Final report

1. Project details

Project title	PolyGas – Polygeneration of bio-oil, electricity, heat and bioashes from thermal gasification of biomass and waste
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Name of the funding scheme	ForskEL
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Project partners	DTU Chemical Engineering DTU Mechanical Engineering Danish Fluid Bed Technology Aps
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2. Summary

The production of electricity and heat from conversion of biomass can complement fluctuating energy sources (wind and solar) and offer several further important advantages, i.e. beyond "just" substituting fossil fuels. This is especially beneficial when the system is able to utilize difficult organic residues such as cereal straw, biogas residue fibers and sewage sludge while recirculating valuable nutrients in biochar. These possibilities have already been demonstrated based on Low-Temperature Circulating Fluidized Bed (LT-CFB) gasification mainly intended for highly effective large-scale power plants. The objective of the present project have been to expand the possibilities based on the LT-CFB gasifier in mainly two directions: 1) ability to shift towards the production of catalytically upgraded pyrolysis oil and biochar in periods with limited need for electricity, and 2) being able to utilize the residual (non-condensing) product gas in an internal combustion engine, - in both ways allowing for very flexible plants, also in smaller scale. Both of these objectives have been met experimentally as well as by mathematical modelling, while - optimizing and documenting the complete system. The demonstrated possibilities in direction of more flexible as well as more readily reachable scale are expected to increase the chances for a next LT-CFB based demonstration plant in an initial small commercial size. Such first plants may also serve as tread-stones to the

originally intended larger power plant scale boilers, based on high pressure and effective steam-circuits, where the improved flexibility from producing catalytically upgraded pyrolysis oil and biochar can also be included.

- *Danish version*

Produktion af elektricitet og varme ved omdannelse af biomasse kan supplere fluktuerende energikilder som vind og sol, samtidig tilbyde yderligere vigtige fordele, dvs. ud over "bare" substituerende fossile brændsler. Dette er især fordelagtigt, når forgasser-systemet er i stand til at udnytte vanskelige organiske restprodukter, såsom halm, biogasrestfibre og spildevandsslam, samtidig med at værdifulde næringsstoffer kan recirkuleres i form af biochar. Disse muligheder er allerede blevet demonstreret baseret på lavtemperatur cirkulerende fluid bed (LT-CFB) forgasning hovedsageligt til direkte afbrænding i stor-skala kraftværker. Formålet med dette projekt har været at udvide mulighederne for LT-CFB forgasningsteknologien i hovedsagelig to retninger: 1) muligheden for produktion af katalytisk opgraderet bioolie og biochar i perioder med begrænset behov for elektricitet, og 2) at kunne bruge restgassen (ikke-kondenserende) produktgas i en forbrændingsmotor - på begge måder muliggør meget fleksible anlæg, også i mindre skala. Begge disse mål er opfyldt eksperimentelt såvel som ved matematisk modellering. De demonstrerede muligheder i retning af en mere fleksibel såvel som en lettere tilgængelig skala forventes at øge chancerne for et næste LT-CFB-baseret kommerciel demonstrationsanlæg i mindre decentral størrelse. Sådanne første anlæg vil også tjene som forløber til de oprindeligt tilsigtede større anlæg i kraftværksskala, baseret på højtryks- og effektive dampkredsløb, hvor den forbedrede fleksibilitet ved produktion af katalytisk opgraderet pyrolyseolie og biochar også kan inkluderes.

3. Project objectives

The purpose of the project was to proof-of-concept operate a multi-purpose biomass based polygeneration plant with high fuel flexibility and similarly flexible co-production of heat, electricity, bio-oil and biochar.

The two main objectives of the project:

1. Experimentally demonstrating and evaluating the option of increased plant flexibility based on being able to shift to the production of catalytically upgraded pyrolysis oil and/or biochar in time periods with low demand for electricity and heat. Further, the project aimed to demonstrate the catalytic treatment of tars from an LT-CFB gasifier for the production of bio-oil with improved properties (see **Error! Reference source not found.**). This required the construction and testing of a catalyst reactor and condensation system and extensive analysis of catalysts and bio-oil properties. One of the project objectives was catalyst development for efficient tar deoxygenation and improvement of the fuel properties of the collected bio-oils. Besides tests conducted at the LT-CFB gasifier, the majority of catalyst development was performed using a separate bench scale fast pyrolysis unit. In addition, the non-condensable gases were analyzed and assessed for their performance in a gas engine.

> Smaller distributed fast pyrolysis/low-temperature gasification plants can be built close to the location of the biomass
> Bio-oil has higher energy density compared to biomass → Savings in transportation costs when bio-oil is transported to centralized oil refinery for further processing
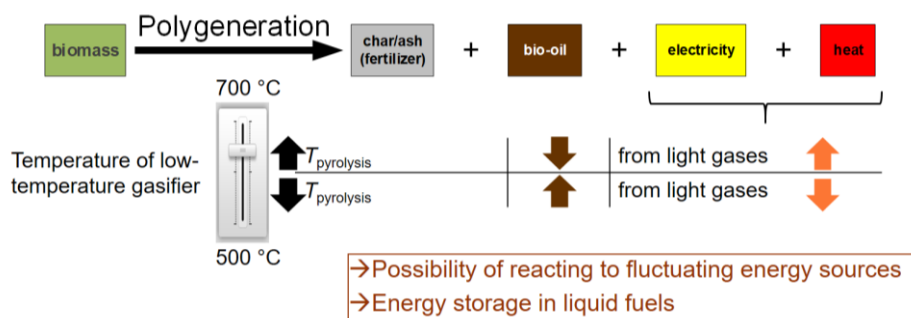

Figure 1. Motivation for the project.

2. Experimentally demonstrating and evaluating the possibility of smaller scale CHP plants based on using also the residual LT-CFB product gas for IC engine(s) instead of producing product gas to large scale CHP boilers in steam circuits.

Developed energy technology

The first solution will offer better economy not only by selling upgraded pyrolysis oil and biochar, but also by better utilisation of the plant investment due to expanded yearly operation time.

The second solution offers reduced economy of scale, but the risk of scaling up the LT-CFB gasifier from the already demonstrated 6 MW is smaller and reduced costs for shorter fuel transportation distances is a further advantage.

4. Project implementation

The project followed the project plan, however some delays have occurred. The project work resulted in a fruitful collaboration with Haldor Topsøe and the refinery Equinor and a number of publications (see Appendix), both in international scientific journals and national scientific magazines. Multiple delays have occurred during the project duration: first, the project work started 9 months later than the project start, according to the grant letter. Second, the postdoc who was hired to do thermodynamic modelling studies left the institute and a PhD student took over the task and met all planned milestones. Lastly, the engine tests have been postponed, as another postdoc left and could not finish the experiments, which were postponed again due to the COVID-19 lockdown. Nevertheless, the delays have been overcome and the aimed milestones were completed, one of them partially completed (M4.2 – Proof of concept operation of a small gas engine with upgraded producer gas), as the engine was not functioning with real upgraded producer gas due to technical issues.

Risks associated with bio-oil production and upgrading
- One of the main obstacles or risks that was noted and addressed during the applied research project was the rapid **deactivation of the zeolite catalyst by coke formation**. Initially, a fresh zeolite catalyst

loses activity to a certain extent by the hydrothermal conditions, but the remaining activity could be regained after catalyst regeneration as long as the regeneration was conducted carefully without generating hot spots in the catalyst bed. During the tar deoxygenation, rapid coke formation occurred on the zeolite and generally on solid acid catalysts. This coke formation decreases the deoxygenation activity and so the catalyst needs to be regenerated once the quality of the bio-oil becomes insufficient. The research in this work addressed this aspect by mapping the quality of the bio-oil against different catalysts and increasing amounts of biomass fed over the catalysts. Particularly for hydrodeoxygenation catalysts, the **coke formation was very low** and therefore a much more stable deoxygenation performance was achieved. This in turn will reduce the frequency of regeneration required and therefore also the number of reactor units that need to be operated in parallel.

- An initial risk of the process was that the **catalyst bed might lose efficiency** after a few regeneration cycles. This **risk was minimized/removed** by the use of a **highly efficient hot gas filter** upstream the catalyst bed to remove any char fines, since the alkaline inorganics present in the char would have poisoned the acid sites on the catalyst.

- Another risk that was considered is that the **oil-collection efficiency** might be **insufficient** for subsequent operation of the gas engine on the residual gas. This issue can be prevented by applying proven oil-collection technologies including wet electrostatic precipitation and organic scrubbers. In this work, wet **electrostatic precipitation** was applied and found **very effective** in collecting tar aerosols. To further protect the gas engine, another option is to install a guard unit.

- In a broader sense, the biggest challenge/risk for the further development/commercialization of this technology is that the **production of fuels from pyrolysis/gasification** of biomass **can not compete with the cheap price of fossil fuel**. As such, government incentives are required that reward production of fuels from technology that does not lead to increased CO_2 emissions.

- It seems that it is possible to produce catalytically reformed LT-CFB pyrolysis oil suited for being taken in at oil refineries and for use as a fuel for large marine engines. But it is uncertain whether the obtainable price will be high enough to make the addition of the necessary – i.e. continuously working - catalytic reforming to the CHP plant a positive business case. A possible fall back solution may be to produce a somewhat relaxed quality bio-oil which just allows easy transportation, stable storing and handling with the intension of being used for e.g. simple (non solid fuel and normally not manned) decentral CHP-plants or larger CHP plants as a start up/auxiliary fuel.

- There may be differences in the **long-term catalyst stability**. Testing that would require an **automated unit to monitor the catalyst activity** during hundreds of reaction/regeneration cycles.

- Insufficient incentives for the non-fossil based plant output products, i.e. bio-oil, electricity, heat and ash containing nutrients and biochar.

- Competition from comparable VE-plants and products

In the following paragraphs, we describe how the project was implemented, the work done for each WP and the milestones completed.

WP0 Project Management

The tasks included in WP0 have been completed according to the plan. The contract between the project participants was made and the kick-off meeting was held on 19/09/2017 at DTU-Risø Campus. There have been regular project meetings with all the project partners as well as meetings between the PhD Student (Andreas Eschenbacher) and his supervisors every two weeks. Half-year financial reports and annual project reports have been prepared and submitted to EUDP.

WP1: Modification of the LT-CFB gasifier

The three milestones have been reached. Hence modifications were made on the LT-CFB gasifier and tar measurements were allowed for before and after the installed filter. The filter was installed before the time period of the current report.

WP2: Design, construction and test of the zeolite unit

At the beginning of the project, the available bench scale unit had to be optimized for catalyst testing. A larger catalyst reactor was constructed. Overall a large number of experiments were performed which provided extensive experimental experience.

The catalytic reactor including the downstream oil condensation train that was installed at the bench scale system was successfully tested in a product gas slip stream after the ceramic filter of the LT-CFB gasifier. An additional condensation equipment was constructed in order to condense a non-catalytic reference bio-oil in parallel to the stream that was deoxygenated in-line prior to condensation. The tests demonstrated the catalytic deoxygenation of the tar vapors and the improved bio-oil quality compared to the raw tars.

For the rapid screening of catalysts, tests were performed using a micro-pyrolyzer set-up coupled to a gas chromatograph at Iowa State University (USA) during a 4 months external stay.

WP3: Bio-oil collection and characterization

The condensation system of the bench scale fast pyrolysis unit needed to be improved in order to achieve better collection of aerosols. To this end, an electrostatic precipitator was installed. This improved the mass balance of the system and avoided plugging issues in the condensation train. Characterization of both the produced raw tars and deoxygenated bio-oils was established and was performed parallel to the experimental campaigns.

A range of different characterization methods has been used to characterize the produced raw tars and bio-oils and detailed structural information was gathered. Size exclusion chromatography (SEC) analysis of the bio-oils allowed to obtain a molecular weight distribution and along with ^{13}C and ^{1}H NMR, TAN, GC-MS/FID, moisture, and elemental analysis (CHNSO) these characterization methods provided an in-depth understanding of the structural changes of tar species during the catalysis and collection processes (WT 3.2.).

WP4: Mapping and optimization of engine operation

The engine setup related to WT4.1 has been prepared. The specific content and operational strategy have been made. The residual gas, after bio-oil condensation, has been analyzed and evaluated as an engine fuel. Initial tests have been successfully performed with an engine with a low compression ratio, yielding god performance results.

WT4.2 The engine setup has been prepared for tests with a high compression ratio engine, but due to several technical problems with the set-up it has not been possible to finalize the high-compression engine tests within the project period. The modified engine set-up will be made operational in a related project, and at that time the remaining tests will be performed and reported.

WP5: Thermodynamic modelling of the biomass based polygeneration system

Key component models of gasifier and catalytic bio-oil upgrading have been made using the software Aspen Plus V11. The polygeneration system using a gas engine for electricity production was optimized through heat recovery. The system was evaluated from an energy and exergy perspective. Additionally, the production of additional fuels (synthetic natural gas and DME) through water electrolysis and oxygen blown gasification was investigated.

5. Project results

5.1.1 Project results summary

The project aimed at operating a highly flexible polygeneration system on a theoretical and experimental level. The experimental work included the production of bio-ashes, upgraded bio-oils, a low-tar producer gas that was used for gas engine operation, based on locally available biomass fuels (e.g. wheat straw). The project focused mainly on the production, catalytic upgrading and collection of bio-oil, so it could be used in oil refineries, where the bio-oil is mixed directly with fossil fuels. Hence, main the results are obtained within the following groups:

A. Catalyst screening and testing of solid acid catalysts

B. Catalyst testing of basic catalyst (Na-Al_2O_3)

C. Catalyst screening and testing of hydrodeoxygenation catalysts under hydrogen atmosphere (atm. pressure)

D. Further processing by catalytic cracking of blends of pyrolysis oil and conventional refinery feed

E. Bio-fuel production by catalytic upgrading of tars generated in a 100 kWth Low Temperature Circulating Fluidized Bed Gasifier (LT-CFB)

The theoretical work focused on evaluating the performance of the complete polygeneration system through thermodynamic modelling using Aspen Plus V11. The results are grouped as follows:

F. Improvement of system efficiency through heat recovery

G. Energetic and exergetic evaluation of the polygeneration system using a gas engine

H. Alternative plant designs for producing additional biofuels

The main results from the gas engine tests are summarized in chapter 5.1.2.

In the following, the main conclusions/results from each area are summarized:

A. Catalyst screening and testing of solid acid catalyst

The performance of microporous HZSM-5 zeolite with different Si/Al ratios was compared to the performance of hierarchical HZSM-5 zeolites that were prepared by desilication with appropriate NaOH concentration followed by acid wash, ion exchange and calcination. In addition, industrially relevant extrudates of HZSM-5/γ-Al_2O_3 were tested and compared to the vapor deoxygenation with bare γ-Al_2O_3. Tests were performed in inert atmosphere at a catalyst temperature of 500 °C. It is known that steam quickly decreases ~50% of the Brønsted acidity of calcined HZSM-5. In order to study the loss in activity by coke and obtain a more representative indication of the performance of equilibrated catalysts, all catalysts were steamed at 0.3 bar H_2O and 500 °C for 5 h before the reaction tests. As shown in Fig. 1, deep deoxygenation could only be achieved at low yields and low ratios of fed biomass to catalyst (B:C). Also HZSM-5/γ-Al_2O_3 and bare γ-Al_2O_3 can be used as deoxygenation catalysts. A lower slope of deactivation resulted for mesoHZSM-5 obtained from desilication of parent HZSM-5 with a Si/Al = 28 and 40. Micropyrolyzer investigations showed that the introduction of mesopores reduced the yield of monoaromatics, but improved the conversion of methoxyphenols up to higher B:C compared to the parent microporous HZSM-5. Both the tests at micro- and bench scale showed that the coke yields increased after introduction of mesopores.
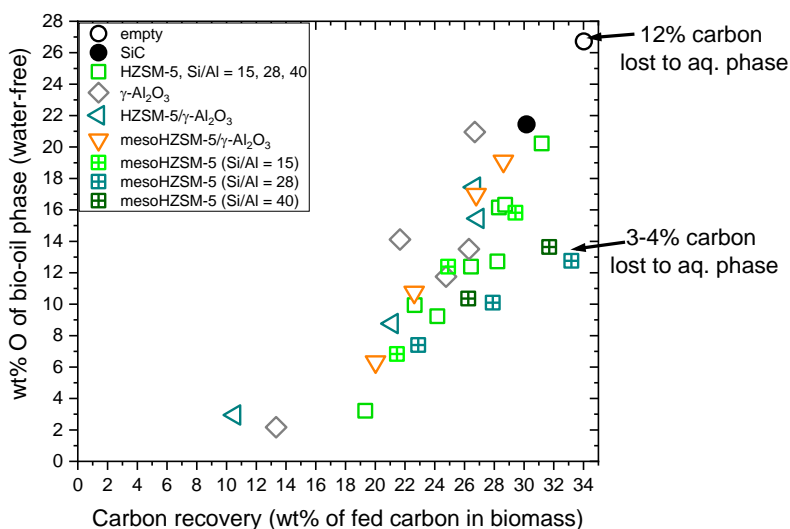
Fig. 1. *Carbon yield and oxygen content (wt% O) of phase-separated bio-oil*

In conclusion, different solid acid catalysts can be used for deoxygenation of biomass-derived pyrolysis vapors and provide improved bio-oil properties. The deactivation by coking leads to the breakthrough of oxygenates and decreases the bio-oil quality. Mesoporous HZSM-5 may allow to operate to higher B:C ratios, and therefore decrease the frequency of regeneration in a scenario of parallel fixed bed reactors for continuous vapor upgrading.

B. Catalyst testing of basic catalyst (Na-Al$_2$O$_3$)

Based on literature, the promotion of γ-Al$_2$O$_3$ or amorphous silica alumina with Na$_2$CO$_3$ resulted in catalysts that are effective in producing bio-oils with low acidity (TAN). However, the data available for continuously operated systems was limited, and the upgrading of pyrolysis vapors derived from wheat straw over Na-Al$_2$O$_3$ had not yet been tested. It was therefore interesting to investigate what yields of bio-oil and at what quality this could be obtained as a function of the biomass-to-catalyst ratio when using wheat straw.

As shown in Fig. 2, for the same level of deoxygenation (~9 wt% O), a similar or higher carbon yield of bio-oil was obtained with lower TAN compared to commonly used acidic catalysts. This can be attributed to highly efficient ketonization of acids, which was confirmed by converting acetic and propionic acid as model compounds.
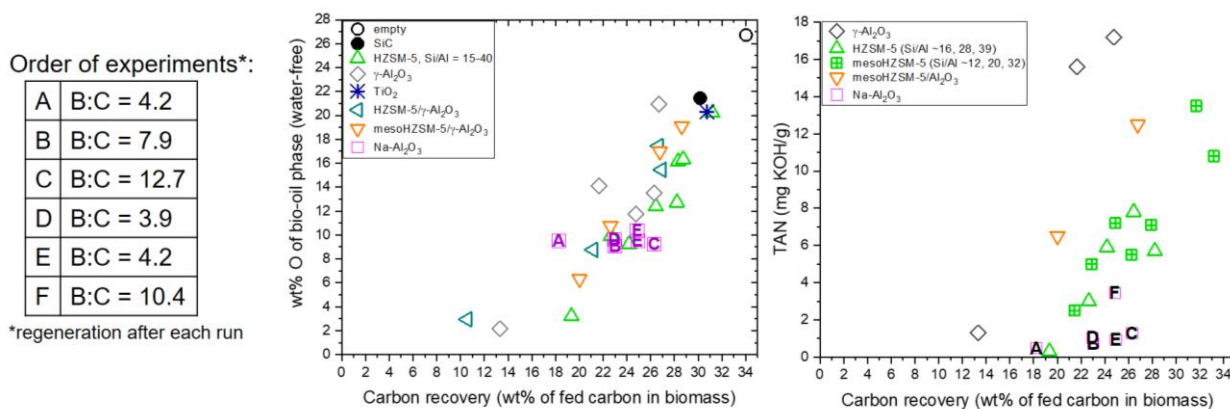

Fig. 2. *Oxygen content (wt% O) and total acid number (TAN) of bio-oil as a function of the obtained carbon yield of bio-oil (wt% of fed carbon in biomass).*

The coke combustion shifted to ~100 °C lower temperature for Na-Al_2O_3 compared to γ-Al_2O_3 (see Fig. 3). At B:C ~4, Na-Al_2O_3 contained ~17% less coke per g catalyst compared to γ-Al_2O_3. The lower coke yield in combination with the easier combustion can decrease the regeneration time considerably. The lower coke yield is attributed to the reduced acidity of Na-Al_2O_3. In addition, it was found that the steam present under operating conditions can result in some coke gasification over Na-Al_2O_3, which may slow down catalyst deactivation.
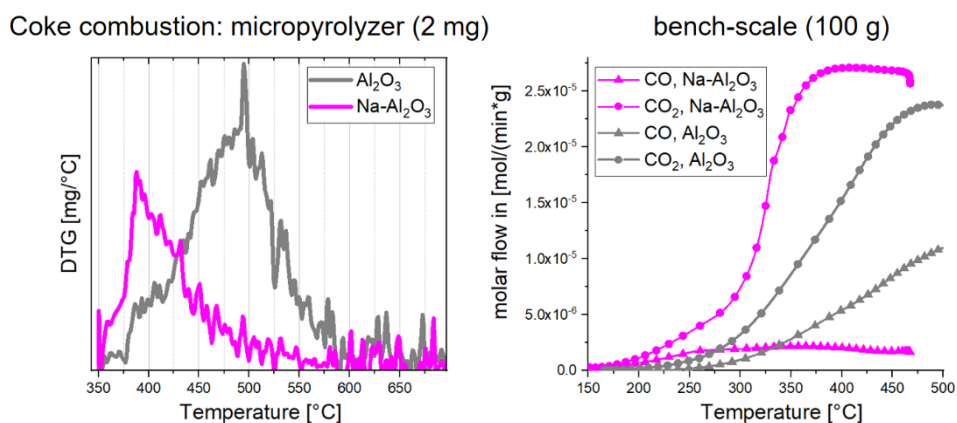

Fig. 3. *Left graph: weight loss during coke combustion of catalyst tested with micropyrolyzer. Right graph: CO/CO₂ flow measured during coke combustion of catalysts tested at bench scale at B:C ~4.*

In conclusion, the selective conversion of acids in bio-oil is highly beneficial, since acids are highly reactive and contribute to reactor plugging for bio-oil hydrodeoxygenation and high TAN numbers >> 1 mg KOH/g lead to severe corrosion in commercial refinery operation (Fluid Catalytic Cracking). The vapor upgrading using low cost Na-promoted Na-Al_2O_3 thus seems to be very attractive, especially for applications without locally available access to hydrogen (see next section).

C. Catalyst screening and testing of hydrodeoxygenation catalysts under hydrogen atmosphere (atm. pressure)

Utilizing hydrogen at atmospheric pressure conditions with catalysts may allow promoting hydrodeoxygenation (HDO) reaction, i.e. the removal of oxygen as water without breaking the C–C bonds and associated carbon losses in the form of CO/CO₂. Based on literature, promising HDO activity was reported for precious metal catalysts supported on TiO_2 and MoO_3-based catalysts. Fig. 4 compares the results obtained with the tested HDO catalysts (blue circle) with solid acid catalysts tested in inert gas. In comparison with a range of other acidic catalysts, better results were obtained with the HDO catalysts. The carbon recovery strongly correlated with the energy recovery of bio-oil, and at 60-70% oxygen removal compared to the non-catalytic bio-oil, the atmospheric HDO allowed to obtain higher carbon and energy recoveries of phase-separated bio-oil phase compared to solid acid catalysts. In particular, TiO_2-supported MoO_3 and Pt catalysts are very promising.
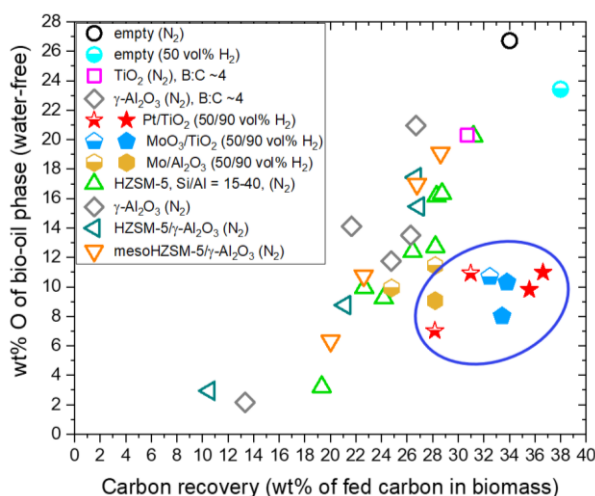
Fig. 4. *Oxygen content (wt% O) of bio-oil as a function of the obtained carbon yield of bio-oil.*

It was further found that the coke deposits on HDO catalysts combusted at lower temperatures compared to solid acid catalysts. Coke yields on TiO_2 based HDO catalysts are remarkably low and insensitive to B:C ratio (see Fig. 5). It is worth pointing out that the coke formation on Pt/TiO_2 and MoO_3/TiO_2 were lower compared to unpromoted TiO2, which suggests that the addition of Pt or MoO_3 might have hydrogenated some of the coke precursors.

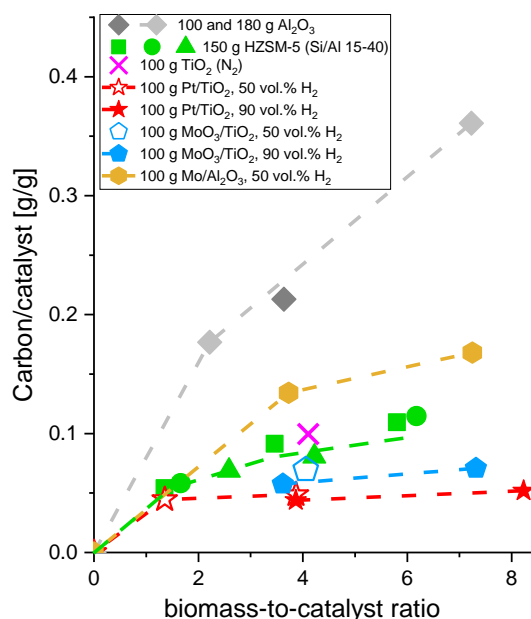Fig. 5. *Deposited mass of carbon in coke per coke-free catalyst for different catalysts and towards higher B:C ratio.*

The cost of hydrogen has to be considered for such a process, but the hydrogen could be produced from electricity using green electricity and electrolysis. An important advantage of the system is that it is not pressurized, and therefore the biomass feeding is easier compared to high pressure systems.
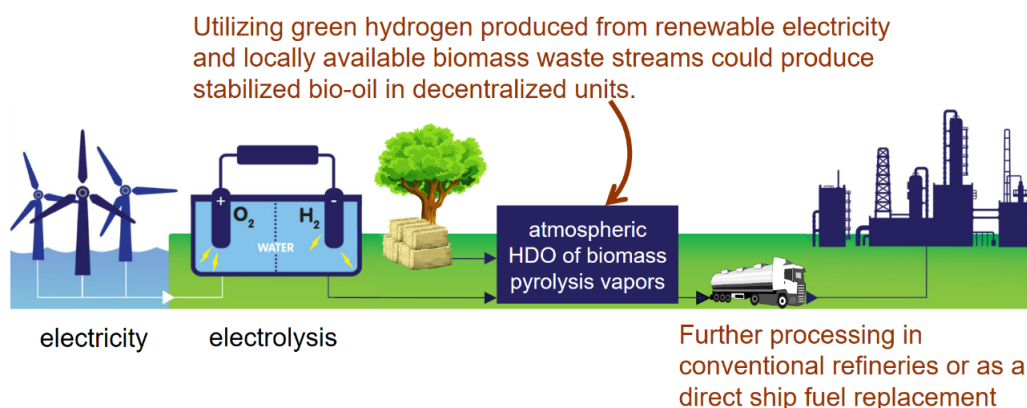
Fig. 6. *Proposed scheme for hydrodeoxygenation (HDO) of fast pyrolysis vapors in decentralized units*

Within this project and as seen from Figure 7. we focused on "decentral" plants based on gas engines, but a similarly flexible LT-CFB based bio-CHP concept - also being able to produce catalytically upgraded bio-oil - could also be for large scale – i.e. "central" - CHP plants and then based on an advanced boiler and steam circuit instead of the gas engine.

D. Further processing by catalytic cracking of blends of pyrolysis oil and conventional refinery feed

Fluid catalytic cracking is a large refinery operation for cracking of vacuum gas oil or atmospheric residue. It was therefore of interest to investigate the co-processing of biomass-derived fast pyrolysis oils with a fossil feed stream. Experiments were performed by Equinor in a fully automated microactivity testing (MAT) unit. The catalyst/oil ratio in the experiments was varied by varying the amount of feed injected over a bed containing 3 g catalyst (525 °C). The conversion was defined as 100%−(light cycle oil (LCO) + heavy cycle oil (HCO)). Table 1 summarizes the properties of the FCC reference feed and bio-oils. The fossil feed had a much lower oxygen content and TAN compared to the untreated wood and straw bio-oils. The bio-oil obtained from vapor treatment with HZSM-5/γ-Al$_2$O$_3$ showed improved properties (lower wt% O, water content, and TAN), however an increased basic nitrogen content resulted for the catalytically treated oil. The FCC cracking tests were performed for blends of 80 wt% fossil oil and 20 wt% bio-oil.

Table 1. *Properties of FCC reference feed and bio-oils.*

FCC reference feed (fossil)		Bio-oils			
			Wood	Straw	Straw, HZSM-5/γ-Al$_2$O$_3$
Conradson Carbon Content (wt.%)†	3.78	H$_2$O content [%]	7.8	14.7	2.3
Sulphur (wt.%)	0.46	wt-% O (d.b.)	29.7	21.4	8.8
wt-% O (d.b.)	~0	Higher heating value (HHV) [MJ/kg]	26.8	30.5	36.2
TAN [mg KOH/g]	~1	TAN [mg KOH/g]	60.8	54.4	3.4
Basic Nitrogen (ppm)	620	Basic nitrogen content [ppm]	30	**3920**	**5670**
†indication of the coke-forming tendencies of an oil		wt% remaining at 300 °C	44	45	18

As shown in Fig. 7 (left graph), the conversion of deoxygenated oil obtained from catalytic fast pyrolysis over HZSM-5/γ-Al$_2$O$_3$ was lowest, while the blending of fossil oil with wood-derived bio-oil showed slightly higher conversions and similar coke yields (see Fig. 7, right graph). The blending with straw-derived bio-oil led to higher coke yields compared to blending with wood-derived bio-oils. The differences in basic nitrogen content of the bio-oils might explain the lower conversion and higher coke yields, since basic nitrogen compounds are very prone to coking on the FCC catalyst. In addition, the deoxygenated bio-oil obtained from catalytic fast

pyrolysis over HZSM-5/γ-Al$_2$O$_3$ contains increased concentration of aromatics and phenolics, which are more difficult to crack.
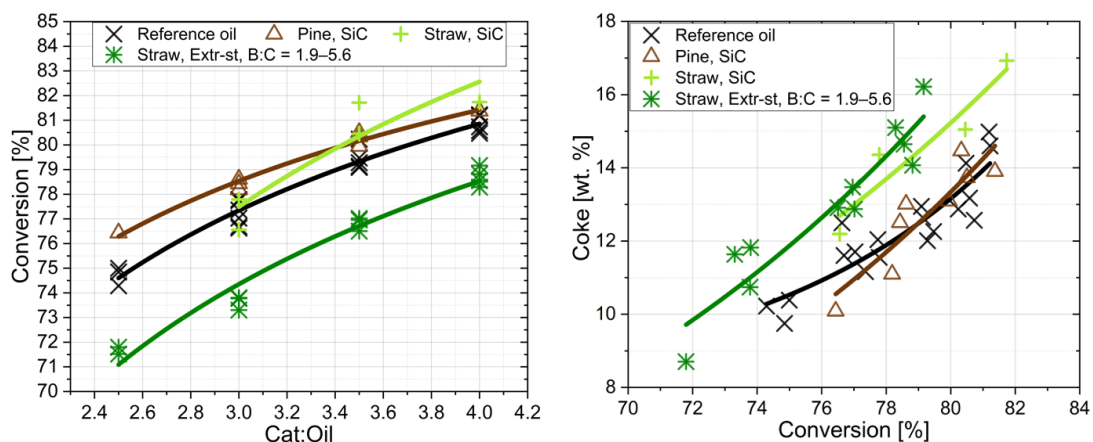

Fig. 7. *Left graph: Conversion as a function of the catalysts-to-oil ratio used for testing. Right graph: Coke (wt% of feed) for different conversions. Raw bio-oils were obtained from loading the catalytic reactor with SiC, a highly inert solid, and HZSM-5/γ-Al$_2$O$_3$ was abbreviated 'Extr' in the legend for the bio-oil obtained from catalytic fast pyrolysis.*

E. Bio-fuel production by catalytic upgrading of tars generated in a 100 kW$_{th}$ Low Temperature Circulating Fluidized Bed Gasifier (LT-CFB)

In order to demonstrate the upgrading of tars generated in a LT-CFB gasifier for production of bio-oils with improved properties (see Fig. 8), a side stream of the filtered gas produced from wheat straw was sampled and split into two parallel streams, of which one was directly condensed and one was passed over a catalytic fixed bed operated at 500 °C. The properties of the raw and upgraded bio-oils are summarized in Table 2. In can be seen that the tar treatment reduced the tar load of the producer gas, which is attributed to carbon losses to light gases and coke. Both γ-Al$_2$O$_3$ and HZSM-5/γ-Al$_2$O$_3$ improved the fuel properties of the obtained bio-oils from the LT-CFB gasifier. In particular, the tar treatment reduced the wt% O, the moisture content, and the TAN of the bio-oil, and it improved its heating value (HHV). In addition, the reheating characteristics of the treated bio-oils were improved in terms of reduced char formation during heating, which should facilitate further processing to transportation fuels.
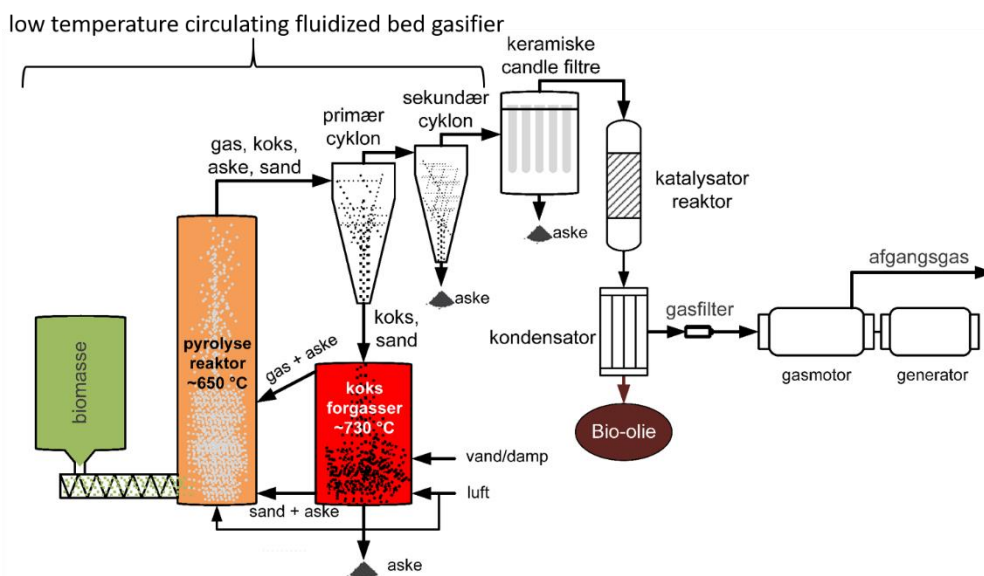
Fig. 8. *Proposed scheme for production of catalytically treated bio-oil from tars produced with an LT-CFB gasifier.*

Table 2. *Properties of bio-oils obtained with and without catalytic treatment of tars produced on wheat straw with a LT-CFB gasifier at a pyrolysis temperature of ~660 °C.*

Catalyst	-	γ-Al$_2$O$_3$	-	HZSM-5/γ-Al$_2$O$_3$
Processed tar g/g catalyst		0.74		1.02
Tar in producer gas [g organics/Nm^3 dry gas]	98	74	123	101
Carbon distribution liquid-range organics/gas/coke	26/74/0	19/73/8	51/49/0	38/53/9
moisture content [wt%]	8.1	2.5	9.9	2.7
wt% N (d.b.)	3.6	4.3	3.1	3.5
wt% C (d.b.)	75.1	77.8	76.7	78.5
wt% H (d.b.)	7.2	7.9	7.6	7.3
wt% S (d.b.)	0.45	0.50	0.32	0.21
wt% O (d.b., by diff.)	14.1	10.0	12.6	10.7
HHV (d.b.) [MJ/kg]	33.2	35.4	34.3	34.9
TAN [mg KOH/g]	14	5	34	3
wt% remaining at 300 °C	38	19	39	18

These test campaigns demonstrated that bio-oil with improved properties can be produced from tars generated in an LT-CFB gasifier, by in-line catalytic treatment. Future research should address the further treatment of the obtained bio-oils and test alternative catalyst formulations to solid acid catalysts.

F. Improvement of system efficiency through heat recovery

For modelling the entire polygeneration system, component models of the LT-CFB gasifier and the catalytic reactor were developed based on data from the experimental campaign on the LT-CFB gasifier from WP2 and WP3. The entire polygeneration system was modelled and analyzed using these component models together with predefined models for simpler standard component, such as heat exchangers, compressors, pumps and a simplified model of a gas engine. Fig. 9 shows a simplified flowsheet of the polygeneration system. Compared to Fig. 8, the pyrolysis reactor, char gasifier and the two downstream cyclones were unified into the LT-CFB gasifier in Fig. 9. Additionally, Fig. 9 shows the temperatures of the different streams in the system for

the specific case of an LT-CFB gas exit temperature of 620 °C and catalyst (HZSM-5/γ-Al2O3) operation temperature of 450 °C.
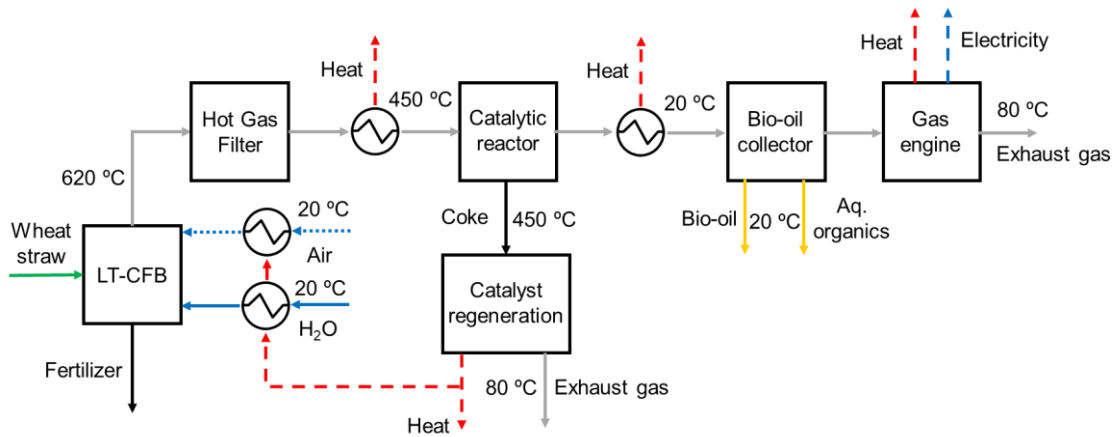

Fig. 9. Simplified flowsheet of the polygeneration system with LT-CFB gas exit temperature 620 °C and catalyst (HZSM-5/γ-Al2O3) operation temperature of 450 °C.

Using the system model, the system was first analyzed under the operating conditions used for the experiments in WP2 and WP3. The surface heat loss (hereafter just named heat loss) of the LT-CFB gasifier was assumed to account for 4 % of the chemical energy input of the straw (See Fig. 10, left). A commercial scale plant would have a lower heat loss due to the relation between volume and surface area. By reducing the heat loss to 1 %, the total energy efficiency is increased by 3 %-points to 74.4 %, as shown in Table 3. Fig. 10 and Table 3 also show that the increased efficiency derived from a higher electricity and heat output from the gas engine, while the energy output in form of bio-oil stays constant.
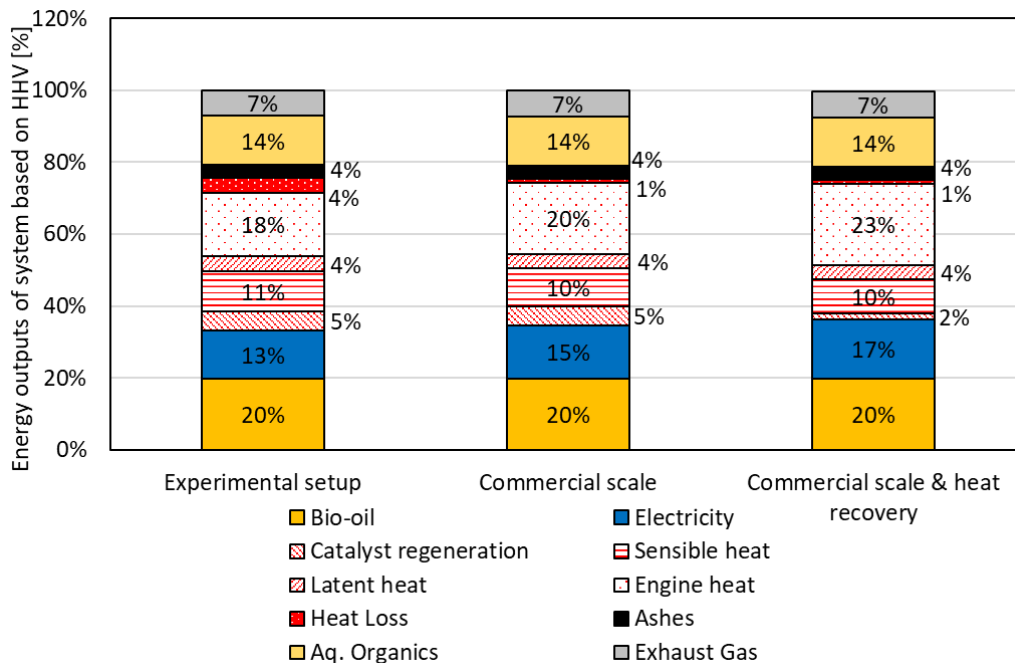
Fig. 10. Distribution of energy outputs of the system for three different cases. All values are normalized to the chemical energy input of straw (HHV).

The next step for improving the performance was to use some of the produced heat in the system in order to preheat the air and water before they enter the LT-CFB gasifier. From Fig. 10, right, and Table 3, right, it can be seen that the heat recovery does not influence the overall energy efficiency of the system. However, the

heat recovery changes the ratio between the produced electricity and heat, leading to a higher electricity production and lower heat output. This is beneficial, because of the higher quality of electricity, as shown in part G.

Table 3. Energy efficiency for three different cases considering different products. All efficiencies are based on the chemical energy (HHV) input of straw.

Energy Efficiency	Experimental setup	Commercial scale	Commercial scale & heat recovery
Bio-oil + Electricity + Heat	71.4 %	74.4 %	74.4 %
Bio-oil + Electricity	33.2 %	34.7 %	36.4 %
Bio-oil	19.8 %	19.8 %	19.8 %

G. Energetic and exergetic evaluation of the polygeneration system using a gas engine

For further understanding of the system, it was analyzed from an exergetic point of view. The concept of exergy allows for distinguishing between high quality energy (like electricity, chemical energy or high-temperature heat) and lower quality (like low-temperature heat). For this analysis, an LT-CFB gas exit temperature of 660 °C was used and γ-Al2O3 at 500 °C was used as a catalyst, as shown in Fig. 11. Compared to the case shown in Fig. 9, the recovered heat is taken from the product gas exiting the gasifier instead of the catalyst regeneration. This allows for preheating air and steam to 560 °C. The heat loss from the LT-CFB gasifier was kept at 1 % of the chemical energy input of straw.
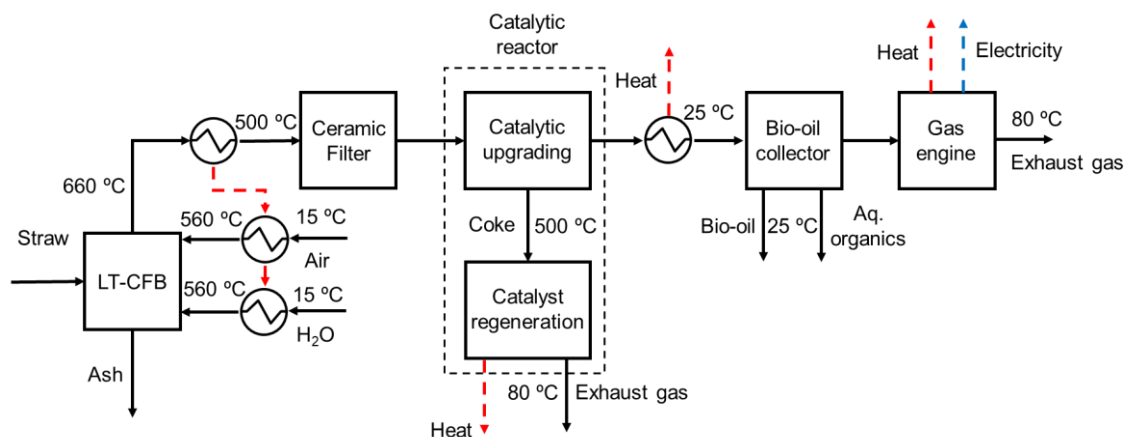
Fig. 11. Simplified flowsheet of the polygeneration system with LT-CFB operation temperature 660 °C and catalyst (γ-Al2O3) operation temperature of 500 °C.

Fig. 12 shows a detailed flowsheet of the polygeneration system, including all heat exchangers and additional components like compressors and pumps. Additionally, chemical energy inputs and outputs, the electricity consumption and production of the components and the heat transferred in the heat exchangers are shown. The surplus heat of the system is used to supply district heating by heating water from 40 °C to 75 °C. From Fig. 12 it can be seen that the energy efficiency based on the LHV is 85.7 %, where 13.4 % of the straw is converted to bio-oil, 19.2 % to electricity and 53.1 % to heat for district heating.

Fig. 12. Detailed flowsheet of the polygeneration system, showing the chemical energy inputs/outputs (LHV), electricity consumption/production and heat transfer.

In an exergy analysis it can be shown, how much of the exergy fuel of the system is converted to the exergy product (E_P). The rest of the exergy fuel is either destroyed (E_D) through irreversibilities in the different components or lost to the environment (E_L) by releasing material streams to the environment, which cannot be used and have temperatures and pressures different than the environment. For the polygeneration system, the exergy fuel is the exergy of the straw input to the system. The exergy product is the sum of the chemical exergy of bio-oil, the net electricity output and the exergy of the supplied district heating.
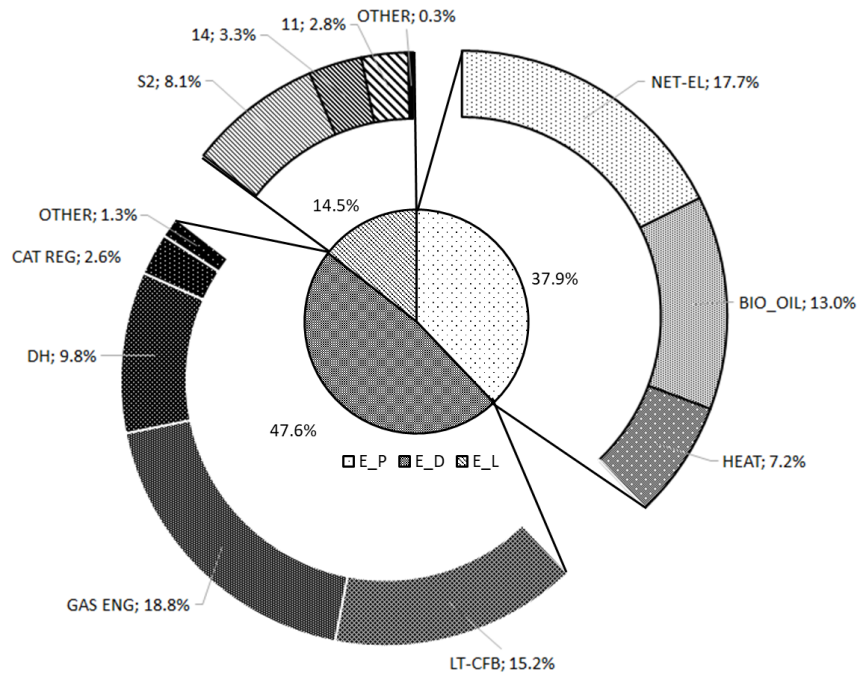
Fig. 13 shows that the exergy efficiency of the polygeneration system is only 37.9 % compared to an energy efficiency of 85.7 %. It can be seen, that the exergy efficiency for converting straw to electricity and bio-oil is similar to the energy efficiency with 17.7 % and 13.0 % respectively. However, the exergy efficiency for the conversion of straw to heat is significantly lower than the energy efficiency with 7.2 % compared to 53.1 %. The large difference between the results of the exergy analysis and the energy analysis derives from considering the low quality of the provided district heating at relatively low temperatures in the exergy analysis.

47.6 % of the exergy fuel is destroyed in the system. The biggest contributors are the gas engine with 18.8 %, the gasifier with 15.2 % and the heat exchangers to the district heating network with 9.8 %. The large exergy destructions in the gas engine and gasifier derive from the chemical reactions occurring within these components, which cannot be avoided. The large exergy destruction in the heat exchangers derives from the large temperature differences between the hot streams in the system and the relatively low temperatures of the district heating. In order to avoid these and to produce a more valuable product than district heating, the possibility of delivering high-temperature process heat or changing the system layout for producing additional fuels instead of electricity and heat will be investigated. It should of course be considered that exergy destruction avoided by producing fuel instead of electricity and heat may just be "postponed" to e.g. using the gas in an similar gas engine in another location. In this case, the purpose of the further fuel production should rather be to be able to distribute and/or store the gas.

Fig. 13. Distribution of exergy product (E_P), destruction (E_D) and losses (E_L) among components and outlet streams of the system.

H. Alternative plant designs for producing additional biofuels

In this study, the possibility of producing additional fuels from the tar-free syngas after upgrading and condensation of bio-oil was investigated. Fig. 14 depicts the three considered systems for comparison. The electricity production system is the same as discussed in section G. Additionally, systems for producing synthetic natural gas (SNG) and dimethyl ether (DME) were considered, where water electrolysis was used for producing additional hydrogen and the oxygen was used for the LT-CFB gasifier.
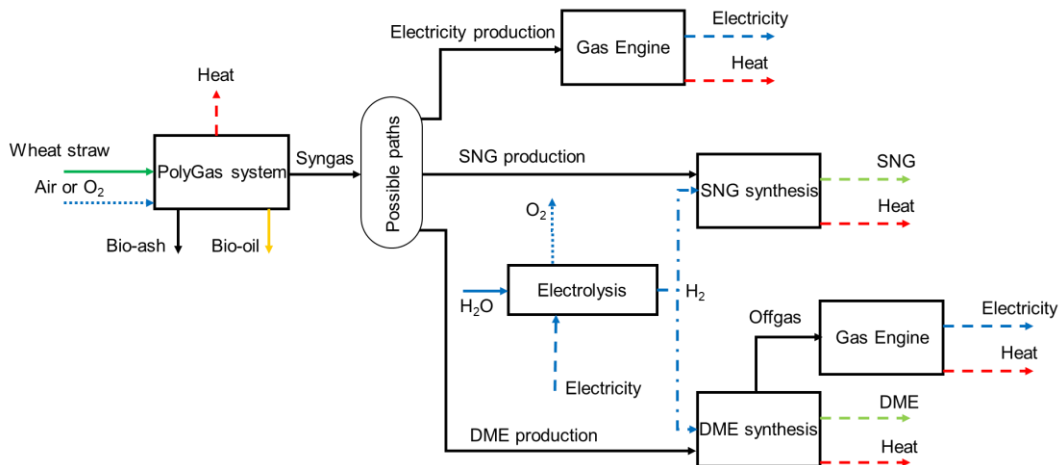

Fig. 14. Three different paths for using the tar-free syngas produced with the PolyGas system.

The SNG synthesis block shown in Fig. 14 consists of a syngas compressor, mixing of the compressed syngas with the added hydrogen, the synthesis reactor and several heat exchangers for preheating the syngas and cooling it down again while delivering heat and condensing the water in order to deliver a dry synthetic natural gas.

The DME synthesis has a more complicated setup consisting of a multi-stage compression with intercoolers before mixing the syngas with hydrogen and a recycling stream coming from the vapor-liquid separator placed

after the DME reactor. The mixture is then synthesized in the DME reactor before being cooled down to a temperature of -50 °C for condensing of DME and other heavy components. 95 % of the separated vapor are recycled to the synthesis reactor. Two distillation columns are used for purifying DME to 99.99 %. The separated fractions from the distillation columns and the non-recycled stream from the vapor-liquid separator contain methanol, CO, methane and other C2-C6 hydrocarbons and are combusted in a gas engine producing electricity and heat.

The heat output from the systems was divided into process heat and district heating in order to assess how much of the heat can be used to deliver higher quality heat (see also explanations in section G). Process heat was defined as heat at temperatures able to supply steam at 200 °C, while district heating is provided at a supply temperature of 75 °C.

The three different systems were compared based on their energy efficiencies and carbon efficiencies as shown in Table 4. Table 4 lists the single input to output efficiencies of the different products of the systems, where the main product is electricity, SNG and DME respectively. Additionally, the energy efficiency without heat is shown, highlighting how much of the energy input (straw + electricity, if applicable) is converted to the two main products, namely bio-oil and electricity/SNG/DME. Eventually, the total energy efficiency is shown.

Table 4. Energy and Carbon efficiencies of the investigated systems. Chemical energies in energy efficiency based on LHV.

Efficiencies	Electricity production	SNG production	DME production
Bio-oil/Input	13.4 %	5.9 %	11.4 %
Main product/Input	19.2 %	53.1 %	32.4 %
Energy efficiency w/o heat	**32.6 %**	**59.0 %**	**43.7 %**
Process heat/Input	40.4 %	16.1 %	26.3 %
District heating/Input	12.8 %	15.5 %	12.9 %
Total energy efficiency	**85.8 %**	**90.5 %**	**83.0 %**
Carbon to Ash	10.0 %	10.0 %	10.0 %
Carbon to biofuels	11.7 %	81.4 %	37.8 %
Carbon efficiency	**21.7 %**	**91.4 %**	**47.8 %**

As already seen in the section G, a big share of the straw is converted to heat in the electricity producing system using a gas engine. Considering also the quality of the heat, it can be seen that a big share (more than 75 %) of the heat is available at temperatures high enough to supply process heat. This highlights that it would be beneficial to locate the system nearby other industry in order to supply process heat. This would firstly increase the economic viability of the polygeneration system and secondly reduce the carbon footprint of the industry sector, as renewable energy sources are used for providing heat. The carbon efficiency is very low for the electricity production system, as all the carbon in the syngas is combusted and emitted as CO_2. The only bound carbon is found in the bio-oil and the ashes/bio-char (if they are returned to the fields), reaching a carbon efficiency of 21.7 %.

The SNG production system reaches the highest energy efficiency, both with and without utilized heat included. This is possible by using more electricity for producing hydrogen through water electrolysis than using chemical energy in form of straw, as shown in Fig. 15. This enables the conversion of most of the CO and CO_2 in the

syngas to methane, reaching a methane content of 90 % in the SNG, which is in the range of usual concentrations in natural gas.

This yields a high carbon efficiency, as nearly all the CO2 and CO in the syngas are converted to methane, while also the higher hydrocarbons (C2-C4) can be injected into the gas grid without problems. The main contributor to the carbon losses in the system is the coke deposition on the catalyst during the catalytic upgrading of the bio-oil, which was assumed to be combusted for regenerating the catalyst as well as the carbon in the aqueous organics, which were assumed to be disposed.
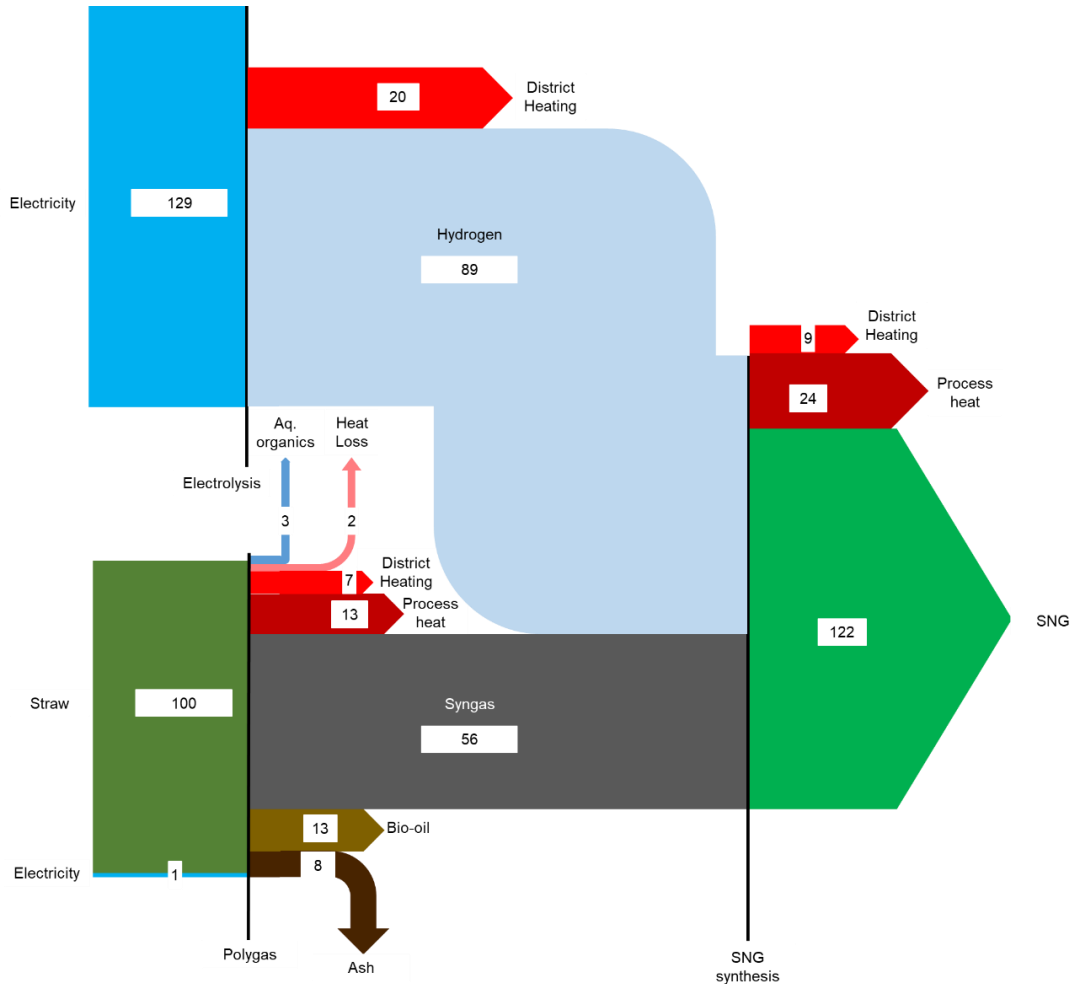
Fig. 15. Energy flows in SNG production system. All values are normalized to the chemical energy input of straw (LHV).

The DME production system has the lowest total energy efficiency, but a higher energy efficiency without heat compared to the electricity producing system. This denotes that more high quality products (DME and bio-oil) are produced, while less heat is produced. However, compared to the SNG production system, significantly less main product is produced. This derives from the fact that only CO is converted to DME, while CO_2 is not converted. Additionally, no hydrocarbons (methane and C2-C6) are converted. This leads to a significant share of energy left in the off-gas from the DME synthesis block, as shown in Fig. 16. The off-gas is then combusted in a gas engine producing electricity and heat. This leads also to a reduced carbon efficiency compared to the SNG production system, as a significant part is emitted as CO2 because of the combustion of the off-gas. 26 % of the carbon are bound in the DME. In order to increase the carbon efficiency of the DME production plant, a more complex DME synthesis should be used, including partial oxidation of the syngas and two-stage DME synthesis.
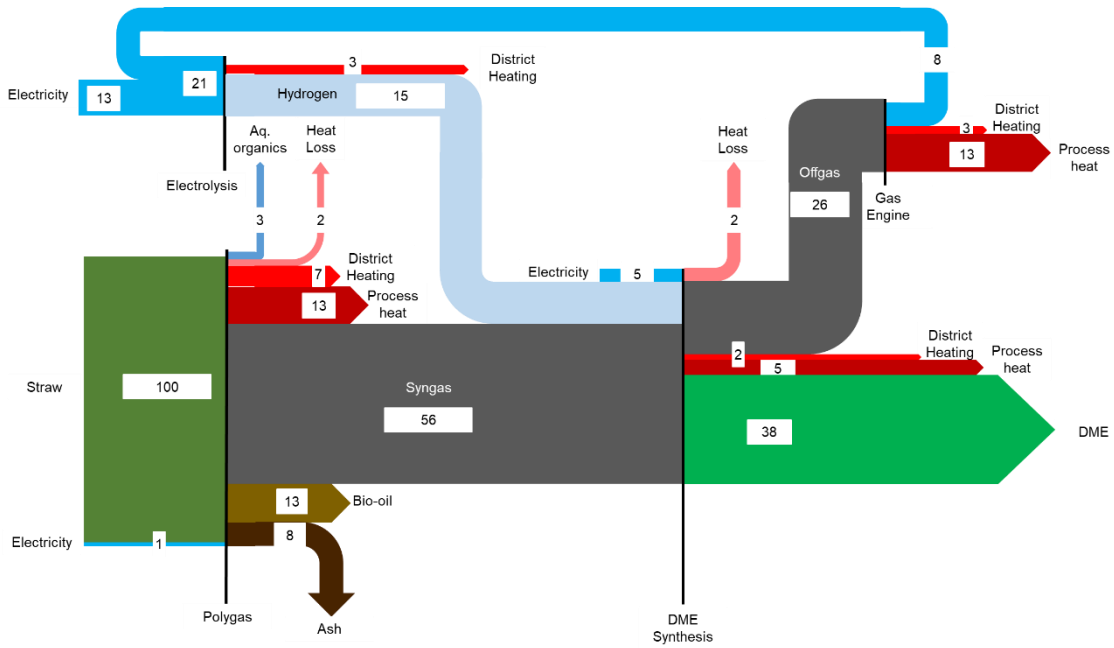
Fig. 16. Energy flows in DME production system. All values are normalized to the chemical energy input of straw (LHV)

5.1.2 Engine tests

5.1.2.1 Experimental setup

The experimental setup is placed in a container, which contains the engine, system controls and auxiliary equipment. The setup acts as a CHP engine, with connection to the electric grid and a cooling system simulating district heating production. The container is connected to external gas and air supply, including the natural gas grid and a manual gas mixer for cylinders. The manual gas mixer is adjusted according to the desired gas composition and the gas composition is measured before the gas enters the container. The engine exhaust is coupled to the TWC and the exhaust is led to the outside environment. A PI-diagram of the setup is shown in Figure 18.
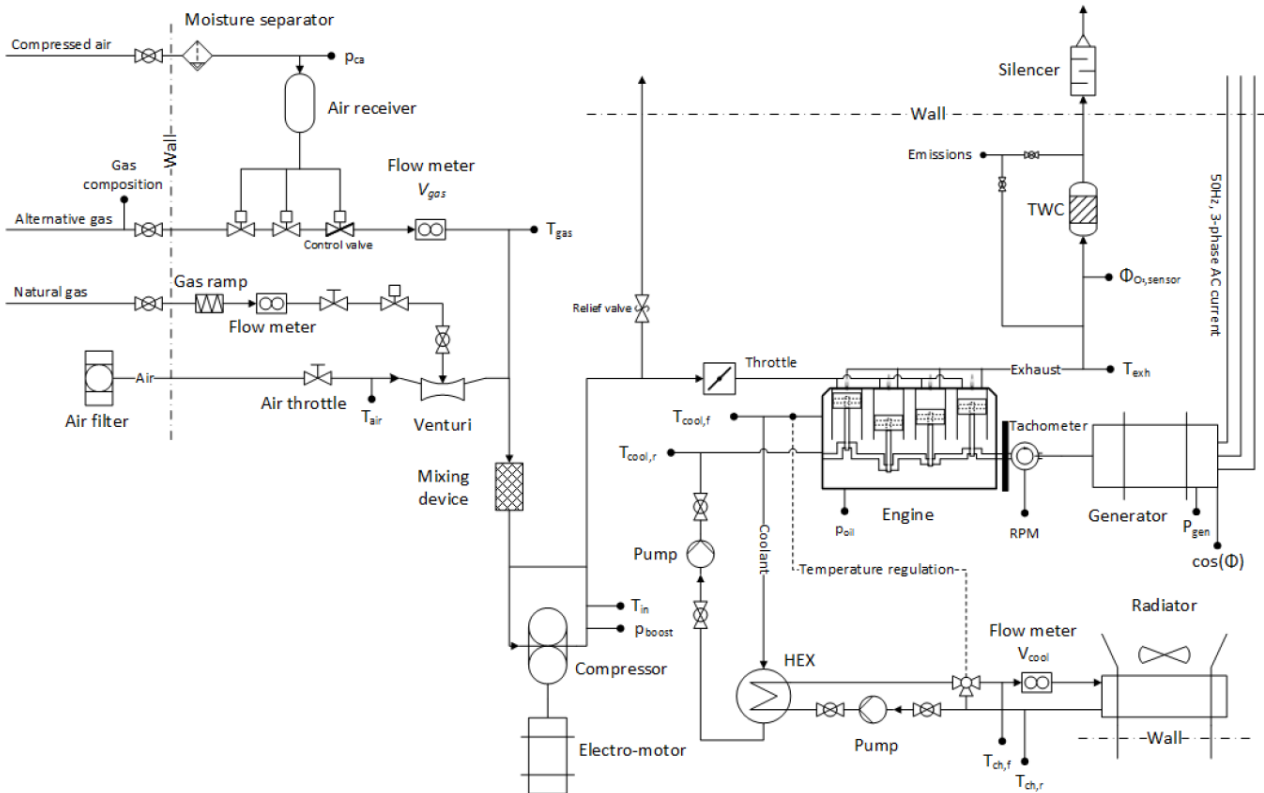
Figure 18. PI-diagram of the engine setup with gas intake, cooling system, generator and exhaust.

5.1.2.2 Intake and exhaust systems

The intake system is designed with two separate trains: natural gas and alternative gas. The engine is started and warmed with natural gas before switching to mixed or real product gas. The alternative gas flow is in the range of 0 - 45 nm^3/h and is adjusted by the exhaust oxygen sensor, while the air (and air-fuel ratio) is adjusted manually on a valve. The engine is naturally aspired, but has a compressor installed between the mixing device and engine to apply a boost pressure of 0 - 2.5 bar. Natural aspiration bypasses the compressor.

The hot exhaust from the engine is lead through the TWC. It is a commercial and mass-produced catalyst designed for cars. The catalyst is heated by the exhaust gas and is operated between 350-450ºC depending on operation. Gas outtakes are placed before and after the converter in order to measure gas compositions. The exhaust is lead through a silencer before being discharged to the outside environment.

5.1.2.3 Engine system

The gas engine is designed to be mounted with two different compression ratios. Both engine configurations are four-stroke, four-cylinder 1.86 L spark ignition Lister Petter models. The applied compression ratio for the initial tests is 9.5:1. The engine runs at a regulated constant speed of 1500 rpm, to match the generator grid frequency. The electric power production is in the range of 0 - 20 kW$_e$.

The engine is internally cooled by simulating a district heating network. The engine's cooling circuit is connected via a heat exchanger to a second cooling cycle that is cooled by forced convection the outside environment. The temperature is measured before and after the forced convection and hence the heat production can be calculated.

In the project the engine set-up has been rebuilt, a new engine block with a compression of 12:1 ratio has been installed and proof of concept tests have been planned for the modified set-up.

5.1.2.4 **Results**

The initial engine test, made prior to the project period, showed stable engine performance with an acceptable efficiency from gas to electricity for this engine, see Figure 19. The gas composition applied for the initial experiments is showed in Table 5.

Measurements of the emissions of CO and NOx can be seen in Fig. 20. The emissions are significantly below Danish emission levels, even without catalytic conversion of CO.

Table 5. The applied gas composition for the initial experiments

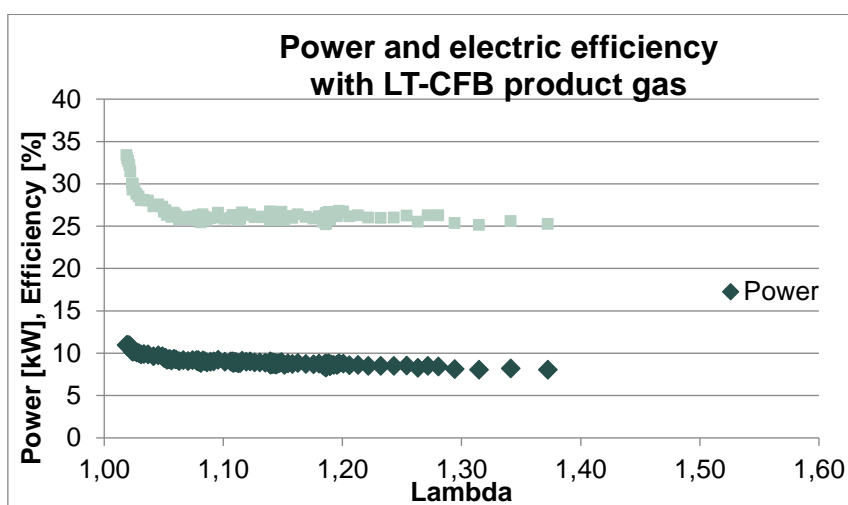| Gas	H_2 [vol%]	CH_4 [vol%]	CO [vol%]	CO_2 [vol%]	N_2 (rest) [vol%]	LHV [MJ/nm³]
LT-CFB residual gas	10.5	5.8	13.1	20.0	50.6	4.82

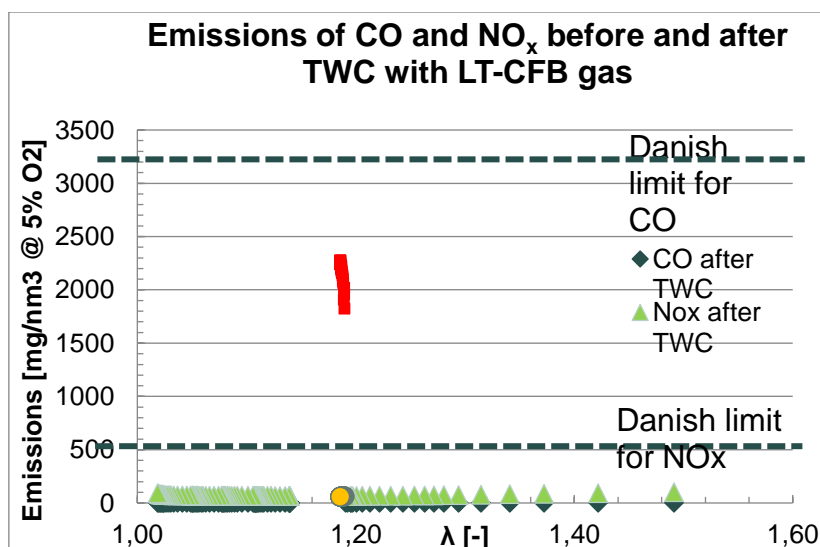Figure 19. The applied gas composition for the initial experiments

Figure 2. Emissions of CO and NOx as a function of λ for LT-CFB gas at ignition timing 18 CADBTDC

Running of the modified engine set-up and test were planned for spring 2020, but due to the corona situation this had to be postponed to the fall of 2020. The running in of the new engine block has been completed with natural gas as fuel, but the valve system, controlling and instrumentation for shifting from natural gas operation to alternative gas operation has been giving unforeseen technical problems, which has not been possible to fix within the project period. The new set-up will be made operational on alternative gas in related projects and at that time the remaining PolyGas engine tests will be performed and reported.

For the planned high compression experiments a new synthetic gas composition has been proposed based on the measurements of the composition of the residual gas form the gasifier experiments. The synthetic gas is adjusted for the content of CxHy in the real gas by increasing the CH_4 content.

Table 6. The composition of the measured residual gas after bio-oil extraction and the proposed composition of the synthetic test-gas for the high compression engine tests.

Measured gas composition	vol%	New gas composition for tests	vol%
H_2	4,7%	H_2	4,7%
CO	11,9%	CO	11,9%
CH_4	3,4%	CH_4	6,4%
C_xH_y	1,8%	C_xH_y	0,0%
CO_2	18,0%	CO_2	18,0%
N_2	59,0%	N_2	59,0%
sum	99%	sum	100%

5.1.3 Dissemination of results

11 publications have been published in scientific journals related to renewable fuel/energy and pyrolysis. In addition to this comes 6 oral conference contributions, 2 poster contributions and 1 popular scientific publication.

Scientific publications:

- Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, C. Li, J.Ø. Duus, U.V. Mentzel, A.D. Jensen, Impact of ZSM-5 deactivation on bio-oil quality during upgrading of straw derived pyrolysis vapors, Energy & Fuels. 33 (2019) 397–412. doi:10.1021/acs.energyfuels.8b03691.

- A. Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, S. Ndoni, C. Li, J.Ø. Duus, U.V. Mentzel, A.D. Jensen, Catalytic deoxygenation of vapors obtained from ablative fast pyrolysis of wheat straw using mesoporous HZSM-5, Fuel Process. Technol. 194 (2019) 106119. doi:10.1016/J.FUPROC.2019.106119.

- A. Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, C. Li, J.Ø. Duus, U.V. Mentzel, A.D. Jensen, Deoxygenation of Wheat Straw Fast Pyrolysis Vapors using HZSM-5, Al2O3 , HZSM-5/Al2O3 Extrudates, and Desilicated HZSM-5/Al2O3 Extrudates, Energy & Fuels. (2019). doi:10.1021/acs.energyfuels.9b00906.

- A. Eschenbacher, T. Myrstad, N. Bech, J.Ø. Duus, C. Li, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, U.V. Mentzel, Co-processing of wood and wheat straw derived pyrolysis oils with FCC feed—Product distribution and effect of deoxygenation, Fuel. 260 (2020) 116312. doi:10.1016/j.fuel.2019.116312.

- A. Eschenbacher, F. Goodarzi, A. Saraeian, S. Kegnæs, B.H. Shanks, A.D. Jensen, Performance of Mesoporous HZSM-5 and Silicalite-1 Coated Mesoporous HZSM-5 Catalysts for Deoxygenation of Straw Fast Pyrolysis Vapors, J. Anal. Appl. Pyrolysis. (2019) 104712. doi:10.1016/J.JAAP.2019.104712.

- A. Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, C.D. Jensen, C. Li, K. Enemark-Rasmussen, J.Ø. Duus, U.V. Mentzel, A.D. Jensen, Catalytic upgrading of tars generated in a 100 kWth low temperature circulating fluidized

bed gasifier for production of liquid bio-fuels in a polygeneration scheme, Energy Conversion and Management 207 (2020) 112538.

- A. Eschenbacher, A. Saraeian, B.H. Shanks, P.A. Jensen, C. Li, Ø. Duus, Enhancing bio-oil quality and energy recovery by atmospheric hydrodeoxygenation of wheat straw pyrolysis vapors using Pt and Mo-based catalysts, Sustain. Energy Fuels. (2020). doi:10.1039/c9se01254k.

- A. Eschenbacher, J.A. Andersen, A.D. Jensen, Catalytic conversion of acetol over HZSM-5 catalysts – influence of Si/Al ratio and introduction of mesoporosity, Catal. Today. (2020). doi:10.1016/j.cattod.2020.03.041.

- A. Eschenbacher, A. Saraeian, P.A. Jensen, B.H. Shanks, C. Li, J.Ø. Duus, T.E.L. Smitshuysen, C.D. Damsgaard, A.B. Hansen, K.I. Kling, U.V. Mentzel, U.B. Henriksen, J. Ahrenfeldt, A.D. Jensen, Deoxygenation of wheat straw fast pyrolysis vapors over Na-Al2O3 catalyst for production of bio-oil with low acidity, Chemical Engineering Journal 394 (2020) 124878.

- A. Eschenbacher, A. Saraeian, B. H. Shanks, U. V. Mentzel, P. A. Jensen, U. B. Henriksen, J. Ahrenfeldt, A. D. Jensen, Micro-pyrolyzer screening of hydrodeoxygenation catalysts for efficient conversion of straw-derived pyrolysis vapors. Journal of Analytical and Applied Pyrolysis, *150*, (2020).

Oral Presentations (4):

- Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, U.V. Mentzel, A.D. Jensen, Deoxygenation of wheat straw fast pyrolysis vapors using HZSM-5, Al2O3, HZSM-5/Al2O3 extrudates, and desilicated HZSM-5/Al2O3 extrudates, 14th European Congress on Catalysis, 2019, Aachen, Germany.

- A. Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, U.V. Mentzel, A.D. Jensen, Performance of Mesoporous HZSM-5 for the Upgrading of Wheat Straw Derived Fast Pyrolysis Vapors in Bench Scale, North American Catalysis Society Meeting, 2019, Chicago (IL), United States.

- A. Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, U.V. Mentzel, A.D. Jensen, Performance of mesoporous ZSM-5 in deoxygenation of straw derived pyrolysis vapors, Thermal & Catalytic Sciences Symposium 2018, Auburn (AL), United States.

- A. Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, U.V. Mentzel, A.D. Jensen, Performance of mesoporous ZSM-5 for the upgrading of straw derived pyrolysis vapors in bench scale, 18th Nordic Symposium on Catalysis 2018, Copenhagen, Denmark

- R. Kofler, L.R. Clausen, Thermodynamic modelling and analysis of a biomass based polygeneration plant producing bio-oil, electricity, heat and fertilizer, 6th Central European Biomass Conference 2020, Graz, Austria

- R. Kofler, L.R. Clausen, Comparison of different biorefinery systems integrating the electricity, heating and transport sector, 6th International Conference on Smart Energy Systems 2020, Aalborg, Denmark

Poster Presentations (2):

- Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, A.D. Jensen, Optimizing tar-deoxygenation of fast pyrolysis vapors over zeolites, 26th European Biomass Conference and Exhibition (EUBCE 2018), Copenhagen, Denmark

- A. Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, A.D. Jensen, Optimizing catalytic deoxygenation of biomass derived fast pyrolysis vapors, Sustain 2017 Conference at DTU, Kgs. Lyngby, Denmark

Popular scientific publication (1):

- Eschenbacher, P.A. Jensen, U.B. Henriksen, J. Ahrenfeldt, A.D. Jensen, Fremstilling af bio-olie med forbedrede brændstofegenskaber fra halmforgasning—en spændende polygenerationsteknologi, submitted to Dansk kemi.

The PhD thesis represents an enormous body of research work, which is on a high scientific level. In addition to challenging experimental work combining both biomass pyrolysis and catalytic upgrading using various catalysts and atmospheres, the work has necessitated extensive characterization of typically 4 product phases (gas, solid, and organic and aqueous liquid phases) by a range of techniques, too numerous to summarize here. Catalyst characterization has involved chemisorption and physisorption studies, compositional analyses

such as XRF, structural analyses such as XRD and TEM, oxidative analyses of carbon deposition and site/element studies by infrared and solid state NMR techniques. The thesis touches upon most of the important topics related to catalytic oil/tar upgrading for production of a higher quality bio-oil. It provides a fundamental understanding of the catalytic conversion while it will provide a strong basis for subsequent work in the field. The work on the potential for co-feeding of catalytic bio-oil in an FCC process, and the upgrading of tar from gasification processes may open new research fields. The importance of the work is illustrated by its direct relevance to the UN Sustainable Development Goals 2, 7, 9, 12 and 13. The work contains several innovative elements such as novel catalyst formulations.

6. Utilisation of project results

The extensive knowledge gained in the project with respect to the catalyst development and the performance of different catalyst systems with respect to the yield and quality of the bio-oil was communicated in scientific journals. It serves as a resource for industry to assess the potential of the technology and the produced research results can lay the basis for future Techno-economic analysis. . In a Danish context, Haldor Topsøe has been cooperating with the project and might be able to utilize some of the results commercially.

The knowledge and know-how regarding bio-oil upgrading, extraction and handling will be used in future demonstration and industrialization of pyrolysis and gasification. Danish companies like MASH Energy, AquaGreen, Frichs Pyrolysis, Stiesdal Fuel Technologies and DFBT all have technology tracks that can commercially benefit from the results gained in this project.

The present project results contribute to realize the following Danish energy policy objectives

- To facilitate a conversion from fossil fuels to biomass

- Greater use of biomass

- To reduce Danish net emissions of CO_2

- Increased flexibility of biomass fuel.

7. Project conclusion and perspective

7.1.1 Conclusions

A bench scale fast pyrolysis unit was successfully extended for studying catalysts for upgrading of fast pyrolysis vapors and condensation of all vapors. Extensive screening of catalysts was performed and the catalysts were thoroughly characterized. The non-condensed pyrolysis vapors derived from wheat straw were analyzed by analytical pyrolysis and the bio-oil obtained at bench scale pyrolysis was analyzed by multiple techniques, which provided a good understanding of its properties. With respect to the catalytic vapor treatment, when using HZSM-5 zeolite, the catalysts rapidly deactivated by coke, which increased the oxygen content of the bio-oils. Adding mesopores to HZSM-5 could delay the deactivation to some extent. Tar deoxygenation can also be achieved using lower cost γ-Al_2O_3. Coke yields were significantly higher compared to HZSM-5, however the coke combusted at lower temperatures. The catalytic treatment of tars from an LT-CFB gasifier operated with wheat straw pellets was demonstrated by using HZSM-5/γ-Al_2O_3 and γ-Al_2O_3, resulting in improved quality of the collected bio-oils.

A low-cost Na-Al$_2$O$_3$ catalyst is highly active in ketonization of carboxylic acids, producing bio-oils with low acidity (TAN), thereby lowering the corrosion potential significantly. This is an important aspect for the storage and further handling of the produced bio-oil by oil refineries. Another benefit for this catalyst is that lower coke yields and coke combustion temperature resulted compared to the parent γ-Al$_2$O$_3$, which facilitates the regeneration procedure.

The hydrodeoxygenation with Pt/TiO$_2$ and MoO$_3$/TiO$_2$ catalysts under atmospheric pressure hydrogen achieved higher levels of bio-oil energy recoveries compared to catalysts tested under inert conditions at remarkably low coke yields. MoO3/TiO2 was not as active in conversion of acids, and Pt/TiO2 showed the highest selectivity to alkanes. An increase in H$_2$ partial pressure further improved the oil properties and/or carbon and energy recovery of bio-oil.

Mathematical modelling focused on the polygeneration system using a gas engine for electricity production and was optimized through heat recovery. The system was evaluated from an energy and exergy perspective. Additionally, the production of additional fuels (synthetic natural gas and DME) through water electrolysis and oxygen blown gasification was investigated.

Engine experiments with a synthetic gas, with a gas composition similar to residual gas after bio-oil extraction, resulted in stable engine performance with a good efficiency. Emission measurements indicate that engine operation can be performed with emissions below the regulatory limit, especially the NOx emissions were very low at all operating conditions. This is mainly associated with low combustion temperatures caused by the high inert content of the residual gas. Future engine tests with a high compression ratio engine will indicate the efficiency limit for engine operation with the residual gas.

7.1.2 Perspectives

In a scenario of parallel fixed beds of catalyst, it is crucial that a high amount of biomass can be converted over the catalysts before the liquid quality deteriorates, in order to limit the frequency of regeneration and hence the number of parallel fixed bed units required for continuous operation. Areas identified in this work that warrant further investigation are listed in the following:
- Further studies using Na-Al2O3 for vapor upgrading to elucidate the nature of Na species during reaction conditions, optimal Na content, long-term behavior, and processing of produced oils in refinery processes such as FCC or hydroprocessing appear highly relevant. In addition, testing of the partly deoxygenated bio-oil as fuel for ship diesel engines may be of interest.
- While good HDO performance of 0.5 wt.% Pt/TiO2 was observed in this work, based on the high cost of Pt it may be of interest to study to what extent the Pt loading can be further lowered without negatively affecting the deoxygenation activity. More investigations are needed with respect to the further processing of bio-oils produced from atmospheric HDO in refinery processes such as FCC/hydroprocessing or its application as a renewable fuel for ship diesel engines.
- It is expected that the partly deoxygenated bio-oils with an oxygen content of ~10 wt.% can be hydrotreated in a single stage. To demonstrate this, hydrotreatment tests require ~2 L of upgraded bio-oil, which would require ~12 repetition experiments at the ablative bench scale unit using 100 g catalyst and operating to B:C ~8. Conducting these tests with the most promising catalysts identified in this study (Na-Al2O3, 0.5 wt.% Pt/TiO2, and 10 wt.% MoO3/TiO2) will at the same time provide additional information on the catalyst stability.
- It is proposed that the performance of the promising Na-Al2O3 and HDO catalysts are studied for upgrading of tars from the LT-CFB gasifier operated at a low pyrolysis temperature, possibly with larger catalysts reactors and condensation equipment to produce larger amounts of bio-oil for further treatment.

Bio-oil from low temperature gasification or pyrolysis of residual biomass, can be a fast track to biofuel production for the transport sector. When used in existing refineries, it can be converted into conventional fuel

products that can be used directly in the transport sector without modification of infrastructure or vehicles. One of the main constraints for this development is the quality of the bio-oil. This project has shown, that hot vapor upgrading of producer gas can be a game changing technology for the implementation of commercial bio-oil production via low temperature gasification or pyrolysis.

Utilization of the residual gas after bio-oil extraction can be done several ways, depending on the need of the future energy system. The gas can be utilized for direct energy production, such as heating or CHP, or the gas can be upgraded to SNG or DME via synthesis.

Biochar will be produced as a byproduct form the thermal process. The biochar is a valuable product both in a climate mitigation perspective because it represents a carbon sink when applied to agricultural soils, additionally the biochar has soil enhancing and fertilizing properties. With the LT-FCB gasifier the amount of biochar produced may be varied to some extent and this represents additional flexibility, which may be of competitive advantage in a future energy system.

8. Appendices

- PhD thesis of Andreas Eschenbacher and publications in scientific journals, listed in 5.1.3