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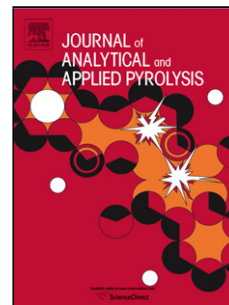
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Production and characterization of a new quality pyrolysis oil, char and syngas from digestate –
introducing the thermo-catalytic reforming process

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Highlights:

Report on commissioning experiments run on a newly designed intermediate pyrolysis reforming reactor

Use of a wet biomass residue (anaerobic digestate) to a novel quality of pyrolysis products

Characterization of feedstock and of various product fractions

Presentation of mass and energy balances

Abstract

A 2 kg/h laboratory scale thermo-catalytic reforming (TCR®) unit was designed and commissioned at Fraunhofer UMSICHT to convert digestate into enhanced pyrolysis products. The TCR® reactor is an intermediate pyrolysis screw reactor connected to a reformer. In the experimental series reported, digestate pellets were used as feedstock. The aim herein was to test and characterize the TCR® reactor for the feedstock digestate and its products for syngas applications and decentralized power production. Prior to the pyrolysis experiments thermal gravimetric analysis was used to analyze the weight loss over temperature. The digestate was pyrolyzed at a constant temperature of 400 °C, whereas the reformer temperature was varied between 500 and 750 °C. Following the cooling and condensation of pyrolysis vapors, these separated into bio-oil, an aqueous phase and permanent gases. Hydrogen concentration increased together with increased reforming temperatures and reached a maximum of 35 vol% at 750 °C. The bio-oil generated at 750 °C had a higher heating value of 33.9 MJ/kg, 1.7 wt% water content and a total acid number of 4.9 mg KOH/g. It was possible to convert over 91 % of the energy content of the biomass into usable products. These results are analyzed together with the extensive feedstock and product characterization and the experimental parameters and discussed.

Keywords: thermo-catalytic reforming, intermediate pyrolysis, digestate, oil, syngas, char

1 Introduction

Bioenergy will play a significant role in the future energy supply [1–3]. The expansion of bio-fuels produced from biomass residues has been deemed essential to meet sustainability and cost criteria [4]. The existent competition of energy crops with food and feed production makes the utilization of agricultural waste streams like straw or digestate necessary. It has therefore emerged as one of the favored future strategies for the bioenergy sector, which is confirmed by the increasing number of residue- and waste-to-energy projects [5,6]. Digestate is the residue following anaerobic digestion of biodegradable feedstock for the production of biogas. In Germany alone, more than 7800 anaerobic digestion units produce over 60 million tons of digestate every year (at approximately 10 wt% dry matter) [7]. As the total energy content of corn or other energy crops, being the main feedstock for agricultural anaerobic digestion units in Germany, cannot be fully used in the digestion process, making use of these residues for power production is an important step to improve overall economics. For example, digestate with a dry matter of 90 % still has a heating value of 15.8 MJ/kg [8]. However due the high ash content, low ash melting point and slagging, digestate is not a favorable fuel for

incineration and necessitates special furnace designs [8–10]. Therefore biomass pyrolysis is a promising conversion technology for the production of biofuels from residue. Moreover, energy from biomass and its residues has the potential to be CO₂ neutral and can therefore have a positive effect on the reduction of greenhouse gas emissions [11].

In the presented work dried and pelletized digestate was processed in a recently developed thermo-catalytic reforming (TCR®) reactor with the objective of quantifying and characterizing the products [12]. The TCR® is an enhanced intermediate pyrolysis screw reactor combined with a reforming process as a part of Fraunhofer UMSICHT's concept of the 'Biobattery' [13–16]. Within this concept bio-oil and gas from TCR® will be used for engine applications for combined heat and power. The utilization of TCR® bio-oil blended with biodiesel has been successfully proven in a diesel engine already [21]. Further the char is of interested as potential fertilizer and soil conditioner.

2 Materials and methods

2.1 Raw material

For the experiments pre-conditioned digestate from an anaerobic digestion plant operated by Neue Energie Steinfurt GmbH, Germany (NESt) was used. Chemical composition and physical properties of digestate are dependent on the blend of substrates used as feedstock for biogas production. The feedstock composition used in the NESt anaerobic digestion (AD) plant from which the pellets were acquired is shown in Table 1. For a better homogenization inside of the AD plant the feedstock has been chopped prior to the input. During the fermentation process the primary anaerobic feedstock is converted to biogas for power generation and digestate as the residue.

Table 1 Composition of primary feedstock of the anaerobic digestion plant

Fresh digestate has a high moisture content of approximately 90 wt% which can be reduced down to 60–70 wt% by mechanical de-watering and reduced further to 10–20 wt% by drying. 1000 kg of homogenized digestate were mechanically de-watered, dried and pelletized by NESt. The pellets had a diameter of 6 mm and about 15–30 mm length (Fig. 1).

Fig. 1. Digestate pellets (as received)

2.2 Feedstock characterization

Volatiles and fixed carbon of the digestate were measured by Thermo Gravimetric Analysis (TGA) in a Netzsch STA 409 PC Luxx TGA device. Prior to TGA, samples of digestate pellets were milled and homogenized with a Fritsch pulverisette 23 ball-mill. Approximately 25 mg of dried digestate was filled into a crucible and pyrolyzed under an inert atmosphere of Argon at a flow rate of 100 ml/min, to a maximum temperature of 1000 °C, with a heating rate of 20 °C/min.

Ash content at 575 °C and total moisture content at 105 °C of the feedstock was determined in a muffle furnace according to ASTM E1755-01 and ASTM E1756-08.

Ultimate analysis was carried out by an external analytical laboratory using a Leco TruSpec CHN analyzer and a Leco SC-144DR for sulfur. The higher heating value in MJ/kg of the digestate was determined with an IKA C5000 bomb calorimeter.

2.3 Thermo-catalytic reforming (TCR®) experiments

The TCR® plant is installed at the laboratory of Fraunhofer UMSICHT Institute Branch Sulzbach-Rosenberg, Germany. The TCR® unit is an intermediate pyrolysis reactor connected to a reformer [12,14–16]. A schematic of the thermo-catalytic reforming is shown in Fig. 2. A picture of the plant is shown in Fig. 3. The reactor is a multi-zone auger pyrolysis reactor which can process a feed in an inert atmosphere of nitrogen at a rate of up to 2 kg/h. The lab-scale reactor is heated externally by electrical heating bands. The feed moves through the different zones of the screw conveyor system and can be heated using a specific temperature profile. On the downstream side of the auger reactor, resulting intermediates are conveyed into the electrical heated reformer, where a reforming between char, vapor and gases takes place, resulting in an upgrading of all phases which can be performed at lower temperatures as described in conventional catalytic coal gasification research [17,18]. The big variability in process control gives the plant a wide range of options regarding gas composition and amount, oil quality and char stability.

The experiment was conducted with a total of 5 kg pelletized feedstock with a mass flow of 1.6 kg/h and an average residence time of 5 min. Three different temperature zones made up the temperature profile used for the TCR® reactor. Temperatures increase from 150 °C at the inlet to 500 °C at the

outlet with a constant temperature in the central pyrolysis zone of 400 °C. The temperature in the reformer was varied between 500 °C to 750 °C. The reactor was heated for 80 minutes prior to the introduction of feedstock. A steady state operation was achieved after 25 minutes. During the experiments the plant was pressurized to 100 Pa overpressure. The resulting TCR® vapors emitted from the reformer were cooled down in a cold trap at a temperature of -10 °C and condensed as liquids. After the runs, the liquids produced which phase separated into an organic bio-oil phase and aqueous phase were separated and accurately weighed. The char produced was also weighed and mass balance closure was obtained with the permanent gases calculated by difference.

Fig. 2. Schematic drawing of the thermo-catalytic reforming reactor

Fig. 3. Laboratory scale TCR® reactor installed at Fraunhofer UMSICHT

2.4 Liquid and solid products analyses

After the experiments the pyrolysis liquids (organic bio-oil phase and aqueous phase) and solid products were analyzed to determine their chemical and physical properties. Most of the analyses were carried out by external analytical laboratories.

- Water content of the char was determined in a muffle furnace at 105 °C according to ASTM E1756-08. Water content of the pyrolysis oil was determined in accordance with ASTM E203-08 with an Analytik Jena AQUA 40.00 Karl-Fischer titration unit.
- The higher heating value of the char and pyrolysis oil was determined with an IKA C5000 bomb calorimeter.
- Ultimate analysis for the pyrolysis oil and the char was measured with a Leco TruSpec CHN analyzer and a Leco SC-144DR for sulfur. Elemental compositions (C, H, N, O and S) are obtained as delivered.
- The density of the pyrolysis oil was determined at 15 °C using a glass hydrometer according to ASTM D1298-12b.
- Kinematic viscosity was measured by Cannon-Fenske routine viscometer according to ASTM D445-12.
- Flashpoint of the pyrolysis oil was measured using an automated closed flashpoint tester according to ASTM D93-13e1 standard test procedure.
- The pH value of the aqueous phase was determined using a WTW pH 325 pH meter calibrated with standard buffer solutions according to ASTM E70-07 standard test procedure.
- TAN of the pyrolysis oil was measured with a Metrohm Dosimat 775 titrator with an alcoholic potassium hydroxide titrant in accordance with ASTM D664-04.
- Ash of the char was determined in a muffle furnace at 575 °C according to ASTM E1755-08. Ash content of the pyrolysis oil was determined at 775 °C in accordance with ASTM D482-03.

2.5 Gas analysis

The gas composition was constantly measured after condensing of the pyrolysis vapors using a Dr. Födisch Umweltmesstechnik AG gas analyzer MGA 12 suitability tested in accordance with EN 15267-3 standard test procedure. The measurement principle based on an infrared photometer (CO, CO₂, CH₄), an electro chemical cell (O₂) and a thermal conductivity detector (H₂). A Union Instruments CWD2005 process gas analyzer was installed to measure the heating value of the gas phase. The gas analyzers were calibrated with a calibration gas prior to the experiments.

3 Results and discussion

3.1 Feedstock characterization

Table 2 presents the proximate, ultimate analyses and the heating value of the digestate feedstock used in thermo-chemical reforming experiments. Considering the high ash content of the digestate, the higher heating value of this feedstock is still in a range comparable to wood with 19-22 MJ/kg on a moisture-free basis [19]. The oxygen content of the digestate is however lower in comparison.

Table 2 Feedstock characterization

The TGA pyrolysis weight loss and rate of weight loss (DTG) curves are shown in Fig. 4. Major weight loss of approximately 50 wt% is seen till 400 °C. The rate of weight loss peaks at around 320–330°C as a direct result of the decomposition of cellulose and lignocellulose fibers which has not been

190 converted to biogas by the bacteria in the digester. At temperatures between 400 °C and 750 °C the decomposition of lignin causes a rate of weight loss up to approximately 38 wt% of the former biomass. At 1000 °C the solid residue has 35.3 wt% of the original sample.

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3 Fig. 4. TGA pyrolysis weight loss curve and weight loss rate curve (DTG)

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5 3.2 Thermo-catalytic reforming experiments

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7 3.2.1 Permanent gas analysis

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10 200 The dependence of the gas composition on an increase of the reformer temperature is shown in Fig. 5. The content of inflammable components increases with increasing reformer temperature. The production of hydrogen starts below 500 °C and increases to 35 vol% at 750 °C. The significant decrease of CO₂ results from the Boudouard reaction where carbon dioxide and carbon is converted to carbon monoxide. The decrease of CO results from the water-gas shift reaction where carbon monoxide and water steam generate carbon dioxide and hydrogen. CH₄ is steam reformed to hydrogen and carbon monoxide. Approximately the double amount of hydrogen is generated compared to carbon monoxide and –dioxide, causing a decrease of carbon dioxide and carbon monoxide in terms of volumetric percentage. The lower heating value of the gas reached an average of 13.1 MJ/kg at 750 °C reformer temperature. The balance was not detected but was assumed to be mainly hydrocarbons due to the measured heating value and density.

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30 220 After condensation of the pyrolysis vapors a phase separation into an aqueous phase and an organic phase of the condensate occurred as shown in Fig. 6. After removal of the aqueous phase, analysis of the organic phase, which hereafter is referred to as product bio-oil, has demonstrated the high quality. Table 3 shows the physical and chemical properties of the generated bio-oil and compares it to the requirements of ASTM D7544-12 Grade D. This ASTM method is currently the only method, which specifies grades of pyrolysis oils from biomass. However the standard does not include use in internal combustion engines. The bio-oils higher heating value was measured to be 33.9 MJ/kg and water content of 1.7 wt% was determined. This is significantly lower than required by ASTM D7544-12. The oxygen value of digestate derived bio-oil is also low (8.7 wt%), thereby increasing the calorific value and stability of the bio-oil. The low oxygen value results from a de-oxygenation process during the reforming step. Furthermore, the low total acid number (TAN) causes the bio-oil to be less corrosive to buffer tanks, combustion equipment like burners or engine components. The higher density and viscosity of the bio-oil (compared to biodiesel) could lower the flow characteristics within fuel pipes, injectors or nozzles. The bio-oil flashpoint of 47 °C meets the requirements to diesel fuel with a minimum of 38 °C according to ASTM D975-14 and is above the 45 °C of the ASTM D7544-12 standard specification for pyrolysis liquid biofuel. Some initial blending of biodiesel and bio-oil was carried out and the bio-oil was found to be directly miscible with biodiesel at all concentrations which indicates a high potential for a future biofuel in stationary CHP engines or upgraded further to transportation grade biofuel.

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40 230 Due to the good phase separation, the aqueous phase consists mainly of water leading to a very low heating value (Table 4). The pH value indicates an alkaline solution which could result from present organic nitrogen and ammonia compounds.

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49 Fig. 6. Bright aqueous phase (top) and brown low-viscous bio-oil phase (bottom)

50 240 Table 3 Physical and chemical properties of bio-oil from digestate compared to ASTM D7544-12

51
52 Table 4 Characterization of the aqueous phase

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55 3.2.3 Char analysis

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59 Fig. 7 shows the pyrolysis char obtained. It can be seen, that the produced pyrolysis char retains the physical structure of the pelleted feedstock. In addition, it is remarkable that only a small percentage of powder is generated, showing the low abrasion rates achieved inside the TCR® unit.

60 250 Fig. 7. TCR® char from digestate (original structure and shape of pelleted feedstock are maintained)

Analytic results of the pyrolysis char are shown in Table 5. The carbon content of the char increased to 65 wt%. The hydrogen content of the char is 1.2 wt% while the oxygen content is 2.2 wt%, being very low compared to other pyrolysis chars [20]. Furthermore the higher heating value of the char has increased to 23.9 MJ/kg which is approximately an increase of about 28 % compared to the feedstock.

Table 5 Characterization of the TCR® char

260 3.2.4 Product yields

The product distribution and yields for the thermo-catalytic reforming at a pyrolysis temperature of 400 °C and increasing reformer temperatures are shown in Fig. 8. The results indicate that with increasing reforming temperature the yield of permanent gases increases and thereby the yields of condensable liquids and pyrolysis char are reduced. The yields of the pyrolysis char from the TCR® experiments are lower as indicated by TGA measurements which are yields of pyrolysis char of 44 wt% at 500 °C, 41 wt% at 600 °C and 38 wt% at 750 °C (see Fig. 4). This is a result of the reforming of the char by pyrolysis vapors leading to higher hydrogen content (see Fig. 8).

270 Fig. 8. Comparison of the product yields from digestate at different reforming temperatures

3.3 Energy balance

The energy balance presented in Fig. 9 results from trials of digestate as feedstock, the products' lower heating values and the product yield at 750 °C TCR® temperature. With 100 % feedstock energy input 36 % was converted to pyrolysis gas, 12 % of the feedstock energy was in the bio-oil and 43 % in the char. The energy content of the aqueous phase was approximately 0.2 %. The conversion loss of the lab-scale TCR® process was 8.8 % for the feedstock digestate.

280 Fig. 9. Energy balance for TCR® of digestate at 750 °C reforming temperature

4 Conclusions

Bio-oil, pyrolysis char and pyrolysis gas from digestate were successfully produced using a novel thermo-catalytic reforming process based on intermediate pyrolysis. Experiments were performed at constant 400 °C pyrolysis temperature and 500 °C to 750 °C reforming temperature. The feedstock and products have been analyzed in terms of their composition and characteristics.

- 290 • Start of hydrogen production below 500 °C reforming temperature with an increase up to 35 vol% at 750 °C reforming temperature has been observed.
- Decrease of CO₂, CO and CH₄ in the product gas with temperature increase due to Boudouard reaction, water-gas shift reaction and steam reforming of hydrocarbons occurs.
- Cracking of hydrocarbons with water steam and higher temperature was shown.
- Production of bio-oil with a higher heating value of 33.9 MJ/kg, low acidity (4.9 mg KOH/g) and oxygen content (11.2 wt%) has been carried out.
- Phase separation of organic bio-oil and aqueous phase under gravity settling was observed, generating a bio-oil with a high HHV and aqueous phase with a very low HHV.
- De-oxygenation of the bio-oil during the presents of high amounts of hydrogen gas within the reformer was observed.
- 300 • Alkaline pH value (pH 9.3) of the aqueous phase was measured.
- Pyrolysis char with a higher heating value of 23.9 MJ/kg and high C:O ratio was produced.
- Reforming of the char with steam out of the origin biomass decreases the char yield with increasing reforming temperatures.
- Over 91 % of the digestate energy content was transferred into usable products.

The presented TCR® process demonstrated the advantage of high product qualities from low grade biomass with minimal higher energy demand due to the reformer heating compared to intermediate pyrolysis only. H₂ rich TCR® gases are a potential feed for synthesis reactions like Fischer-Tropsch or alcohol production. Due to the reforming temperatures of up to 750 °C the chars' C:O ratio indicates highly stable biochar and indicates potential as fuel, soil conditioner or for carbon sequestration. Overall the TCR® process is a promising technology to utilize biomass residues for the production of biofuels and sustainable energy from CHP engines.

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6 References

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Figures and Tables

Table 1 Composition of primary feedstock of the anaerobic digestion plant

Component	wt%
Cattle slurry	17
Pig slurry	17
Corn silage	62
Others	4



Fig. 1. Digestate pellets (as received)

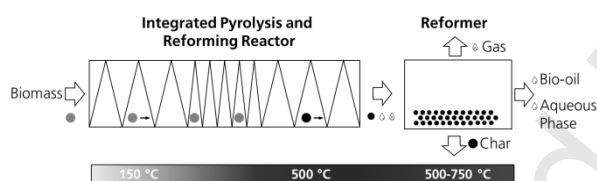


Fig. 2. Schematic drawing of the thermo-catalytic reforming reactor



Fig. 3. Laboratory scale TCR® reactor installed at Fraunhofer UMSICHT

Table 2 Feedstock characterization

Ultimate analysis		
	Unit	Value
C	wt%	41.6
H	wt%	5.1
N	wt%	1.6
S	wt%	0.3
O (diff.)	wt%	31.6
Proximate analysis		
	Unit	Value
Moisture	wt%	11.1
Volatiles	wt%	53.6
Fixed carbon	wt%	26.6
Ash	wt%	8.7
LHV	MJ/kg	15.8
HHV	MJ/kg	17.1

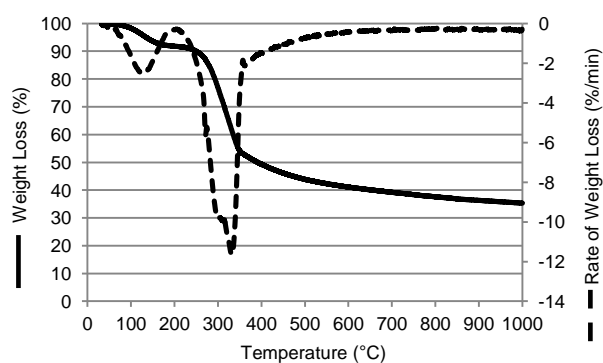


Fig. 4. Digestate: TGA pyrolysis weight loss curve and weight loss rate curve (DTG)

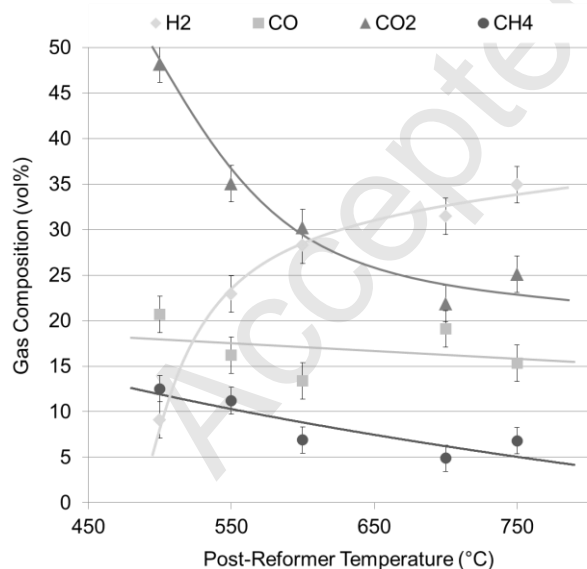


Fig. 5. Gas composition from constant 400 °C pyrolysis temperature and increasing reformer temperature



Fig. 6. Bright aqueous phase (top) and brown low-viscous bio-oil phase (bottom)

Table 3 Physical and chemical properties of bio-oil from digestate compared to ASTM D7544-12

	Units	TCR® at 750 °C	ASTM D7544-12 Requirements Grade D
440 C	wt%	76.6	
H	wt%	7.7	
N	wt%	2.2	
S	wt%	0.6	< 0.05
O (diff.)	wt%	11.2	
Water content	wt%	1.7	< 30
Ash	wt%	<0.05	< 0.15
LHV	MJ/kg	32.5	
HHV	MJ/kg	33.9	> 15
TAN	mg KOH/g	4.9	
450 Viscosity (40 °C)	mm ² /s	40.0	< 125
Density (15 °C)	kg/m ³	1063	1100-1300
Flash Point	°C	47	> 45

Table 4 Characterization of the aqueous phase

	Units	TCR® at 750 °C
460 C	wt%	4.9
H	wt%	1.7
N	wt%	1.0
S	wt%	0.02
O (diff.)	wt%	11
Water content	wt%	81.3
Ash	wt%	< 0.1
LHV	MJ/kg	< 0.2
HHV	MJ/kg	2.4
pH	-	9.3

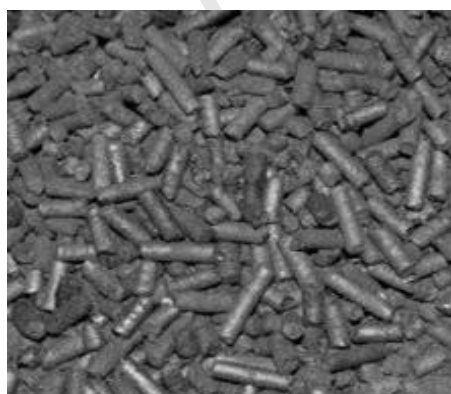


Fig. 7. TCR® char from digestate (original structure and shape of pelleted feedstock are maintained)

Table 5 Characterization of the TCR® char

	Unit	TCR® at 750 °C
C	wt%	65.0
H	wt%	1.2
N	wt%	1.5
S	wt%	0.3
O (diff.)	wt%	2.2
Moisture content	wt%	0.7
Ash	wt%	29.1
LHV	MJ/kg	23.5
HHV	MJ/kg	23.9

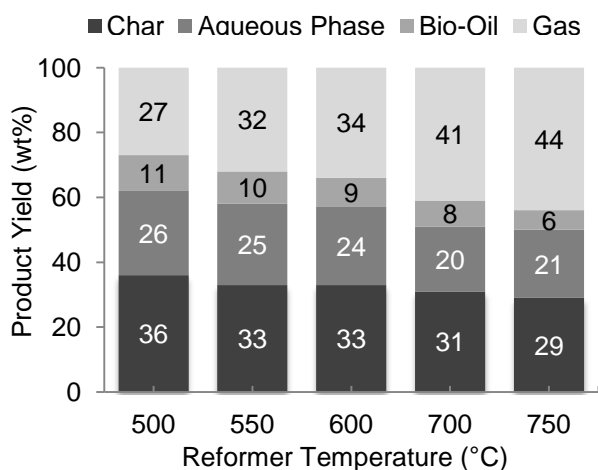


Fig. 8. Comparison of the product yields from digestate at different reforming temperatures

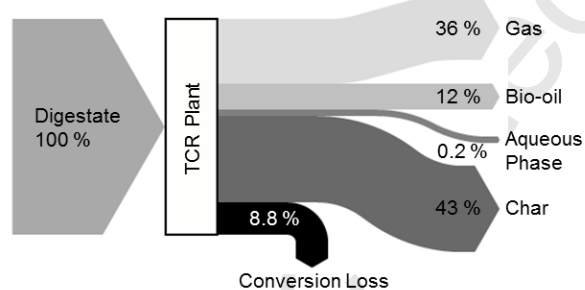


Fig. 9. Energy balance for TCR® of digestate at 750 °C reforming temperature