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Thermo-Catalytic Reforming of spent coffee grounds

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Abstract

Conversion of spent coffee grounds through the Thermo-Catalytic Reforming system (TCR®) is evaluated in this study. While, the TCR® is a technology that has been developed by Fraunhofer UMSICHT, which combines an intermediate pyrolysis and a catalytic reforming. The temperature of the catalytic reformer is varied between 500 and 700 °C to achieve an optimum yield quantities and qualities of the products. The hydrogen concentration is maximized at a reforming temperature of 700 °C, and a gas yield up to 52 wt% is achieved. The thermal stable bio-oil produced at 700 °C has the highest calorific value of 36.8 MJ/kg with significantly low oxygen and water content, low viscosity and low TAN (total acid number). Furthermore, the maximum bio-oil and char yields are obtained at the lowest reforming temperature of 500 °C. Overall spent coffee grounds show a great potential as feedstock in the Thermo-Catalytic Reforming for energy and bio-chemicals production.

Keywords: Intermediate pyrolysis, TCR®, Spent coffee grounds, Catalytic reforming, Sustainable fuels

Introduction

Increase in the global energy demand and the greenhouse gases crisis is one of the most important topics nowadays. The fossil based oil is an important source of energy but it is one of the reasons for an increasing carbon concentration in the atmosphere. Therefore, it is necessary to develop other renewable sources and replace the traditional fuel sources. One of these sources is the biomass, which is considered as an indirect form of solar energy. The biomass can originate from various sources, such as botanical plants, vegetation, algae, animals and organisms living on land or in water. Biomass as an initial feedstock is able to supply energy in forms of syngas, liquid bio-oil and solid fuel (Cho et al. 2016; Rao and Parulekar 1997).

Coffee is one of the highest global consumer products; the consumption of coffee beans in 2018 was estimated to be around 10.5 million tons worldwide. The coffee beans processing produce 91% of waste in the form of spent coffee grounds (SCG), while the worldwide production of SCG in 2014 was predictable to be 8 million tons per year. The spent coffee grounds are the residual waste that remain after using the coffee beans through dehydration, milling and brewing. Around 50% of SCG worldwide are produced industrially, and the remaining 50% are generated domestically (Blinová et al. 2017; Cho et al. 2017; Karmee 2018; Kelkar et al. 2015; Kim et al. 2017; Li et al. 2014; Scully et al. 2016; United States Department of Agriculture 2018).

The spent coffee grounds are regularly moved to a landfill or combusted as solid fuel. These utilization ways can cause serious pollution due to the high oxygen consumption during the decomposition of the organic components and releasing of caffeine, tannin, and polyphenols into the atmosphere (Bok et al. 2012; Kim et al. 2017). The incineration or combustion of coffee waste is also challenging, because the emissions level are not within the European standard of emissions, as it produces a higher amounts of CO and NO_x (Galanakis 2017; Kang et al. 2017; Limousy et al. 2013). On the other hand, small parts of SCG are used as animal feed (Kelkar et al. 2015).

Furthermore, the spent coffee grounds have 2.1–3.9 wt% ash content, which categorizes it as 2nd and 3rd grade wood pellets. Due to the high generation of ash, the

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combustion of SCG is unstable compared to the combustion of wood pellets (Allesina et al. 2017; Kang et al. 2017).

Spent coffee grounds are valuable as biomass feedstock for bio-fuels and bio-refinery production (Li et al. 2014), due to the high organic compounds in it, such as fatty acids, lipid, cellulose, hemicellulose, lignin, carbohydrate, and nitrogen containing compounds (Cho et al. 2017; Karmee 2018). Consequently, there is a great interest in the conversion of spent coffee grounds through thermochemical processes into a syngas, bio-oil, biodiesel, or bioethanol, and char (Bok et al. 2012; Galanakis 2017; Karmee 2018; Tsai et al. 2012).

One of the treatment methods of spent coffee grounds into biogas is the anaerobic digestion. Several studies show that spent coffee grounds have a great potential for biogas production (Karmee 2018; Kim et al. 2017; Neves et al. 2006). A detailed study is carried out on anaerobic digestion of coffee residues mixed with activated sludge. The study reveals that the highest methane yield of 0.28 m^3 CH_4 per 1 kg of initial volatile solids is reached, and it achieves 75–89% methane production efficiency (Neves et al. 2006).

Furthermore, the gasification of spent coffee grounds through a thermochemical conversion system has been investigated in a narrow scope, and reported a gas yield of 70%, with a high heating value of 14.6 MJ/m^3 (Kan et al. 2014).

Chemical composition of the spent coffee grounds makes it possible to be directly used as solid fuel for energy and heat generation (Tsai et al. 2012). Therefore, different investigations are carried out on direct combustion of SCG. It is noted that the coffee residue has a high water content of more than 55%, which leads to a lower heating value of 8.4 MJ/kg; thus, it should be dried to around 15 wt% to enhance the lower heating value up to 18.8 MJ/kg. Spent coffee grounds as a solid fuel could be combusted 20% higher and longer than kiln-dried wood, and generate higher thermal power about 8.86 kW compared to the wood pellets with power of 8.02 kW. However, the direct combustion generates less emission by 80% than the landfill of SCG (Allesina et al. 2017; Bio-bean Co. 2018; Kang et al. 2017).

In addition, several studies are carried out for a biodiesel production from the bio-oil that is extracted from the SCG. While the studies show that the produced biodiesel can offer a 10–15% reduction in CO_2 emissions compared to the traditional diesel. As well a bio-hydrotreated biodiesel has successfully achieved the physical–chemical specification of commercial biodiesel (Bio-bean Co. 2018; Phimsen et al. 2016, 2017).

The pyrolysis as a thermochemical conversion technique is a promising technology and has a great potential as an alternative treatment process for biodegradable wastes. Pyrolysis provides a better conversion rate of feedstock into bio-oil, gas and solid fuel, with a high feed to bio-fuels efficiency, that could be developed worldwide as a bio-fuel and bio-chemical resource (Cho et al. 2017; Daschner et al. 2016; Hornung et al. 2011; Li et al. 2014; Tsai et al. 2012).

The conversion of spent coffee residue into valuable products through fast and slow pyrolysis has been reported in detailed in the literature. Both pyrolysis technologies have different operating parameters such as heating rates, reaction temperatures, and residence time, accordingly having different products distribution and various products' qualities (Hornung 2014).

The results from slow pyrolysis of spent coffee grounds show that increasing the heating rate or raising the pyrolysis temperature leads to a reduction in the char yield and the heating value of the char. The maximum char yield was in the range of (25–40 wt%) (Tsai et al. 2012), the gas yield (21–24 wt%), and the bio-oil yield (27.2–28 wt%) (Galanakis 2017). With slow pyrolysis, the calorific value of char could reach to 31.9 MJ/kg; it is relatively high as compared to the char from fast pyrolysis (29.1 MJ/kg) (Kelkar et al. 2015; Tsai et al. 2012).

The results from fast pyrolysis of coffee grounds into bio-oil show that the yield and characteristics of the products are highly dependent on the heating rate and the reaction temperature. Furthermore, increasing the residence time in the reactor promotes the cracking of bio-oil to gas and re-polymerization to char. The produced char from the fast pyrolysis is achieved a yield in the range of (16–20.6 wt%). Bio-oil yield is increased up to (54.8–65 wt%) with raising the temperature, and then is decreased again at a higher temperature of 600 °C to 51 wt% (Bok et al. 2012; Kelkar et al. 2015; Li et al. 2014).

The fast pyrolysis oil from SCG has high heating value HHV in range of 17.2–23 MJ/kg. On the contrary, The quality of the bio-oil is relatively low, with the water content to be between 20 and 32 wt%, nitrogen content is around 0.8–5.0 wt%, and high oxygen content of 35–59 wt% in the bio-oil (Bok et al. 2012; Kelkar et al. 2015; Li et al. 2014).

In addition, the non-condensable gas yield is increased to 12–20 wt% at the expense of both bio-oil and solid char at higher temperature that is an indication of the secondary cracking reactions of the bio-oil. It is noted that the pyrolysis gas compositions' yield is slightly increased by raising the reaction temperature, when the maximum yield of CO_2 is 13.11 wt%, CO 4.79 wt% and the yield of H_2 is very low <1 wt% (Bok et al. 2012), and HHV reaches up to 14.8 MJ/kg (Bok et al. 2012; Kelkar et al. 2015; Li et al. 2014).

To enhance the qualities of pyrolysis products, and reduce the acidity, the oxygen and water content in the bio-oil, catalytic pyrolysis of spent coffee grounds is recommended, which consequently leads to improvement of the non-condensable gases (Galanakis 2017; Li et al. 2014; Yu et al. 2018).

Catalytic pyrolysis of spent coffee grounds was intensively investigated, and the results show a promotion in thermal cracking, dehydrogenation, thermal decomposition of methane and the water–gas shifting reactions due to the addition of the catalyst. While, the catalyst causes significantly increasing in the hydrogen concentration and a reduction in the C_xH_y. From the mass balance point of view, the catalyst encourages the conversion and cracking of bio-oil into non-condensable gases, which leads to a reduction in bio-oil yield and increasing in non-condensable gases yield (Cho et al. 2017; Kan et al. 2014).

In general, the spent coffee grounds contain about 15 wt% of oil that can be extracted. Furthermore, pyrolysed bio-oil from coffee residue has a high amount of hydrophobic compounds such as fatty acids, fatty acid esters, medium-chain paraffins, olefins, and caffeine (Kelkar et al. 2015), giving it a great potential to be upgraded into biodiesel (Li et al. 2014). However, spent coffee grounds bio-oil has a HHV around 20–37 MJ/kg (Cho et al. 2016; Galanakis 2017). Nevertheless, the quality of bio-oil from coffee residue is still low because of its high oxygen and water content. In another references, the bio-oil contains very high oxygen ranging from (35–59%), water content of (20–37%), with low HHV below 20 MJ/kg (Bok et al. 2012; Kelkar et al. 2015; Li et al. 2014). Adding catalyst into the reaction increases the bio-oil qualities and thermally decomposes the linear hydrocarbons, furans compounds and the phenols compounds (Cho et al. 2017; Galanakis 2017).

The TCR® system as an intermediate pyrolysis combined with catalytic reforming was tested with different wastes like sewage sludge, woody biomass, agriculture residues or digestate. It is an applicable and effective technology to produce three main products (gas, bio-oil and char) with various distribution and various qualities. It was reported that increasing the catalytic reforming temperature enhances the gas yield and gas quality. Furthermore, it produces lower yield of bio-oil with high heating value, lower oxygen and water content, and low TAN number compared to other pyrolysis systems (Conti et al. 2017; Jäger et al. 2016a, b; Neumann et al. 2016a, b).

However, the applications of the biofuels from the traditional pyrolysis of SCG as an energy source are limited due to the drawback of bio-oil, such as high water and oxygen contents. In addition, the low qualities of the pyrolysis gas, low heating value and presence of tar are also derived (Galanakis 2017; Kan et al. 2014; Li et al. 2014). Moreover, the spent coffee grounds need to be dried before the fast pyrolysis up to 90–98% dry (Bok et al. 2012; Kan et al. 2014; Tsai et al. 2012).

Therefore, the aim of the present study is to investigate the possibility of the conversion of wet spent coffee grounds residue through the Thermo-Catalytic Reforming (TCR®) technology, and to characterize the product distribution and products quality obtained from different range of reforming temperatures by using a laboratory TCR® scale (2 kg/h plant).

Materials and methods

Thermo-Catalytic Reforming TCR® technology

The Thermo-Catalytic Reforming TCR® system is installed at Fraunhofer UMSICHT, Institute Branch Sulzbach-Rosenberg-Germany, as shown in Fig. 1. As illustrated in Fig. 2, the TCR® lab-scale plant is a batch system, containing a screw-conveyor reactor based on intermediate pyrolysis, which is capable of processing approximately 5 kg of biomass, with a maximum mass flow up to 2 kg/h. The auger speed motor controls the residence time of the solid biomass to be an average of 10 min. Three heating zones along the horizontal reactor maintain and control the temperatures between 400 and 500 °C, and a heating rate of 200 °C–300 °C/min (Ahmad et al. 2018; Conti et al. 2017; Elmously et al. 2019; Hornung et al. 2011; Hornung 2014; Jäger et al. 2016b; Neumann et al. 2016b).

The pyrolysis step is combined with an additional vertical post-reformer, while the post-reformer is the stage where the produced char acts as a catalyst at high temperatures in the range of 500 °C–700 °C. Due to the contact of the hot char with the pyrolysed gases, the reaction between carbon dioxide and the fixed carbon in the char is stimulated and improves the water–gas shifting reactions, and enhances the secondary cracking reactions of pyrolysis products. The post-reformer is electrically heated in two heating zones, and keeps the reforming temperature in the range of 500 °C to 700 °C. Leaving the post-reformer, the vapors pass through two series steps of shell and tube condensers that are controlled at -5 °C and 0 °C. The liquid phase is separated by gravity into an aqueous phase and a water phase. The non-condensable gases are driven through a washing unit, an active carbon filter, candle filter and then silica wool filter to eliminate the particles and to purify the non-condensable gases. The char is removed from the post-reformer at the end of each experiment (Ahmad et al. 2018; Conti et al. 2017; Elmously et al. 2019; Hornung et al. 2011; Hornung 2014; Jäger et al. 2016b; Neumann et al. 2016b).

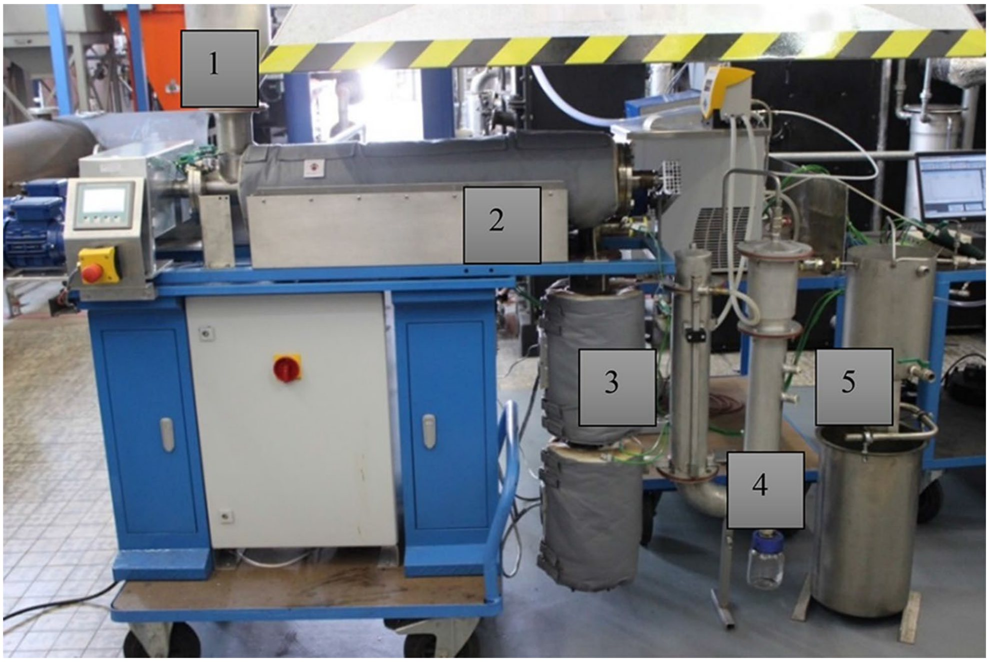

Fig. 1 TCR® 2 (lab scale)—maximum capacity 2 kg/h. (1) feed hopper, (2) reactor, (3) post-reformer, (4) gas cooler/condenser #1, (5) gas cooler/condenser #2

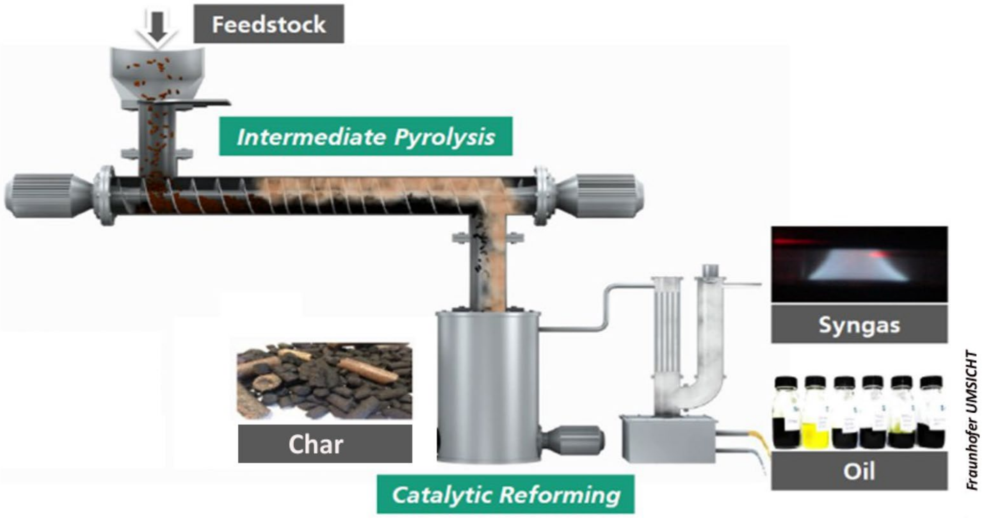

Fig. 2 Schematic principle of the TCR® process (Jäger et al. 2016b)

Compared to other technologies, the TCR® process provides a variety of higher-quality products. It converts the wet coffee residue into storable high-quality energy carriers, produces a clean gas fraction, with high H_2 and CO concentration, free of dust or tar, produces lower-molecular weight condensable organics, and char with high carbon content.

Analytical methods and measurements

A calibrated gas detector from Dr. Födisch Umweltmesstechnik AG (MGA 12) measures the produced gas.

The principle of the measurement is built on an infrared photometer (CO, CO_2, CH_4, and C_xH_y), an electrochemical cell (O_2), and a thermal conductivity detector (H_2). The heating value of the gas and the density measurement are carried out with an online gas-calorimeter CWD 2005 from Union Instruments GmbH (Ahmad et al. 2018; Elmously et al. 2019; Jäger et al. 2016b). The total volume of the non-condensable gases is calculated by difference (Feed − ($\Sigma_{char+condensate}$)) (Apfelbacher et al. 2016; Elmously et al. 2019; Jäger et al. 2016b).

Elemental analysis (CHNS) of feedstock and by-products (bio-oil, char, and water phase) is carried out on a dry basis, and then the oxygen content is calculated by difference (100 − ($\Sigma_{CHNS+ash}$)). The high heating value is measured by a combustion bomb calorimeter IKA C2000 series from IKA (Elmously et al. 2019; Jäger et al. 2016b).

Total acid number (TAN) in the bio-oil is determined by 916 Oil Ti-Touch (Metrohm AG). Besides, the water content in the bio-oil is determined by Karl Fischer titration using a 915 KF Ti-Touch titrator from Metrohm AG (Elmously et al. 2019; Jäger et al. 2016b).

The gas chromatography–mass spectrometry (GC/MS) analysis of the bio-oil is performed on a gas chromatograph coupled with a mass spectrometer Shimadzu GC/MS-QP2020. The carrier gas is Helium with 5.0 purity, and the injection volume is set to 1 µL. The bio-oil samples are diluted by 10 mg of Sample in 1 mL of methanol (MeOH), and with split 1:20.

Fig. 3 Feedstock spent coffee grounds pellets, scale in cm

Raw materials

The spent coffee ground as a raw material is a waste from the roast and ground coffee beans, which are supplied from JACOBS DOUWE EGBERTS GmbH. The spent coffee grounds are pelletized to improve its consistency, handling characteristics, increase the homogeneous of the process and reduce the dust formation. Final pellets have a diameter of 4 mm to 10 mm, length < 20 mm, and a moisture content in the range of 30–37 wt % with a fragile pellets structure, as shown in Fig. 3. However, 100% dry biomass is not applicable in this technology, as the water content in the feed has a big role in the reforming reactions; while at high temperature, there is a notable increase in the conversion of water (feed water + pyrolysis water) and CO to hydrogen. The dry basis ultimate analysis of the feedstock is reported in Table 1. It has to be noted that spent coffee grounds contain a relatively high amount of nitrogen due to a higher content of protein and caffeine. Compared to woody and agriculture biomass, the SCG residue contain low ash content 0.24 wt%; whereas in woody biomass, it is about 2–4 wt%. The SCG has slightly higher H/C ratio of 0.13 compared to woody biomass of 0.12, and lower O/C ratio of 0.69 in SCG (woody biomass is 0.82–1.0). In addition, SCG has a higher heating value of an average 22 MJ/kg, compared to the woody biomass with an average of 19 MJ/kg. (Campos-Vega et al. 2015; Jäger et al. 2016b; Kelkar et al. 2015; Tsai et al. 2012).

Results and discussion

Investigation of the spent coffee grounds as a sustainable biomass feedstock in the TCR® process is studied in terms of quality of the products, mass and energy balance. The data from the results are determined as average values from minimum of two consecutive trials at the same temperature gradient. Whereas, the pyrolysis temperature is 400 °C in the reactor and reforming temperature is varied between 500 °C, 600 °C and 700 °C in the post-reformer.

Table 1 Ultimate analysis of some properties on dry basis and some of physical properties of the tested SCG feedstock

Feedstock	Ultimate analysis (wt%)					H/C ratio	O/C ratio	HHV (MJ/kg)	Proximate analysis (wt%)	
	C	H	N	O (diff.)	S				Ash	H_2O
SCG	52.75	7.21	2.17	36.4	0.24	0.13	0.69	21.9–23.0	1.24	30–37

Table 2 Mass balance of products from SCG through TCR® system and other technologies

System	Heating rate (°C/min)	Char (wt%)	Gas (wt%)	Condensate[b] (wt%)	Bio-oil (wt%)	Aqueous phase (wt%)	References
TCR® at 500 °C	200–300	10.80	35.12	54.08	7.33	46.75	
TCR® at 600 °C		8.26	36.87	54.87	6.22	48.65	
TCR® at 700 °C		6.28	52.16	41.56	5.23	36.33	
Fast pyrolysis, 450 °C to 600 °C	40,000	29–17	13–20.2	57.3–46	–[a]	–[a]	Bok et al. (2012), Kelkar et al. (2015)
Slow pyrolysis	50	27	21	27.2	–[a]	–[a]	Galanakis (2017)
Catalytic pyrolysis, 500 °C to 700 °C	10	43.2–41.8	0.5–22	56.5–36.2	–[a]	–[a]	Cho et al. (2017)

[a] Data are not available

[b] Bio-oil + aqueous phase

Mass balance

The product yields from the utilization of spent coffee grounds in TCR® systems at different reforming temperatures are shown in Table 2.

In accordance with the previous studies with the TCR ® system, the gaseous product fraction is increasing by raising the post-reformer temperature. The amount of char and bio-oil tend to decrease. The higher temperature enhances the cracking of bio-oil and increases the water–gas shifting reactions between the gas and the char, which led to an increase in the gas yield from 32.5 to 52.2 wt%. Consequently, the char yield is reduced from 10.8 to 6.3 wt%. In the meantime, the bio-oil is significantly reduced from 7.3 to 5.2 wt%. It has to be considered that the yield of condensate is separated into two phases including bio-oil and aqueous phase. In general, the aqueous phase yield, as a separated water phase from the total condensate fraction, is highly dependent on the initial moisture content of the feedstock. Therefore, the total aqueous phase amount is high in the range of 36.3–48.6 wt%, because of the initial moisture content in the feedstock.

The mass balance distribution of products varies according to pyrolysis and reforming conditions. Moreover, the influence of temperature on the products yield in the three-pyrolysis categories (slow, intermediate, and fast) has similar trend. While it is observed in several studies that fast pyrolysis with high heating rate and significantly short residence time, produces the maximum liquid phase yield about 57.3 wt% and reduced to 46 wt% at higher temperature. On the other hand, the slow pyrolysis focuses on production of char with highest qualities and yield about 27 wt% at low heating rate and long residence time. The TCR® technology is based on an intermediate pyrolysis with an integrated catalytic reforming step. Therefore, it is in between the reaction conditions of slow and fast pyrolysis, whereas the products qualities are determined by the post-reformer temperature. This enables diverse product yields and qualities. Additionally, the TCR® system is distinctive by producing two separate liquid phases (organic and aqueous phase). Depending on the composition of the feedstock and the operating conditions, the product yields and composition are adjustable (Bok et al. 2012; Galanakis 2017; Hornung 2014; Kacprzak et al. 2017; Kelkar et al. 2015; Yang et al. 2014).

This is in line with Cho et al. who implemented a catalyst during the fast pyrolysis process to enhance the gas production yield from 0.5 to 22 wt%. Additionally, it resulted in a reduction in the total condensate yield to 36.2 wt%, due to the enhancement of the secondary cracking reactions (Cho et al. 2017).

It is obvious, that up to 52% of the product is an engine ready gaseous form, with the high quality and free of tar it could easily be used directly in engine. Although the bio-oil has low yield, it has high energy content and high quality which make it possible and economically for biofuel production.

Bio-oil characterization

The bio-oil characteristics from spent coffee grounds through TCR® system at different reforming temperatures and a comparison with fast pyrolysis are reported in Table 3. Raising the reforming temperature from 500 to 700 °C leads to an increase in the secondary cracking reaction of the bio-oil, whilst the high reforming temperature has a high positive impact on the bio-oil qualities in favor of the yield. A slight increase in the heating value is observed from 36 to 36.8 MJ/kg at temperature of 500 °C–700 °C, respectively. TCR® oil is in the top of the range of the average heating value that reported by fast pyrolysis bio-oil of 20–37 MJ/kg (Bok et al. 2012; Cho et al. 2016; Galanakis 2017).

Moreover, it is confirmed by (Ahmad et al. 2018; Conti et al. 2017; Neumann et al. 2016a) that the presence of

Table 3 Properties of TCR® bio-oil from spent coffee grounds through TCR® system and other technologies

System	Heating rate (°C/min)	Ultimate analysis (wt%)					HHV (MJ/kg)	H_2O (wt%)	TAN (mgKOH/g)	References
		C	H	N	O (diff.)	S				
TCR® at 500 °C	200–300	75.9	9.6	3.3	10.8	0.41	36.0	3.9	27	
TCR® at 600 °C	200–300	78.1	8.3	4.3	8.4	0.8	36.2	3.6	16	
TCR® at 700 °C	200–300	79.3	6.8	3.8	9.2	0.76	36.8	1.9	8.1	
Fast pyrolysis at 500 °C	60	28.9–44.9	6.5–12.0	0.8–5.0	42.0–59.5	0.07–0.12	17.2	10–15	pH 3.1	Kelkar et al. (2015), Li et al. (2014)
Fast pyrolysis at 450 °C	1000 k/s	54.3	7.4	3.0	35.3	0.0	23.1	23.9	pH 3.1	Bok et al. (2012)

a catalytic reforming step and higher reforming temperatures have a positive impact on the reduction of the oxygen and water content and the acidity of the bio-oil. Because of the enhancement of cracking reactions and the thermal decarboxylation of organic acids in the bio-oil by the catalyst. The oxygen content is reduced from 10.8 to 9.2 wt%. The TAN number is reduced from 27 to 8.1 mg·KOH/g, by increasing the reforming temperature from 500 to 700 °C, respectively.

Noticeably, the bio-oil phase is separated from the aqueous phase by gravity, due to the differences in density and polarity. With the gravitational separation, a low water content of the bio-oil of 3.9 wt% at 500 °C could be achieved and reduced to 1.9% at higher reforming temperature of 700 °C. As mentioned earlier, the coffee residues have higher contents of nitrogen containing compounds, which leads to increase the nitrogen content in the bio-oil. In comparison to TCR®-bio-oils from different feedstock, the nitrogen content is significantly higher in SGC-bio-oil of 3.3–4.8 wt% in comparison to 2.5 wt% in bio-oil from woody biomass. However, a previous study at Fraunhofer UMSICHT succeeded in reducing the nitrogen content in the produced TCR ® bio-oil from digestate by hydrodeoxygenation (HDO), from 4.6 to <0.1 wt% (Jäger et al. 2016b; Neumann et al. 2016b).

On the other hand, due to the high concentration of phenols compounds, the bio-oil has high potential for chemicals production. While, the phenols could be recovered from the bio-oil and used in the production of plastics, explosives such as picric acid, and drugs such as aspirin, and in the dye industry (Shah et al. 2017; Zhang et al. 2018).

Compared to the fast pyrolysis, the bio-oil quality is significantly lower than TCR®-bio-oil. As shown in Table 3, fast pyrolysis bio-oils have a higher oxygen content of 35–59 wt% and water content 10–23 wt%. Besides, the low carbon content with maximum 54.3 wt%, with HHV up to 23.1 MJ/kg. Contrary to the TCR®-bio-oil, the fast pyrolysis oils have lower nitrogen and sulfur yields; this is related to the variation of the feedstock composition (Bok et al. 2012; Kelkar et al. 2015; Li et al. 2014).

The influence of the post-reformer on the improvement of the bio-oil is illustrated by the absolute intensity of the main chemical compounds obtained from the gas chromatography–mass spectrometry (GC–MS) analysis in Fig. 4. The 25 highest concentrated components are listed in Additional file 1: Table S1, while the small peaks and unidentifiable peaks are neglected.

It is notable that raising the reforming temperature from 500 to 700 °C has a great impact on the reduction of the acids and oxygenated compounds. In addition to,

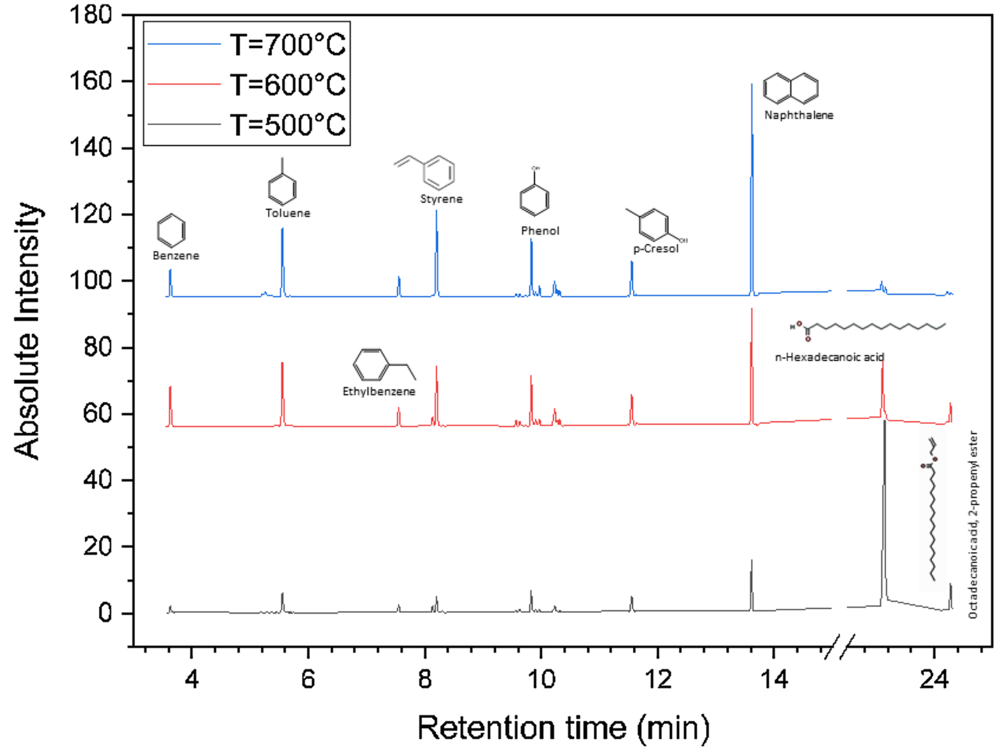

Fig. 4 GC–MS analysis of the bio-oil from SCG at reforming temperature of 500 °C, 600 °C and 700 °C

there is a remarkably cracking of the caffeine compounds in the bio-oil, due to the catalytic reforming and the secondary cracking reactions. Comparing to the fast pyrolysis where there is an apparent detection of caffeine in the bio-oil (Bok et al. 2012; Cho et al. 2016; Kelkar et al. 2015).

Gas composition and characterization

The influence of catalytic reforming temperature on the gas composition is represented in Table 5. As shown from the results, raising the reforming temperature increases the volumetric content of hydrogen in the gas composition, and reduces the concentration of carbon dioxides. Consequently, increasing the temperature enhances the steam reforming and secondary cracking reactions.

As shown in Table 4, due to the contact of the gases with the hot TCR® char in the post-reformer, the reaction between carbon dioxide and the carbon in the hot char is stimulated, which leads to a formation of carbon monoxides. By the water–gas shifting reaction, the CO and water vapor can be further transformed into CO_2 and H_2. Furthermore, the higher reforming temperature increases the de-carbonization and decarboxylation of the oxygenated compounds in the products, which leads to the production of more CO and CO_2.

Such reactions and equilibriums are sensitive to the temperature, while the reaction rate is increasing at higher temperature, and the conversion of reactants to products is reduced, and the tendency of reverse reaction is raised (Castro-Dominguez et al. 2016; LeValley et al. 2014; Xie et al. 2013). This explains the observed reduction of CO from 15.2 vol% at 500 °C to 11.6 vol% at 600 °C; then it is increased again to 12.1 vol% at higher temperature of 700 °C. On the other hand, the CO_2 content kept reducing from 31.1 to 22.6 vol% with increasing temperatures from 500 to 700 °C, respectively. These results are in line with the results reported by Neumann et al. (2016a).

Table 4 Post-reforming reactions (Neumann et al. 2016a)

Reaction	Enthalpy (kJ/mol)
$CO_2 + C \rightleftharpoons 2CO$	+172
$C + H_2O \rightleftharpoons CO + H_2$	+131
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	+206
$CO + H_2O \rightleftharpoons CO_2 + H_2$	−41.2
$C + 2H_2 \rightleftharpoons CH_4$	−74.8

The significant increase in the H_2 content by 29.5% from reforming temperature 500 °C to 700 °C is as a result of water–gas shifting and the methane reforming reactions. The decomposition of methoxy and methylene groups and the cracking of the oxygenated compounds in the bio-oil produce the methane or hydrocarbon compounds in general, and reduce the density of the gas from 1.2 kg/m^3 at 500 °C to 0.97 kg/m^3 at 700 °C in combination with the increased hydrogen content. Hence, the methane reacts with steam and produces hydrogen and carbon monoxide as shown in Table 5 (Kan et al. 2014; Xie et al. 2013). The HHV is slightly decreasing with increasing reforming temperatures from 23.1 to 20.6 MJ/m^3, because of the reduction in the CO and C_xH_y content and the increase of the hydrogen content in the gas. However, at all temperature ranges, the heating value of the TCR® gas is still higher than other technologies for syngas production from spent coffee grounds (Li et al. 2014).

It is highlighted by Cho et al. 2016 that adding a catalyst during the fast pyrolysis has a great influence on thermal degradation of the bio-oil and converting it into gaseous phase. Nonetheless, the hydrogen and carbon monoxide are significantly lower than those produced by the TCR® unit (Cho et al. 2016, 2017).

Compared with anaerobic digestion of SCG for biogas production, Luz et al. 2017 studied the conversion of spent coffee grounds into gas through anaerobic

Table 5 Properties and gas composition from spent coffee grounds through TCR® system and other technologies

System	Gas composition (vol%)					Density (kg/m^3)	HHV (MJ/m^3)	LHV (MJ/kg)	References
	H_2	CO	CO_2	CH_4	C_xH_y				
TCR® at 500 °C	24.3	15.2	31.1	0.0[b]	4.9	1.24	23.1	17.5	
TCR® at 600 °C	34.2	11.6	24.2	0.04[b]	4.8	1.06	22.6	19.2	
TCR® at 700 °C	38.7	12.1	22.6	0.23[b]	3.7	0.97	20.6	19.1	
Catalytic pyrolysis at 500 °C to 700 °C	0.5–2.2	4.5–7.0	–[a]	0.2–0.7	–[a]	–[a]	–[a]	–[a]	Cho et al. (2016, 2017)
Anaerobic digestion	–[a]	–[a]	30–40	50–59	–[a]	–[a]	–[a]	28.66	Luz et al. (2017)

[a] Data are not available

[b] The high content of hydrocarbons in the gases influences the detection of the other gases, especially methane caused by a crosswise relation between these compounds

Table 6 Ultimate analysis and physical properties of the char from SCG through TCR® and other technologies

System	Ultimate analysis (wt%)					H/C ratio	HHV (MJ/kg)	Ash (wt%)	References
	C	H	N	O (diff.)	S				
TCR® at 500 °C	78.6	2.4	3.8	6.3	0.12	0.03	30.8	8.6	
TCR® at 600 °C	80.0	1.2	3.0	2.1	0.20	0.015	29.5	12.8	
TCR® at 700 °C	70.6	1.4	1.8	2.6	0.38	0.019	25.5	23.2	
Slow pyrolysis	80.0	3.0	5.0	12.0	–	0.037	31.9	23.0	Tsai et al. (2012)
Fast pyrolysis at 500 °C	75.3	3.5	4.4	11.1	0.12	0.046	29.1[a]	5.5	Kelkar et al. (2015)

[a] Calculated value

Fig. 5 The produced char from spent coffee grounds, scale in cm

digestion with animal manure. The produced gas composition was measured as shown in Table 5. The majority of the gas is methane by maximum yield of 59 vol% and carbon dioxide by 40 vol%. The low heating value LHV of 28.9 MJ/kg is higher than TCR® gas (Luz et al. 2017).

The TCR® gas balance is not closed as shown in Table 5, due to a limitation of the gas analyser. The high content of hydrocarbons influences the detection of the other gases, especially methane caused by a crosswise relation between these compounds; the missing gas composition percentage could be nitrogen, methane or hydrogen.

Char characterization

The chemical characteristics of the TCR® char and slow pyrolysis char are presented in Table 6. The char is produced in powder form caused by mechanical abrasion in the reactor and the thermal degradation, as shown in Fig. 5. The carbon content of the TCR® char at the two reforming temperatures 500 °C and 600 °C is similar (78.6–80 wt%). It is reduced significantly to 70.6 wt% at the higher reforming temperature of 700 °C. This can be explained by the increasing of the cracking reactions of the products at high temperature of 700 °C.

Table 7 Energy balance of products from spent coffee grounds through TCR® system

System	Energy balance (%)		
	Char	Gas	Bio-oil
TCR® at 500 °C	25.8	52.3	18.5
TCR® at 600 °C	18.9	55.7	16.4
TCR® at 700 °C	11.4	72.8	14.0

Raising the reforming temperature enhances the steam reforming and water–gas shifting reactions, which causes a reduction in the high heating value of the char along with the temperature from 30.8 to 15.4 MJ/kg on a dry basis. In addition, it shows a rise in the ash content with increasing the reforming temperature. Furthermore, the improvement in the heating value compared to the initial feedstock shows a potential for consumption of the char as a solid fuel. It is noticeable that the nitrogen content in the char is relatively high (3.8–1.8 wt%); this is in line with the high initial nitrogen content in the feedstock. While, this could cause an increase in the production of nitrogen oxides (NO_x) in the emissions during the char combustion (Tsai et al. 2012).

Compared to the slow and fast pyrolysis, the produced char from TCR® technology is inferior, due to the catalytic reforming reactions between the char and the condensable and non-condensable gas. The TCR® char has less oxygen content and less H/C ratio. The low H/C ratio gives the TCR® char the stability to be used for a carbon storage in soil (Kelkar et al. 2015; Yu et al. 2018). An alternative utilization of the char could be, for example, as an adsorbent material for filtering system (Kelkar et al. 2015).

Energy balance

Table 7 presents the energy balance of the products at different temperatures. The balance is calculated using the mass balance, water content and the LHV values of the feedstock and each product feedstock. Increasing the reforming temperature improves the energy content of the gaseous fraction from 52.3 to 72.8%. Additionally, a reduction of the energy content of the char to 11.4% and the bio-oil to 14% at reforming temperature of 700 °C is observed. In general, about 90% of the energy content in the feedstock is transferred to the products and mainly to the gaseous phase by 70% of the total energy. However, it is noticed from the results that the products at 700 °C have high energy content about 98%, due to increasing in the endothermic reactions in the post-reformer.

Conclusion

The pyrolysis of spent coffee grounds is investigated by the Thermo-Catalytic Reforming technology. The results show that the TCR® system delivers a better products distribution and better bio-fuels properties compared to typical fast pyrolysis of SCG, which creates an opportunity for bioenergy production. Because of the additional values in the products, spent coffee grounds conversion by TCR® offers a valuable utilization pathway instead of the state of the art technologies like landfilling or incineration and other conversion technologies. More combustible gases with high hydrogen content are obtained from conversion of SCGs in the TCR® system. Moreover, the obtained bio-oil has a high HHV of 36.8 MJ/kg, low oxygen and low water content, and lower corrosive properties compared to the fast pyrolysis bio-oil. Likewise, the produced char with less oxygen and less H/C ratio can be utilized in various utilization pathways such as gasification, adsorption, and soil enrichment. In the summary, the main differences between the TCR® system and the typical pyrolysis systems is the combination of the intermediate pyrolysis and post-reforming reactions, while it gives the advantages of production of higher-quality products.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s40643-019-0281-5.

Additional file 1. A summary of gas chromatography–mass spectrometry (GC–MS) analysis of the bio-oils from TCR® system at different reforming temperature are represented in Table S1, it shows only the highest 25 concentrated components obtained from the analysis, while the small peaks and unidentifiable peaks are neglected.

Abbreviations

TCR®: Thermo-Catalytic Reforming®; SCG: spent coffee grounds; NiCu/γ-Al_2O_3: nickel copper/gamma-aluminum oxide; TAN: total acid number; GC–MS: gas chromatography–mass spectrometry; HDN: hydro-denitrification; HHV: high heating value; LHV: low heating value.

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Authors' contributions

ME performed the experiments and the analyzing of the products. NJ and AA contributed in analyzing the results and writing the manuscript. RD and AH contributed to the assessment of the results and conclusion. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets generated and/or analyzed during the current study are not publicly available due confidentiality of the research but are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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