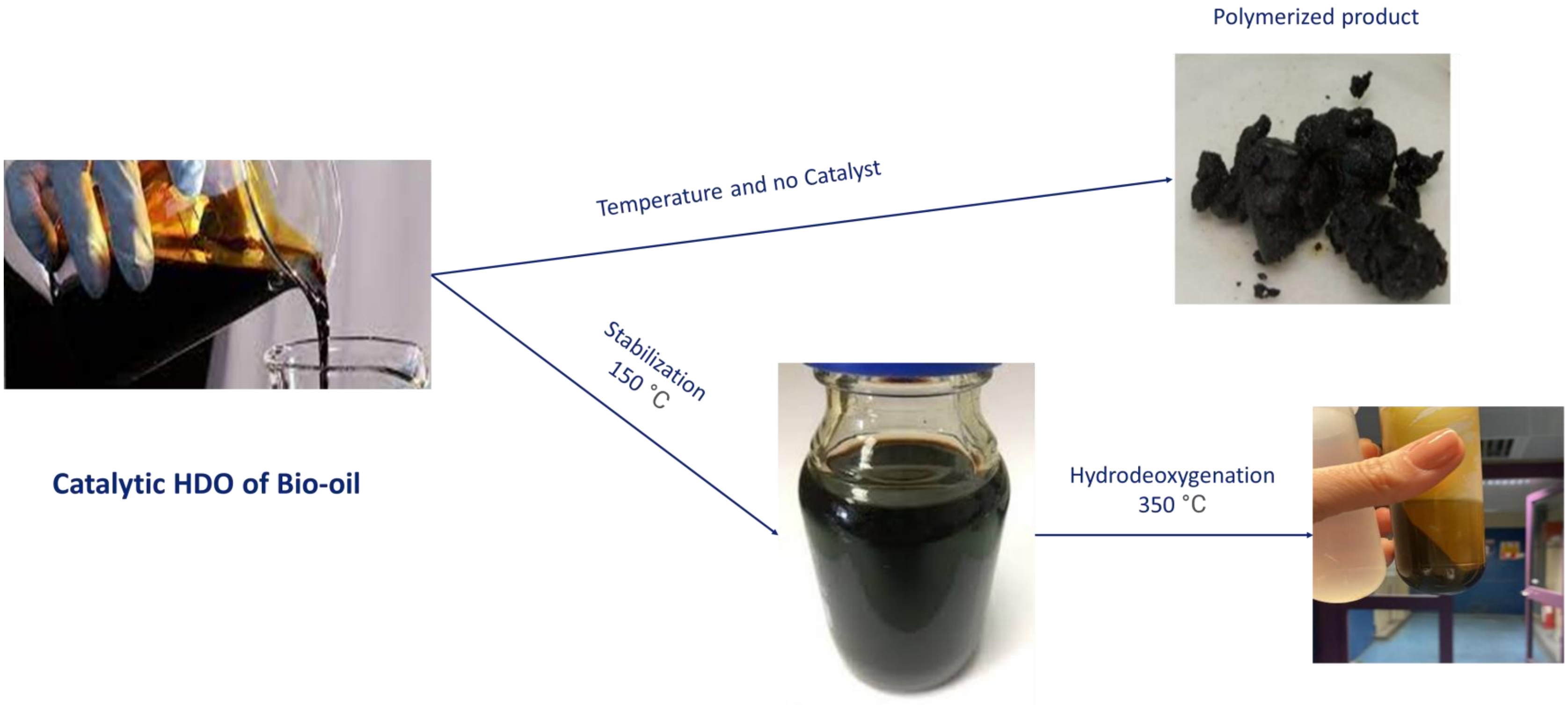

Results – Fast Pyrolyzed oil from Wheat Straw produced at bioliq® (KIT)

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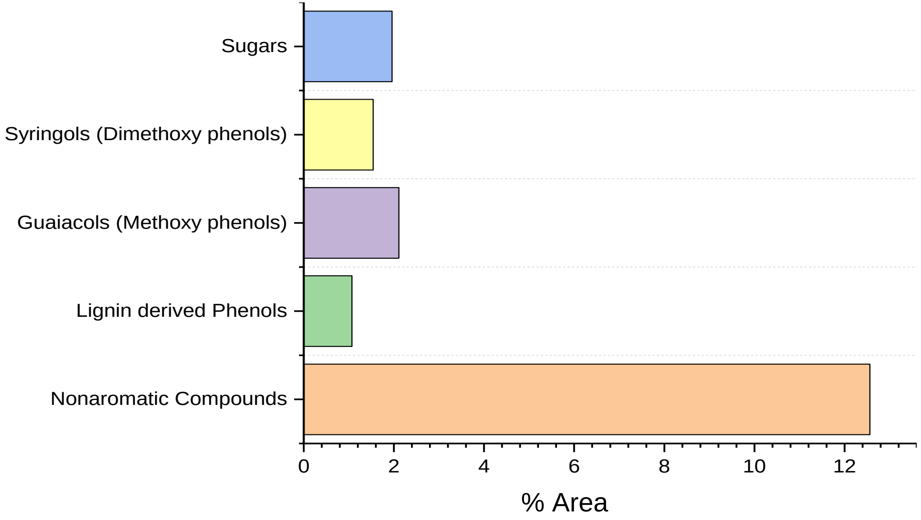
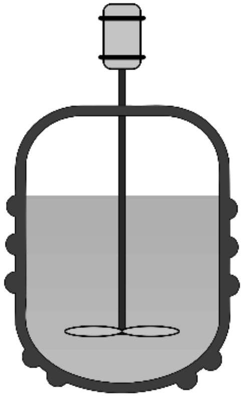
GCMS/FID Wheat Straw FPBO composition





- Temperatures: 80, 150, 250, 350 and 150/350 °C,
- 14.0 MPa H2 at room temperature
- 50 g oil + 2 g Catalysts

Results – Fast Pyrolyzed oil from Wheat Straw produced at bioliq® (KIT)

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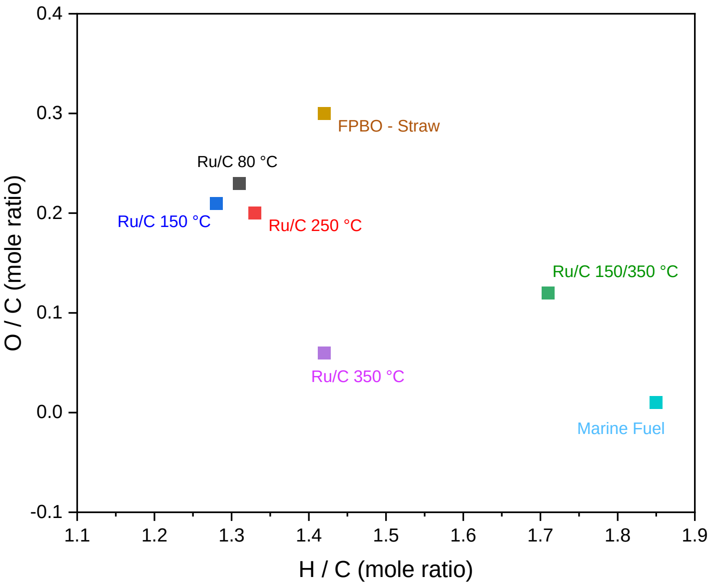
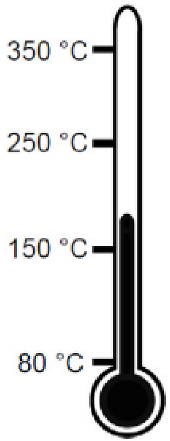
Sample	C (%)	H (%)	O (%)	N (%)	water (%)	DOD
FPBO Straw	49.7	8.5	40.6	1.2	23.7	-
80 Ru/C	63	7.9	27.4	1.7	9.2	17
150 Ru/C	62.1	8.3	28.1	1.6	12.7	25
250 Ru/C	58.4	8.2	31.8	1.6	17.5	23
350 Ru/C LP	77	10	11	1.8	1.7	64
150;350 Ru/C LP	77	10	11	1.6	1.8	62
350 Ru/C HP	60	11	28	2	21	55
150;350 Ru/C HP	49.3	10	39	1.4	40	75

Boscagli, C., Tomasi Morgano, M., Raffelt, K., Leibold, H. & Grunwaldt, J. D. Influence of feedstock, catalyst, pyrolysis and hydrotreatment temperature on the composition of upgraded oils from intermediate pyrolysis. Biomass and Bioenergy 116, 236–248 (2018).

Results – Fast Pyrolyzed oil from Wheat Straw produced at bioliq® (KIT)

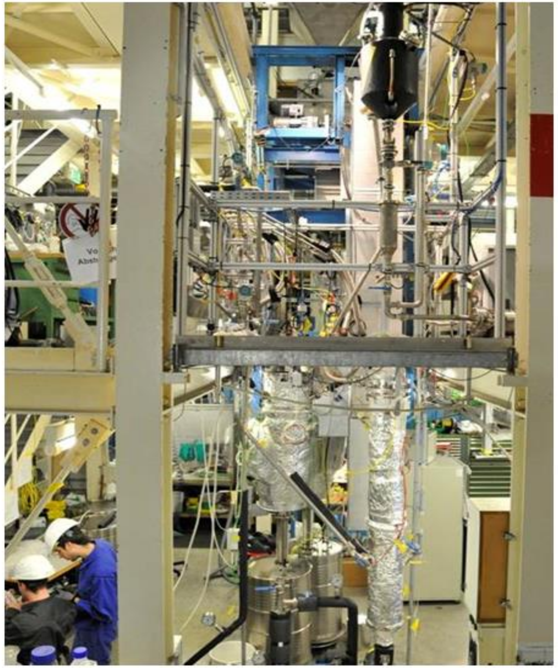




- Higher hydrogenation activity at low temperatures – Stabilized oil
- Deoxygenation, together with an increase of the H_2 content at higher temperatures
- Maximum HHV value at 350 ˚C with stabilization at 150 ˚C.

Boscagli, C., Tomasi Morgano, M., Raffelt, K., Leibold, H. & Grunwaldt, J. D. Influence of feedstock, catalyst, pyrolysis and hydrotreatment temperature on the composition of upgraded oils from intermediate pyrolysis. Biomass and Bioenergy 116, 236–248 (2018).

Pyrolysis Oil – Sugarcane Bagasse Biomass

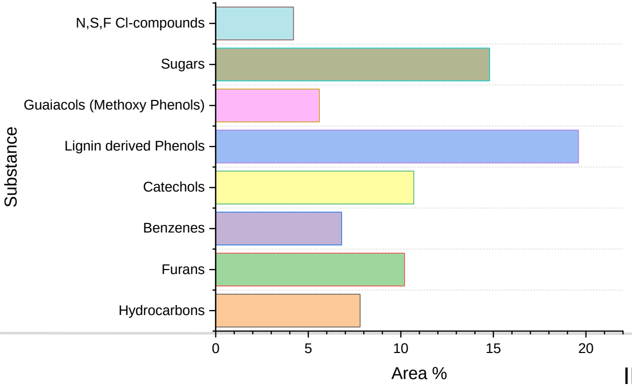


Python Pilot Pyrolysis Plant - KIT

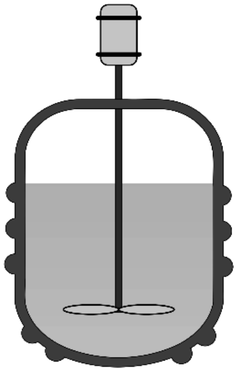
	C (%)	H (%)	O (%)	N (%)	H_2O (%)	HHV (MJ.Kg)
Sugarcane Bagasse	46	6	41.8	0.4	13.2	18.44
FPBO - Sugarcane Bagasse	58	6.4	34.8	0.8	1.1	23.2

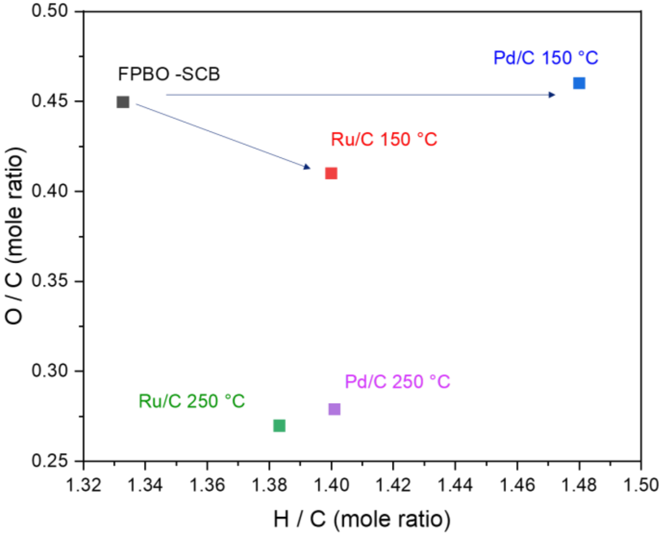
- Low water content

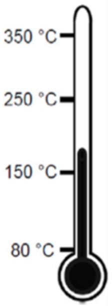
GCMS/FID composition



Results – Fast Pyrolyzed oil from Sugarcane Bagasse produced at Python (IKFT- KIT)





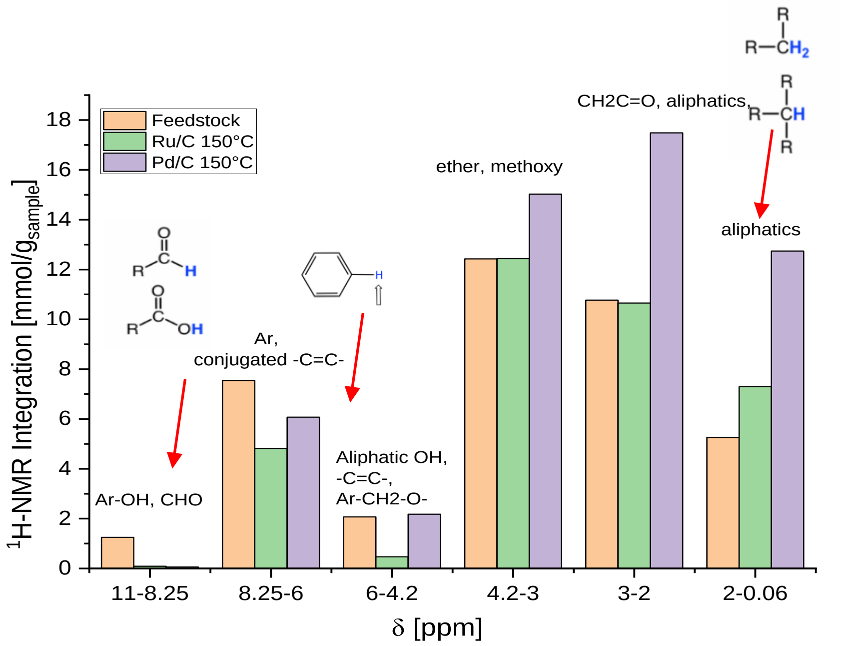


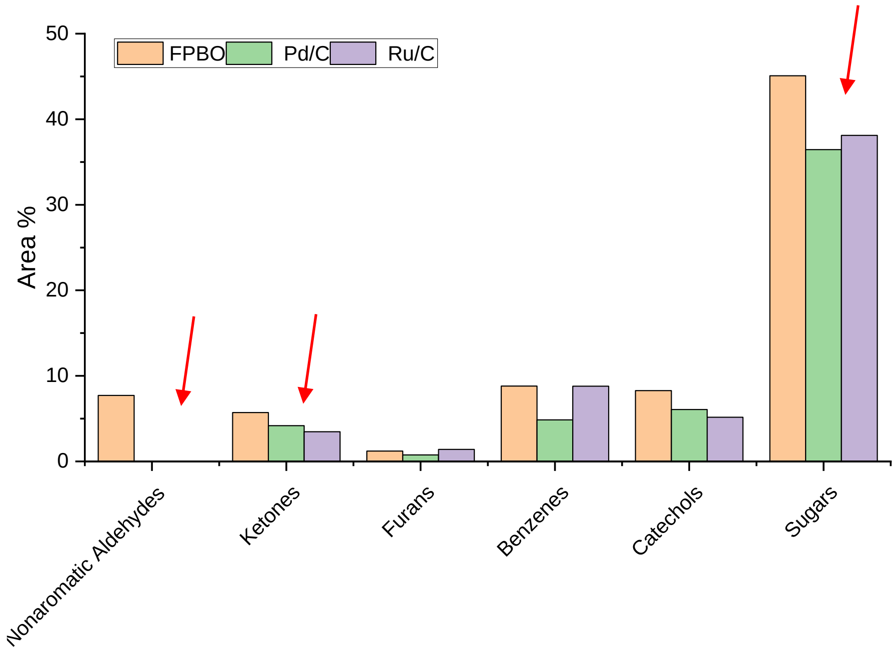
At 150 °C - Aldehyde hydrogenation

- **Stabilization Temperature:** 150 °C
- 8.0 MPa H_2 at room temperature
- 50 g oil + 2 g Catalysts

Sample	C (%)	H (%)	O (%)	N (%)	H (%)	DOD
FPBO - Sugarcane Bagasse	58.0	6.4	34.8	0.8	1.1	-
150 Ru/C	59.4	6.9	32.8	0.9	0.8	6
150 Pd/C	60.1	6.9	32.2	0.9	1.1	7

^{1}H-NMR – GCMS Results





Results – Fast Pyrolyzed oil from Sugarcane Bagasse produced at Python (IKFT- KIT)

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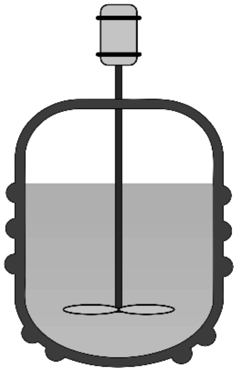
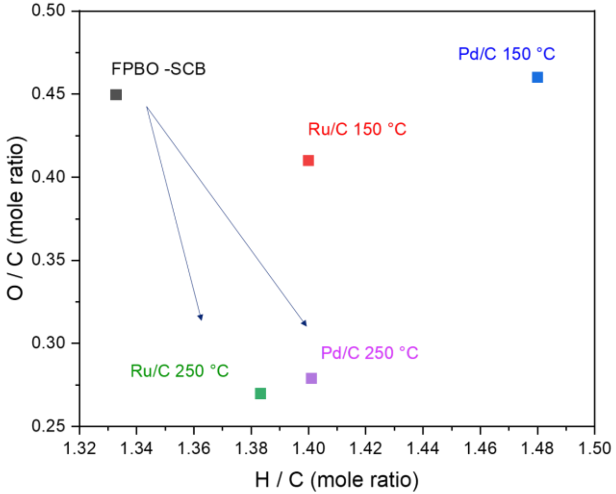
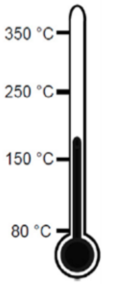




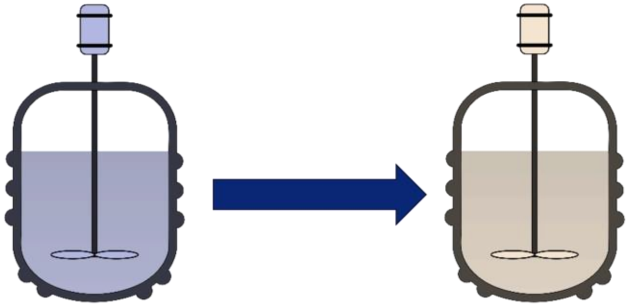


At 250 °C - Hydrogenation of ketones to alcohol

- **Stabilization Temperature:** 250 °C
- 8.0 MPa H_2 at room temperature
- 50 g oil + 2 g Catalysts

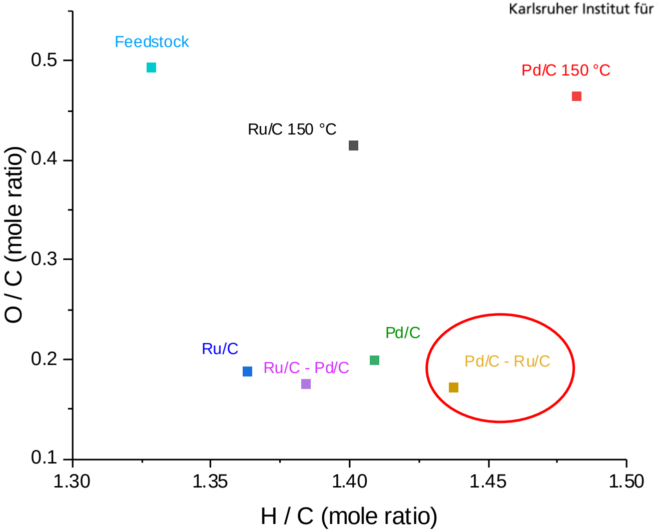
Sample	C (%)	H (%)	O (%)	N (%)	H_2O (%)	DOD
FPBO - Sugarcane Bagasse	58.0	6.4	34.8	0.8	1.1	-
150 Ru/C	59.4	6.9	32.8	0.9	0.8	6
150 Pd/C	60.1	6.9	32.2	0.9	1.1	7
250 Ru/C	67.3	7.8	24.2	0.7	-	30
250 Pd/C	66.5	7.8	24.7	1.0	1.0	29

Two step Results



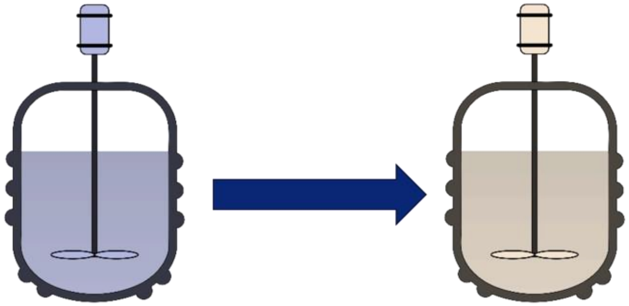
- **Stabilization Temperature:** 150 ˚C,
- 8.0 MPa H2 at room temperature
- 50 g oil + 2 g Catalysts

- **HDO Temperature:** 350 ˚C
- 8.0 MPa H2 at room temperature
- 50 g oil + 2 g Catalysts



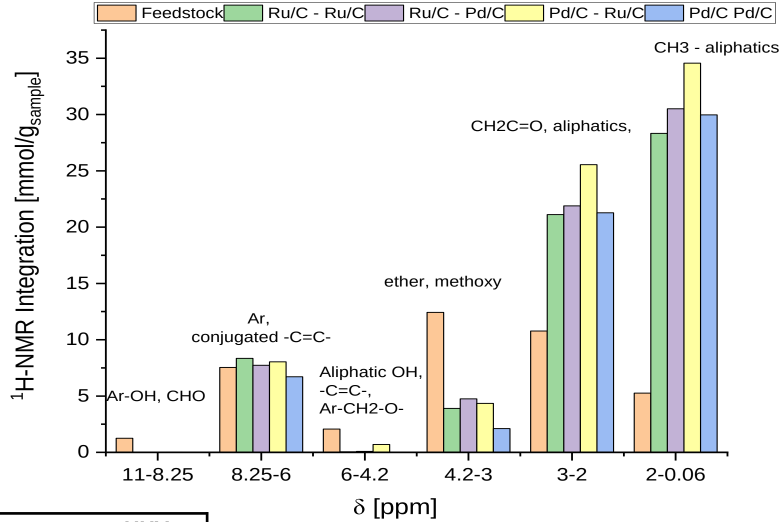
	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	H_2O (wt.%)	DOD (%)	HHV (MJ/Kg)
Feedstock	59.7	7	0.9	32.4	0.6		24.2
Two Steps - Upgraded oil							
Ru/C 350 °C	65.4	7.9	0.7	26.1	1.2	19.44	29.4
Pd/C 350 °C	72.6	8.4	1.0	18.1	1.3	44.14	33.4
Ru/C 150/350 °C	69.1	7.9	1.0	22.0	1.5	32.11	31.1
Pd/C 150/350 °C	71.6	8.4	1.1	18.9	1.2	41.67	32.9
Ru/C 150 °C - Pd/C 350 °C	73.4	8.5	1.2	17	0.9	47.53	33.9
Pd/C 150 °C - Ru/C 350 °C	73.3	8.8	1.1	16.8	1.2	48.15	34.2

Two step Results



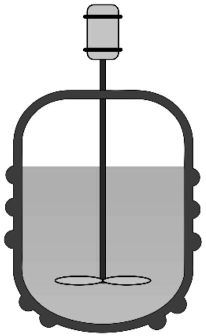
- **Stabilization Temperature:** 150 °C,
- 8.0 MPa H2 at room temperature
- 50 g oil + 2 g Catalysts

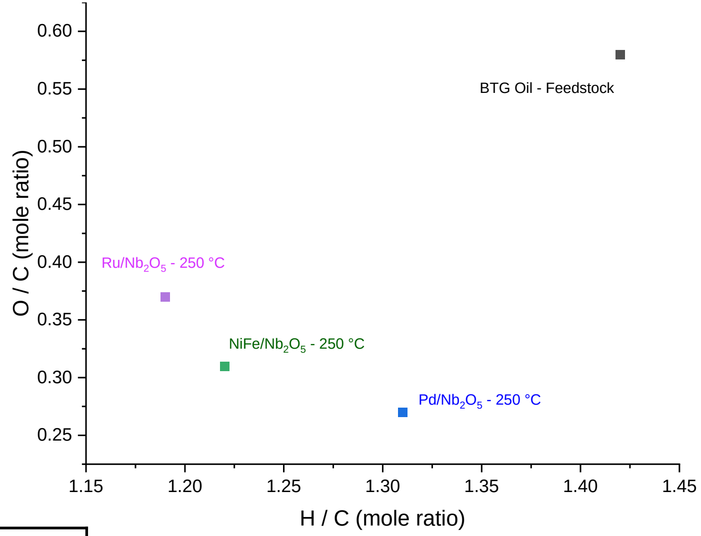
- **HDO Temperature:** 350 °C
- 8.0 MPa H2 at room temperature
- 50 g oil + 2 g Catalysts



	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	H_2O (wt.%)	DOD (%)	HHV (MJ/Kg)
Feedstock	59.7	7	0.9	32.4	0.6		24.2
Two Steps - Upgraded oil							
Ru/C 350 °C	65.4	7.9	0.7	26.1	1.2	19.44	29.4
Pd/C 350 °C	72.6	8.4	1.0	18.1	1.3	44.14	33.4
Ru/C 150/350 °C	69.1	7.9	1.0	22.0	1.5	32.11	31.1
Pd/C 150/350 °C	71.6	8.4	1.1	18.9	1.2	41.67	32.9
Ru/C 150 °C - Pd/C 350 °C	73.4	8.5	1.2	17	0.9	47.53	33.9
Pd/C 150 °C - Ru/C 350 °C	73.3	8.8	1.1	16.8	1.2	48.15	34.2

New Catalysts – Stabilization Process



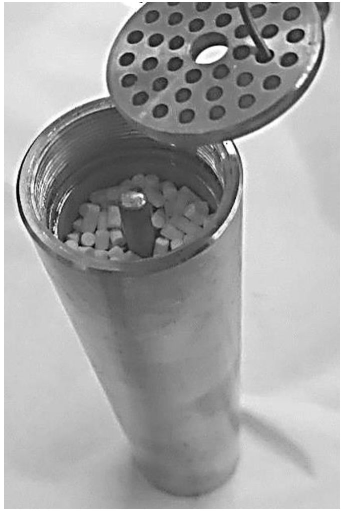


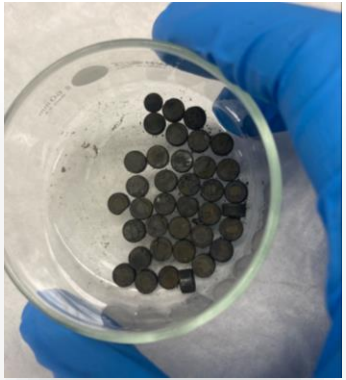
- **Stabilization Temperature:** 250 °C
- 8.0 MPa H_2 at room temperature
- 50 g oil + 2 g Catalysts

Sample	C (%)	H (%)	O (%)	N (%)	H_2O (%)	H/C	O/C	DOD
FPBO BTG	52.9	6.3	40.7	0.3	37.8	1.42	0.58	-
250 °C Ru/Nb_2O_5	62.9	6.2	30.7	0.2	7.4	1.19	0.37	24.57
250 °C Pd/Nb_2O_5	67.8	7.4	24.5	0.3	8.8	1.31	0.27	39.81
250 °C NiFe/Nb_2O_5	65.9	6.7	31.8	0.2	7.4	1.22	0.31	21.89

Upscaling

- Continuous trickle bed reactor
  - 0.2-1 L/h liquid capacity
  - Catalysts in the continuous reactor must be in the form of pellets or tablets in the order of 3-4 mm
  - Preparing pellet catalysts with same composition





Conclusions

- Different Biomass types lead to different bio-oils

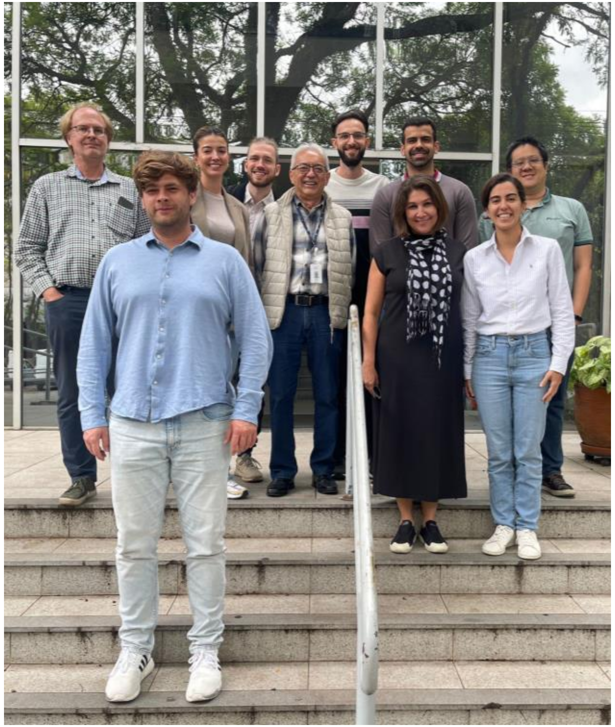
- Different bio-oils require different treatment

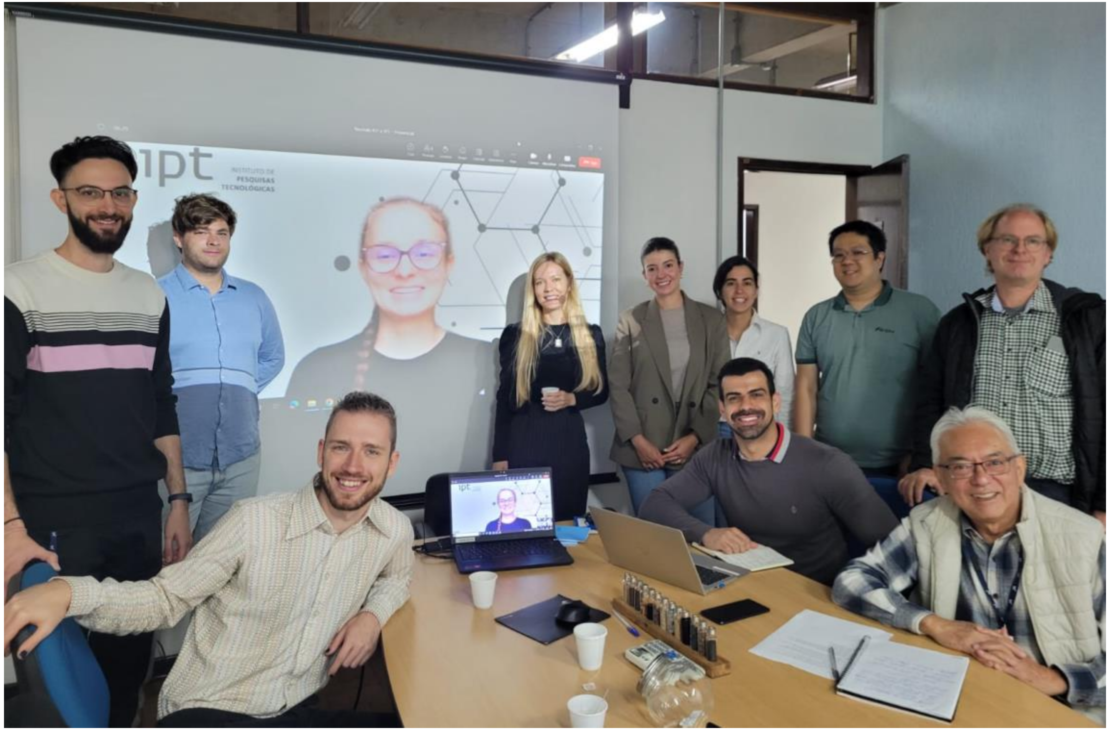
- Catalyst Efficiency: Pd/C and Ru/C catalysts demonstrate high efficiency in transforming FPBO into more stable and energy-dense fuels.

- Optimal Conditions: Higher temperatures (250-350°C) in combination with dual-step upgrading significantly enhance the quality of the bio-oil. However 150 °C is enough to bring more stability for the oil

Sugarcane Bagasse Preparation – IPT (Sao Paulo)

Final meeting at IPT October 2023 – Germany + Brazil Cooperation





Thank you

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