



A state-of-the-art review on spent coffee ground (SCG) pyrolysis for future biorefinery

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HIGHLIGHTS

- Spent coffee ground is a promising organic waste for biochar & bio-oil production.
- Fast pyrolysis is the best technique to obtain optimum yield of bio-oil.
- The maximum bio-oil yield has been reported at 500 °C.
- Bio-oil contains a considerable amount of hydrocarbons and phenol.
- Therefore, it can be used either as a fuel or pesticide.

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ABSTRACT

Coffee is a globally consumed beverage that produces a substantial amount of valuable organic waste known as spent coffee grounds (SCG). Although SCG is a non-edible biomass, research initiatives focused on valorizing/ utilizing its organic content, protecting the environment, and reducing the high oxygen demand required for its natural degradation. The integration with biorefinery in general and with pyrolysis process in specific is considered the most successful solid waste management strategy of SCG that produce energy and high-value products. This paper aims at providing a quantitative analysis and discussion of research work done over the last 20 years on SCG as a feedstock in the circular bioeconomy (CBE). Management strategies of SCG have been thoroughly reviewed and pyrolysis process has been explored as a novel technology in CBE. Results revealed that explored articles belong to Chemical, physical, biological and environmental science branches, with Energy & Fuels as the most reporting themes. Published works correlate SCG to renewable energy, biofuel, and bio-oil, with pyrolysis as a potential valorization approach. Literature review showed that only one study focused on the pyrolysis of defatted spent coffee grounds (DSCG). The insightful conclusions of this paper could assist in proposing several paths to more economically valorization of SCG through biorefinery, where extracted oil can be converted to biofuels or value-added goods. It was highlighted the importance of focusing on the coupling of SCG with CBE as solid waste management strategy.

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1. Introduction

Coffee is a refreshing drink processed via heated coffee beans (*Coffea arabica* or *Coffea robusta*) (Bedmutha et al., 2011). It is an agricultural product utilized extensively around the world in everyday life. In 2019–2020, Global coffee production hit 169.34 million bags of 60 kg, and the consumption was estimated at 168.39 million bags. As a result,

environmentally sustainable alternatives to sustain its systematic conversion into one or the other products is recommended worldwide.

One of the proposed treatments and reuse of the SCG is through what is called as circular bioeconomy (CBE). The CBE system has gained increasing attention during the last 10 years, and it was proposed to replace the non-sustainable linear system that involves ‘extract-produce-use-dispose’. The European Union (EU) anticipated that economic

Nomenclature

CBE	Circular bioeconomy
CCCRD	Central composite rotatable design
CO	Carbon monoxide
CO ₂	Carbon dioxide
CPB	Colorado Potato Beetle
CS	Corn stalk
DSCG	Defatted spent coffee grounds
FT-IR	Fourier transform infrared spectroscopy
GC/MS	Gas chromatography–mass spectrometry
HHV	Higher heating value

EU	European Union
NO _x	Nitrogen oxides
O ₂	Oxygen
PF	Paper filter
RSM	Response surface methodology
SCG	Spent coffee grounds
TAN	Total acid number
TCR®	Thermo-catalytic reforming system
TGA	Thermogravimetric analysis
WP	White pine
WoS	Web of Science

there was an estimated surplus of 952,000 bags (International Coffee Organization, 2020). The general consumption trends indicate that the global coffee consumption is increasing continuously. For example, the annual global coffee production in 2018–2019 was increased by 83.35 %, 50 %, and 20 %, compared to the annual production in 1990–1991, 2000–2001, and 2010–2011, respectively (International Coffee Organization, 2020).

The industry associated with this global drink generates a large amount of valuable organic globally, known as spent coffee grounds (SCG), which is generally wasted. The SCG contains valuable organic materials such as polysaccharides, tannins, lipids, amino acids, minerals, aliphatic acids, polyphenols, proteins, alkaloids, oligosaccharides, melanoidines, trigonelline and phenolics, lignin, and volatile compounds. The direct disposal of SCG having such rich organic components in landfills creates ecotoxicological concerns and many environmental problems. Historically, SCG was either incinerated as a solid fuel or moved to a landfill ignoring its valuable organic content. Incineration of SCG has been reported to cause environmental issues due to the excessive emissions of carbon monoxide (CO) and nitrogen oxides (NO_x). This could increase air pollution and speed-up the global warming. On the other hand, the elevated oxygen supply is required to decompose SCG to releases caffeine, tannins, and polyphenols into the atmosphere. Additionally, landfilling requires large areas with a potential pollution risk and groundwater contamination.

Some previous studies proposed alternative uses of the SCG as compost, deodorizer, or animal feed (Bok et al., 2012; Elmously et al., 2019; Kelkar et al., 2015; Matrapazi and Zabaniotou, 2020; Primaz et al., 2018). All previous waste management strategies focused on the disposal or reuse of the SCG, ignoring its valuable organic matter content. Recently, more scientific works focused on developing appropriate processing technology to take advantage of the valuable content of SCG. The high organic content of this solid waste can have a promising pathway to use in the production of various biofuels (biodiesel, biogas, bio-oil, bio-ethanol, fuel pellets, and bio-hydrogen) and value-added products (bio-plastics, bio-polymers, antioxidants, etc.) (Atabani et al., 2019a, 2019b). Its potential for valorization led to establishing a roadmap for the coffee-based integrated biorefinery (Ktori et al., 2018). This concept is based on valorizing the SCG as low-cost, non-edible biomass and source of energy. This approach would also protect the environment by reducing the disposed amount of SCG that is toxic and require a large amount of oxygen during natural degradation. Therefore, careful management of SCG using economically viable technologies and

benefits due to the shift to CBE could reach up to six hundred billion Euros (Matrapazi and Zabaniotou, 2020). In the transition to a sustainable CBE, pyrolysis-based biorefinery is finding a new impetus within this concept. The pyrolysis technologies prevent the generation of secondary pollutants while ensure establishing this SBE. The pyrolysis of SCG has enormous potential to produce a wide variety of products and supplement renewable energy sources. The emissions of harmful gases during SCG pyrolysis would be relatively low, and the scale-up plants are more simple, convenient, and portable, which allows them to move from one site to another.

Thus, this critical review aspires to shine a light on the pyrolysis opportunities and the potential of using SCG and defatted spent coffee grounds (DSCG) to produce added-value products and bio energy resources. This review is the first work on such topic, and to the best of the authors' knowledge, no previous work has highlighted this aspect.

As a result of this review, it is believed that the scientific community will be more aware of the bio-oil potential of SCG as one of the promising options in this industry. This will lead to developing and integrating the SCG biorefinery concept in which various products will be produced. This review will highlight the importance of SCG pyrolysis and thus helps in promoting the CBE concept in many countries.

2. Bibliometric analysis

Bibliometric analysis is utilized as a tool for collecting scientific publications by specifying the research field to examine the relationship of potential key areas in the research domain and provide emerging trends. This quantitative analysis was conducted using the Web of Science (WoS) database over the last 20 years. The important indicators of this analysis include the distribution of WoS meta-disciplines, a timeline database of the total number of publications over the last 20 years, bump graph to show a temporal evaluation of WoS subject categories and keywords for SCG pyrolysis, as well as top contributors. Quantitative analysis of the literature was carried out using WoS catalog on October 01, 2020. 721 documents were retrieved from WoS where spent coffee grounds (SCG) was mentioned as a topic.

2.1. Topic structure

The distribution of the documents among different subject areas is shown in Fig. 1 (a).

The spread map of WoS was categorized into five meta-clusters

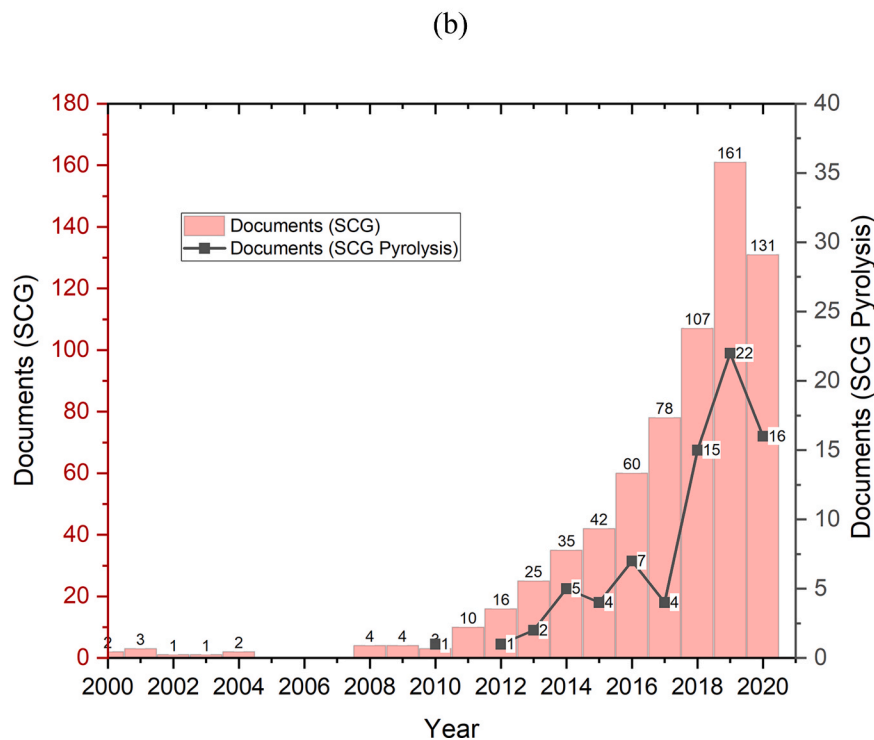
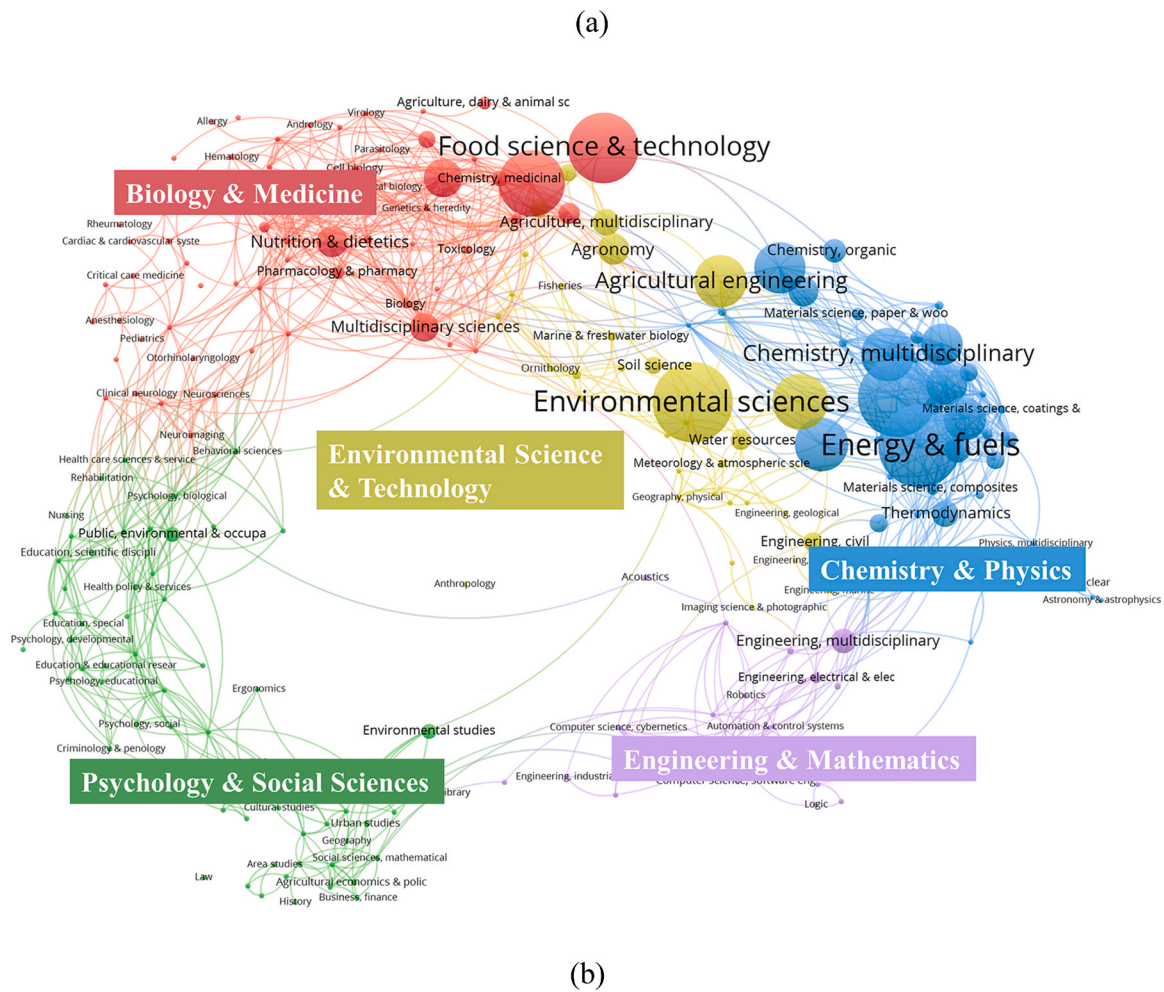


Fig. 1. (a) Distribution of Web of Science (WoS) meta-disciplines for spent coffee ground (SCG), and (b) historical evolution of WoS documents on “SCG” and “SCG pyrolysis”.

indicating that SCG was mostly explored in *Chemistry & Physics*, *Environmental Science & Technology*, and *Biology & Medicine*.

Only 80 studies were found where “SCG pyrolysis” was mentioned in the topic. The first study on the pyrolysis of SCG was published in 2010. The evolution of publications over the last two decades can be seen in Fig. 1 (b).

The temporal evolution of WoS subject categories for SCG pyrolysis is shown in Fig. 2 (a). *Energy & Fuels* was the most occurring WoS subject category. The temporal evolution of keywords is shown in Fig. 2 (b). Pyrolysis, SCG, and biochar were the three most frequently used

keywords.

2.2. Top cited articles on SCG pyrolysis

The top ten most cited articles on SCG pyrolysis process are shown in Table 1. The article entitled “Complete Utilization of Spent Coffee Grounds To Produce Biodiesel, Bio-Oil, and Biochar” by (Vardon et al., 2013) was the most cited document on SCG pyrolysis. Only two articles received more than 100 citations, whereas three others received more than 50 citations.

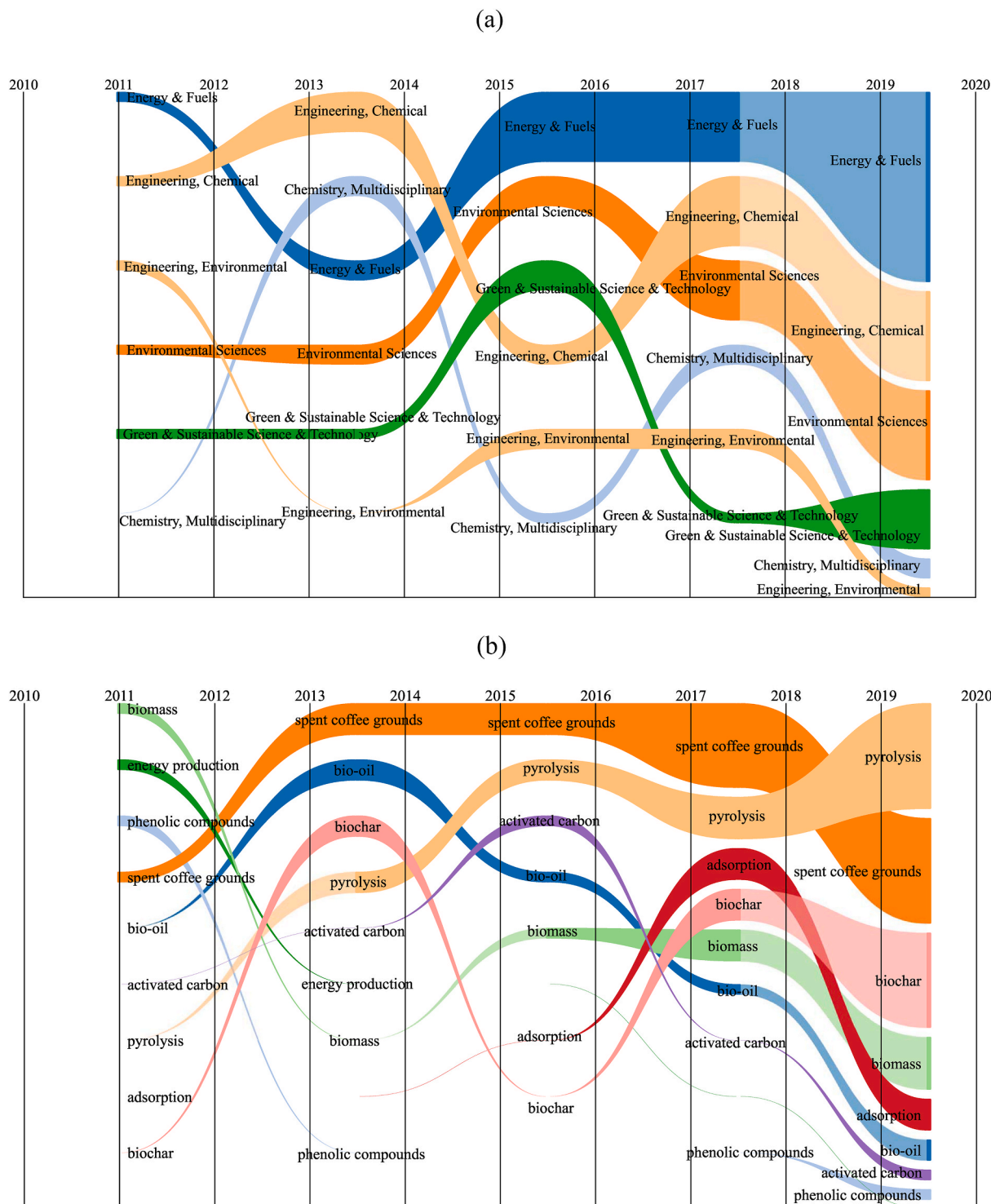


Fig. 2. Temporal evolution of (a) Web of Science subject category and (b) keywords for SCG pyrolysis.

Table 1
Top ten most cited articles on SCG pyrolysis.

Rank	Title	First Author	Source	Year	Citations	Ref
1	Complete utilization of SCG to produce biodiesel, bio-oil, and biochar	Vardon, Derek R.	ACS Sustainable Chemistry & Engineering	2013	118	(Vardon et al., 2013)
2	SCG as a valuable source of phenolic compounds and bioenergy	Zuosro, Antonio	Journal Of Cleaner Production	2012	115	Zuosro and Lavecchia (2012)
3	Gaseous products and particulate matter emissions of biomass residential boiler fired with SCG pellets	Limousy, L. et al.	Fuel	2013	76	Limousy et al. (2013)
4	Energy recovery potential analysis of SCG pyrolysis products	Li, Xiaofeng	Journal Of Analytical And Applied Pyrolysis	2014	54	Li et al. (2014)
5	Carbon dioxide assisted sustainability enhancement of pyrolysis of waste biomass: A case study with SCG	Cho, Dong-Wan	Bioresource Technology	2015	51	Cho et al. (2015)
6	The effectiveness of spent coffee grounds and its biochar on the amelioration of heavy metals-contaminated water and soil using chemical and biological assessments	Kim, Min-Suk	Journal Of Environmental Management	2014	48	Kim et al. (2014)
7	Hydrothermal liquefaction of SCG in water medium for bio-oil production	Yang, Linxi	Biomass & Bioenergy	2016	47	Yang et al. (2016)
8	Bio-syngas production from agro-industrial biomass residues by steam gasification	Pacioni, Tatiana Ramos	Waste Management	2016	42	Pacioni et al. (2016)
9	Spent coffee enhanced biomethane potential via an integrated hydrothermal carbonization-anaerobic digestion process	Luz, Fabio Codignole	Bioresource Technology	2018	41	Luz et al. (2018b)
10	Insights into the thermolytic transformation of lignocellulosic biomass waste to redox-active carbocatalyst: Durability of surface active sites	Oh, Wen-Da	Applied Catalysis B-Environmental	2018	40	Oh et al. (2018)

2.3. Most productive authors and institutions on SCG pyrolysis

A list of ten most productive authors and their contributions in terms of citations is shown in Table 2. Eilhann E. Kwon from Sejong University topped the list with the highest number of articles, citations, and h-index. However, the works of Mejdi Jeguirim and Lionel Limousy from the Université de Haute-Alsace on SCG pyrolysis received the highest citation count per unit publication.

The Sejong University of South Korea is the most productive institution with the highest h-index. The Dalhousie University of Canada is ranked first based on the number of citations per publication.

2.4. Journals and countries

Table 3 lists the top ten most contributing journals based on the number of articles, citations per document, and h-index. Fuel (ISBN: 0016–2361) and Bioresource Technology (ISBN: 0960–8524) are the top two journals covering the content related to SCG pyrolysis. However, two articles published in Fuel Processing Technology (ISBN: 0378–3820) received the highest citations per article. The contingency matrix of the journals and countries with keywords is shown in Fig. 3.

From Fig. 3 (a), the strongest pairing of keywords with journals appears for “carbon dioxide” and “Energy Conversion and Management”. Additionally, worth mentioning pairs are “SCG” & “Renewable Energy”, “Adsorption” & “Science of the total environment”, and “bio-oil” & “Fuel Processing Technology.” Among the distinguishable pairing of countries with keywords appear from Fig. 3 (b), for Greece as a circular economy and Brazil with bio-oil.

Table 2
Ten most contributing authors for their work on SCG pyrolysis.

Rank	Authors	Affiliation	Publications (P)	Citations (C)	C/P	h-index	Rank C/P	Rank h-index
1	Eilhann E. Kwon	Sejong University	11	196	17.82	7	6	1
2	Dong-Wan Cho	Korea Institute of Geoscience & Mineral Resources	6	125	20.83	6	3	2
3	Hocheol Song	Sejong University	6	125	20.83	6	3	2
4	Mejdi Jeguirim	Universite de Haute-Alsace	4	130	32.50	4	1	4
5	Lionel Limousy	Universite de Haute-Alsace	4	130	32.50	4	1	4
6	A. E. Atabani	Erciyes University	3	38	12.67	2	8	8
7	Elina B. Caramao	Universidade Federal do Rio Grande do Sul	3	16	5.33	2	10	8
8	Gopalakrishnan Kumar	Yonsei University	3	38	12.67	2	8	8
9	Joonhak Lee	Korea Institute of Geoscience & Mineral Resources	3	54	18.00	3	5	6
10	Yong Sik Ok	Korea University	3	52	17.33	3	7	6

3. An overview of pyrolysis, pyrolysis process types, and its applications

The energy density of organic substances, biomass, or agro-industrial waste can be enhanced through bio-chemical (anaerobic digestion and fermentation) or thermo-chemical (pyrolysis, gasification, and liquefaction) processes (Abbas et al., 2020; Hameed et al., 2021; Inayat et al., 2020a, 2020b, 2020b; Luz et al., 2018a). Thermo-chemical processes are swift and proficient methods where varied and different feedstocks are converted into unique chemicals and valuable fuels from composite structural matrices of organic biomass. Additionally, they are renowned as being apposite for mass manufacturing (Cho et al., 2016; Khan et al., 2019). Pyrolysis is considered among the majority of developed and capable thermo-chemical alteration techniques applied to accomplish the thermal decomposition of organic substances (Li et al., 2014). Disintegration occurs because of the inadequate thermal firmness between the bonds of the compounds resulting in the creation of smaller compounds (Matrapazi and Zabaniotou, 2020). The pyrolysis process is performed in limited or no oxygen atmospheres under inert conditions (nitrogen as the inert gas) and at very elevated temperature ranges 500–1000 °C to convert the organic matter into three valuable products, namely; liquid bio-oil (pyrolytic liquid), solid biochar (charcoal), and combustible gas (non-condensable gases/syngas) (Aslam et al., 2020; Bedmutha et al., 2011; Kim et al., 2019; Luz et al., 2018a; Primaz et al., 2018; Zanella et al., 2013). The product bio-oil is normally dark-colored with a typical aroma and is deemed as a blend of diverse complex organic molecules. Almost three hundred or more compounds have already been acknowledged in their chemical make-up, such as carboxylic acids, hydrocarbons, aldehydes, alcohols, phenols, esters,

Table 3
Top ten most productive institutions.

Rank	Affiliation	Publications (P)	Citations (C)	C/P	h-index	Rank	Rank
						C/P	h-index
1	Sejong University	11	196	17.82	7	5	1
2	The Hong Kong Polytechnic University	4	77	19.25	4	4	2
3	Aristotle University of Thessaloniki	3	27	9.00	2	9	4
4	Korea University	3	77	25.67	3	2	3
5	University of Stavanger	3	38	12.67	2	7	4
6	Chonbuk National University	2	40	20.00	2	3	4
7	Centre National de la Recherche Scientifique	2	26	13.00	2	6	4
8	Dalhousie University	2	63	31.50	2	1	4
9	Erciyes University	2	20	10.00	1	8	9
10	Khon Kaen University	2	15	7.50	1	10	9

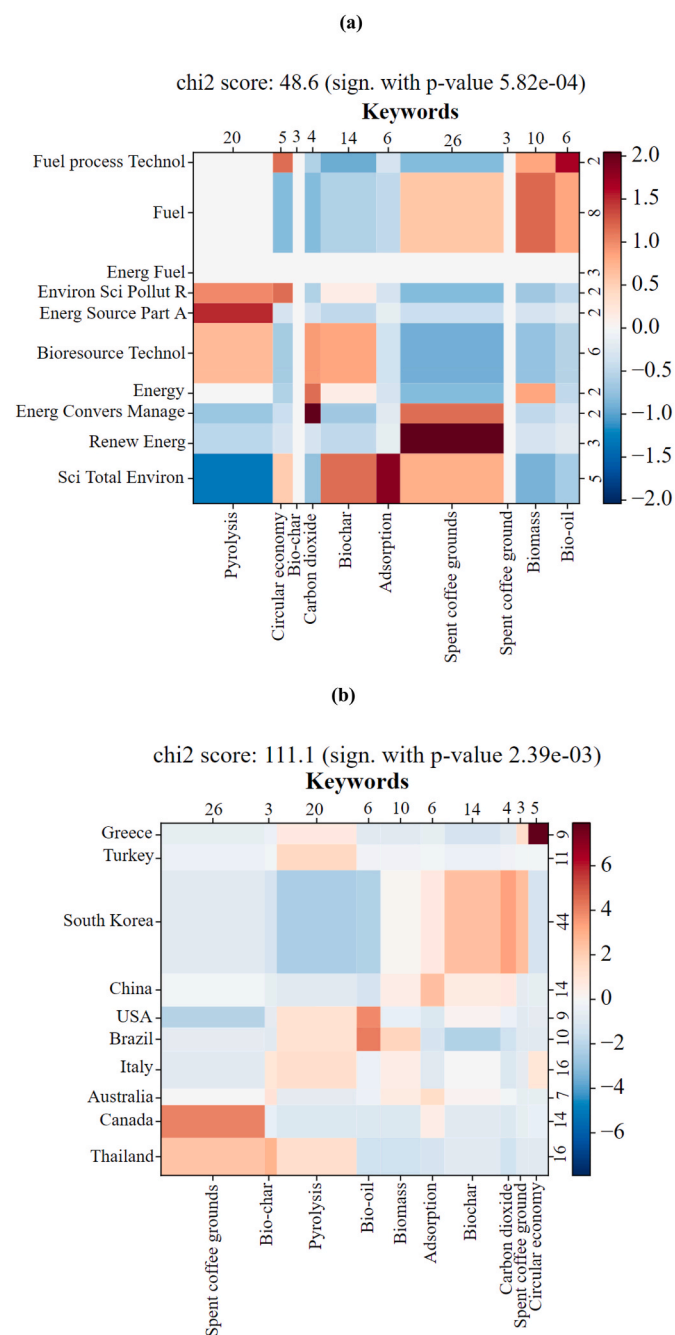


Fig. 3. Contingency matrix of (a) journals, and (b) countries with keywords.

furans, aromatic, ketones, and N-molecules (Krause et al., 2019; Matrapazi and Zabaniotou, 2020; Primaz et al., 2018). It can be utilized for many purposes such as fuel for burners, gas turbines, furnaces & for engines running on diesel (Bok et al., 2012; Krause et al., 2019), chemicals (Krause et al., 2019), as a natural pesticide (Bedmutha et al., 2011) and for the production of polymers and in the pharmaceutical and agrochemical industries (Krause et al., 2019). Moreover, this bio-oil can be enhanced to produce a fuel with superior value making it fitting for engines (Li et al., 2014). Biochar, on the other hand, can be utilized as an energy resource, for carbon storage, as an adsorbent, for soil up-gradation (due to its high surface area), for carbon sequestration, and also as a material for green roofing as it has high heat insulation properties (Ahmed et al., 2020; Kelkar et al., 2015; Ktori et al., 2018; Li et al., 2014; Matrapazi and Zabaniotou, 2020; Vardon et al., 2013). Syngas can also be used as a combustible fuel (Li et al., 2014). The proportions and yield of bio-oil, biochar, & syngas are based on the sort of pyrolysis method, reaction parameters, and heating rate (slow or fast pyrolysis) (Li et al., 2014; Luz et al., 2018a). (Matrapazi and Zabaniotou, 2020) depicted the cause of temperature on the overall pyrolysis yield (bio-char, bio-oil and gases). The total amount of bio-oil and gas increases with increase in temperature, while the overall total yield of biochar decreases with increasing temperature.

Pyrolysis can be divided into three main processes known as slow (conventional) pyrolysis, fast pyrolysis, and the latest called as flash pyrolysis that vary based on the procedural conditions. Their product compositions are affected by the operating environment. Slow or conventional pyrolysis comprises a decomposition course that generates maximum biochar yield with a moderate amount of tar (by-product) at low heating and temperature rates while the residence time is much longer. Slow pyrolysis typically occurs between 400 and 600 °C, with an average heating rate range between 0.1 and 1 °C/s. Slow pyrolysis causes a secondary cracking of the primary products and thus reduces the overall yield of the bio-oil produced. However, the bio-oil produced via slow pyrolysis has an increased energy density on a moisture-free basis (20–37 MJ/kg) that directs to crude oils (41–48 MJ/kg). Additionally, the energy density of biochar may allow it to be co-fired as a solid fuel with an energy density comparable to that of solid fossil fuels. On the other hand, the main product via fast pyrolysis is simply bio-oil generated at temperatures of about 425–600 °C, brief vapor process time (<2 s) controlled by nitrogen gas, a heating rate greater than 200 °C/s and rapid product gas quenching. The high yield of bio-oil is caused by the speedy course of organic gas vapors into the furnace, diminishing the second-rate reactions. Additionally, the short time period helps keep fatty acids & ethers inside the bio-oil and raise their yield. Fast pyrolysis has many benefits, including flexible alteration of different biomass mixtures, energy densification of the biomass, and relatively little capital costs. The drawback of this type of pyrolysis (fast) is that the oil produced is highly oxygenated, thus requiring advanced upgrading. During the process of flash pyrolysis, the total time of reaction is shorter, while the heating rate is almost greater than 1000 °C/s (Bedmutha et al., 2011; Bok et al., 2012; Elmously et al., 2019; Kelkar et al., 2015; Kim

et al., 2019; Lee et al., 2019; Luz et al., 2018a; Matrapazi and Zabaniotou, 2020; Primaz et al., 2018; Vardon et al., 2013). Table 4 lists the main pyrolysis technologies (Bok et al., 2012).

The pyrolysis process yields more bio-oil than carbonization and gasification processes (Mohan et al., 2006). In the past, woody biomasses were the only renewable feedstock that can be used for the production of bio-oil through the pyrolysis process (Bok et al., 2012; Kelkar et al., 2015). In recent times, different types of other biomasses have been identified, like agricultural wastes, energy crops, etc. due to their lignocellulosic content, corresponding to a high energy content (Bok et al., 2012; Primaz et al., 2018). Equipment cost for pyrolysis is high. Therefore, it is vital to select and identify low-cost feedstocks such as organic waste (Matrapazi and Zabaniotou, 2020). In this regard, SCG is expected to be a valuable feedstock due to its availability (food waste) and excellent higher heating value (HHV) as compared to other biomasses (Bok et al., 2012). Shredded waste plastic and tires are also potential sources for the production of bio-oil. The bio-oil yield and characteristics are the most important parameters determining the pyrolysis process's effectiveness (Bok et al., 2012). Previous studies indicated that every biomass has its own optimal pyrolysis conditions, bio-oil features, and yield (Bok et al., 2012). The most common reactor configurations for bio-oil production are fluidized bed, circulating fluidized bed, vortex ablative, rotating cone, vacuum, auger-type reactors, and screw-conveyor reactors (Bok et al., 2012; Kelkar et al., 2015).

4. Valorization of SCG through pyrolysis process

The characterization of biomass and bio-oil is of great significance in order to find out their most suitable uses either for biofuels production or as an input for value-added products (Kelkar et al., 2015). Due to its excellent characteristics, pyrolysis technology has one of the most promising potentials for the valorization of SCG. According to (Matrapazi and Zabaniotou, 2020), the anticipated capacity of 2566 t/yr of SCG pyrolysis could bring revenue of 47€/t of SCG. The study reported positive economic indicators of return on investment (ROI) and payout time (POT) of 0.24 % and 2.6 year, respectively.

In the last 10 years, numerous studies examined the potential of producing bio-oil and biochar from SCG (Bedmutha et al., 2011; Bok et al., 2012; Cho et al., 2016; Kan et al., 2014; Kelkar et al., 2015; Ktori et al., 2018; Li et al., 2014; Luz et al., 2018a; Matrapazi and Zabaniotou, 2020; Primaz et al., 2018; Yang et al., 2016). On the other hand, many researchers (Krause et al., 2019; Matrapazi and Zabaniotou, 2020;

Table 4
Main pyrolysis technologies (Bok 2012).

Pyrolysis technology	Residence time	Heating rate	Temperature (°C)	Products
Carbonization	Days	Very low	400	Charcoal
Conventional	5–30 min	Low	600	Oil, gas, char
Fast	0.5–5 s	Very high	650	Bio-oil
Flash-liquid ^a	<1 s	High	<650	Bio-oil
Flash-gas ^b	<1 s	High	<650	Chemicals, gas
Ultra ^c	<0.5 s	Very high	1000	Chemicals, gas
Vacuum	2–30 s	Medium	400	Bio-oil
Hydro-pyrolysis ^d	<10 s	High	<500	Bio-oil
Methano-pyrolysis ^e	<10 s	High	>700	Chemicals

^a Flash-liquid \equiv liquid obtained from flash pyrolysis accomplished in a time of <1 s.

^b Flash-gas \equiv gaseous material obtained from flash pyrolysis within a time of <1 s.

^c Ultra (pyrolysis) \equiv pyrolysis with a very high degradation rate.

^d Hydro-pyrolysis \equiv pyrolysis with water.

^e Methanopyrolysis \equiv pyrolysis with methanol.

Vardon et al., 2013) proposed to first extract the lipids from SCG and process it into biodiesel (fatty acids methyl esters) while the DSCG can be processed into bio-oil and biochar. Additionally (Zanella et al., 2013), studied the co-pyrolysis of SCG with polypropylene while (Yang et al., 2017) reported co-pyrolysis of SCG with paper filter (PF), corn stalk (CS), and white pine (WP). It has been reported that the co-pyrolysis of different feedstocks leads to improvements in both bio-oil quality and yield (Atabani et al., 2019a).

The chemical composition of SCG depends on certain factors such as the kind of the coffee plant, the site where the plant grew, its age, the climate condition, and the soil of the area. Table 5 shows the chemical composition of SCG. It can be seen that the SCG contains different types of chemical compositions with hemicellulose, lignin, cellulose, protein, fat, fibers, and carbohydrate as the main components. This indicates that the SCG can be utilized as raw materials for many value-added products, chemicals, and food. Compared to other lignocellulosic materials, SCG contains small amounts of cellulose (about 10 wt%) and has a high content of hemicelluloses (30–40 wt%) (Matrapazi and Zabaniotou, 2020). Table 6 shows the proximate analysis of SCG (Bok et al., 2012; Li et al., 2014; Primaz et al., 2018). It can be seen that the SCG contains a high amount of volatile matter (VM) (77.51–93.84 %) followed by fixed carbon (FC) (3.92–19.83 %), moisture (1.31–11.37 %), and ashes (1.35–2.24 %). The high amount of VM present in the SCG is an indication that SCG can be a potential candidate for bio-oil production (Primaz et al., 2018). Further results can also be obtained from the literature (Atabani et al., 2019a). The fiber and inorganic components of SCG can be seen in (Kelkar et al., 2015).

Table 7 presents the results of elemental compositions and HHV of SCG, DSCG, and the obtained bio-oils from SCG and DSCG, and their comparison with other types of biomass and biochar. It can be seen that the carbon content of both the SCG (13.93–23 %) and the DSCG (20.1–21.54 %) is generally higher than the carbon content of some other biomasses such as PF, CS, and WP (15.1–18.1 %). The hydrogen content for SCG (1.57–7.31 %) and DSCG (6.3–6.74 %) were comparable to PF, CS, and WP (6.2–6.8 %). However, it has been seen that both SCG (2.1–6.42 %) and DSCG (2.8–16.7 %) have higher nitrogen content compared to PF, CS, and WP (0–0.5 %). This is attributed to the existence of caffeine which is an organic group that includes.

The HHVs of bio-oil resulting from SCG is higher than that of bio-oil resulting from woody biomass (16–19 MJ/kg) (Bok et al., 2012; Mohan et al., 2006). Moreover, the bio-oil properties produced via co-pyrolysis of SCG with other different feedstocks such as CS, PF, and WP have also been noted in this table. Generally, the oil manufactured from SCG exhibits better carbon density & lower oxygen amount in comparison to SCG (Matrapazi and Zabaniotou, 2020). Additionally, bio-oil from SCG has lower oxygen & hydrogen amounts as compared to bio-oil produced from mallee (Bok et al., 2012). The physio-chemical properties of the bio-oil derived from SCG have been reported by (Bok et al., 2012).

The method of fast pyrolysis of SCG using fluidized bed reactors was addressed by researchers (Bedmutha et al., 2011; Bok et al., 2012; Krause et al., 2019; Primaz et al., 2018) while other authors (Kelkar et al., 2015; Luz et al., 2018a) demonstrated fast pyrolysis using a screw-convey reactor. The influence of temperature on bio-oil yield from SCG has been reported by (Bok et al., 2012; Kelkar et al., 2015; Primaz et al., 2018). The result of two heating rates (10 °C/min & 60 °C/min) on SCG pyrolysis has been reported by (Li et al., 2014).

During the pyrolysis of SCG, three main phases of pyrolysis have been reported as follows (Krause et al., 2019; Li et al., 2014; Primaz et al., 2018):

- 1 The evaporation of water and release of carbon dioxide (CO₂) (until 200 °C). This phase corresponds to about ~7 % (wt%).
- 2 Pyrolysis reactions: This stage starts at ~200 °C and finishes at ~550–600 °C. This phase corresponds to about ~70 % (wt% loss of mass of sample) in which the disintegration of hemi-celluloses & celluloses occurs, liberating a huge array of volatiles. In this stage,

Table 5
Chemical composition of SCG.

Components	wt %										
	References	Giroto et al. (2018)	Ali et al. (2018)	Cruz-Lopes et al. (2017)	Barbero and Fiore (2015)	Yang et al. (2017)	Mussatto et al. (2011)	Caetano et al. (2017)	Lavecchia et al. (2016)	Vítez et al. (2016)	Cho et al. (2016)
Cellulose		24.3		10.78	13.2–18.4		8.6	14.8	12.4		9
Hemicellulose		24.8		28.36	33.6		36.7				
Lignin		13.5		10.72	3	27.7		2.82	23.90		29.8
Moisture			7.47								
Protein			8.97	9.28	10.3–12.2	13		10.7	17.44	13.44	12.9
Fat			13.89						2.29	13.54	
Ash			2.77	1.8	4.5–6.3				1.30	1.43	2.3
Crude fiber			51.86								
Carbohydrate			78.5								
Tannins				30.36	1.2–1.5						
Extractives				14.27		10.5					5.0
Melanoidins					7.2						
Caffeine					0.02–0.08						
Holocellulose						61.4					
Arabinose							1.7		3.60		1.2
Galactose							13.8		16.43		13.8
Mannose							21.2		19.70		23.4
Total dietary fiber									60.46		
Total fibres										20.11	
Acid detergent fibre (ADF)										43.03	
Neutral detergent fibre (NDF)										57.68	
Acid detergent lignin (ADL)										14.97	
Crude starch										2.39	
Acetyl group											2.6

Table 6
Proximate analysis of SCG.

wt.%	Reference		
	Bok et al. (2012)	Primaz et al. (2018)	Li et al. (2014)
VM	77.51	93.84 ± 0.5	82.0
FC	19.83	3.92 ± 0.1	16.30
Ashes	1.35	2.24 ± 0.5	1.70
Moisture	1.31	11.37 ± 0.08	8.1

thermal breakdown of hemi-cellulose starts roughly at ~365 °C (~51 % wt% of loss of mass of sample), while the thermal decomposition of cellulose occurs at ~400 °C (~19 % wt% of loss of mass of sample)

3 The decomposition of residual carbonaceous solids and the ultimate mass creation of biochar. This phase occurs in between the range of 600–1000 °C.

According to (Bedmutha et al., 2011), SCG bio-oil is more uniform and doesn't split into aqueous (aq) & organic parts compared to most bio-oils available. However, it almost contains 40–50 % water. This makes SCG bio-oil unattractive as a fuel. Therefore, the authors proposed an alternative pathway of utilizing SCG bio-oil applications as a pesticide. The authors indicated that SCG bio-oil processed at range of 500–550 °C was mainly energetic against *Streptomyces scabies* & *Clavibacter michiganensis* subsp. *Michiganensis* bacteria, while the bio-oil formed at 400 °C was the most active against the Colorado Potato Beetle (CPB).

Thermogravimetric analysis (TGA) permits the forecast of the kinetic factors of a thermo-chemical route, such as the process of pyrolysis (Krause et al., 2019). TGA of SCG has been examined in several studies (Bok et al., 2012; Cho et al., 2016; Kelkar et al., 2015; Kim et al., 2019, p. 20; Li et al., 2014; Primaz et al., 2018). (Bok et al., 2012) observed that the maximum peak for SCG occurred at 581 K while it was 651 K for mallee where lignin decomposed after 673 K. This is similar to (Kelkar et al., 2015), who indicated that the highest rate of weight loss was

detected around 593 K (Primaz et al., 2018). reported that the thermal decomposition of SCG up to 550 °C correlates to 70.33 % of the preliminary mass; hence the process of pyrolysis of the waste mass can be performed at temperatures ranging around 550 °C. This observation has also been mentioned by (Kelkar et al., 2015).

Fourier transform infrared spectroscopy (FT-IR) provides good information regarding the chemical composition of biomass (Krause et al., 2019). FT-IR of SCG before and after pyrolysis was reported by (Primaz et al., 2018) and (Li et al., 2014). FT-IR of SCG, DSCG, and biochar was reported by (Krause et al., 2019). FT-IR of bio-oil derived from SCG and DSCG has been reported by (Vardon et al., 2013).

Gas chromatography-mass spectrometry (GC/MS) offers information regarding the sample, making it likely to provide future endeavors in the different energy-derived industries (Krause et al., 2019). Analysis of bio-oil via GC/MS derived from SCG have already been examined by (Bedmutha et al., 2011; Bok et al., 2012; Cho et al., 2016; Kelkar et al., 2015; Li et al., 2014; Primaz et al., 2018; Yang et al., 2016; Zanella et al., 2013) while via GC/MS of DSCG was scrutinized by (Krause et al., 2019) and (Matrapazi and Zabaniotou, 2020). They reported the produced gas after the pyrolysis process using GC. The major compounds in the bio-oil from SCG samples were *n*-hexadecanoic acid (palmitic acid) (19 %), 9-octadecenoic acid (oleic acid) (11 %), and octadecanoic acid (stearic acid) (10 %). Considering the classes of chemical species, the major types were hydro-carbons (122 compounds), acids (25 compounds), ketones (36 compounds), esters (19 compounds), including phenols (43 compounds), and N-compounds (40 compounds) (Primaz et al., 2018). (Kelkar et al., 2015) identified the top five chemicals in bio-oil derived from SCG as hydroxy acetone, acetic & palmitic acid, pentadecane, and caffeine (Li et al., 2014). indicated that the primary products in the collected bio-oil from SCG were also present in C16–C20 (~40 %). These compounds were largely linoleic, palmitic, and 1-eicosanoic acids. The rest of the compounds include catechol, hydroquinone, phenol, and caffeine (Bedmutha et al., 2011). reported that SCG and tobacco bio-oils have a related chemical make-up regarding phenol-related molecules (Yang et al., 2016). indicated that the bio-oil product produced from

Table 7

Higher heating values (HHV) and elemental analyses of SCG, DSCG, bio-oils derived from SCG and DSCG, other biomasses and biochars.

	Reference	HHV	C%	H%	O%	N%	S%	
SCG	Kelkar et al. (2015)	–	52.37	7.31	36.5	2.42	0.14	
	Bok et al. (2012)	22.74	54.61	6.59	34.83	3.97	–	
	Li et al. (2014)	23.2	54.5	7.1	34.2	2.4	0.1	
	Yang et al. (2016)	20.2	50.4	7.2	40.3	2.1	–	
	Vardon et al. (2013)	23.4	56.1	7.2	34.0	2.4	0.14	
	Yang et al. (2017)	21.5	51.4	7.7	38.8	2.1	–	
	Kan et al. (2014)	–	54.9	7.90	33.75	3.51	0	
	Matrapazi and Zabaniotou (2020)	13.93	47.96	1.57	44.05	6.42	–	
Elmously et al. (2019)	21.9–23.0	52.75	7.21	36.4	2.17	0.24		
DSCG	Vardon et al. (2013)	20.1	51.8	6.3	38.8	2.8	0.17	
	Atabani et al. (2017)	21.54	49.59	6.74	–	16.7	0.851	
Woody biomass	Bok et al. (2012)	17.32	48.4	6.3	45.2	0.1	–	
PF	(Yang et al., 2017)	18.1	50.1	6.2	43.5	0.2	–	
CS		15.2	44.4	6.3	48.9	0.5	–	
WP		15.1	42.7	6.8	50.5	0	–	
Bio-oil (SCG)	Kelkar et al. (2015)	–	44.97	12.03	42.07	0.80	0.12	
	Bok et al. (2012)	20.38	54.27	7.41	35.26	3.06	–	
	Li et al. (2014)	17.23	28.9	6.5	59.5	5.06	0.07	
	Yang et al. (2016)	31.0	71.2	7.1	18.7	3.0	–	
	Vardon et al. (2013)	23.3	74.0	9.8	13.4	2.6	0.17	
	Yang et al. (2017)	40.4	73.9	12.3	13.0	0.8	–	
Thermo-catalytic reforming system (TCR®)	500 °C 600 °C 700 °C	Elmously et al. (2019)	36.00	75.90	9.60	3.30	10.80	0.41
			36.20	78.10	8.30	4.30	8.40	0.80
			36.8	79.30	6.80	3.80	9.20	0.76
Bio-oil (DSCG)	Vardon et al. (2013)	27.0	70.9	8.0	16.4	4.3	0.39	
Bio-oil (Woody biomass)	Bok et al. (2012)	–	42.3	8.2	49.4	0.1	–	
	(Mohan et al., 2006)	16–19	54–58	5.5–7.0	35–40	0–0.2	–	
Bio-oil (SCG/PF)	Yang et al. (2017)	25.6	60.4	7.4	30.5	1.7	–	
Bio-oil (SCG/CS)		33.3	71.7	8.5	17.9	1.9	–	
Bio-oil (SCG/WP)		26.2	61.9	7.3	28.8	2.0	–	
Biochar (SCG)	Kelkar et al. (2015)	–	75.30	3.52	0.11	4.40	0.12	
Biochar (SCG)	Li et al. (2014)	31.1	82.10	2.90	4.70	4.10	0.08	
Biochar (SCG) ^a	Matrapazi and Zabaniotou (2020)	25.56	70.69	2.85	23.26	3.20	–	
Biochar (SCG) ^b		26.18	72.92	2.59	21.90	2.59	–	
Biochar (SCG)	Vardon et al. (2013)	31.00	76.2	5.60	–	3.90	0.05	
Biochar (DSCG)		28.30	72.6	5.0	–	4.30	0.10	

^a ≡ formed at 500 °C.^b ≡ formed at 600 °C.

SCG via HTL contains 48.15 % of n-hexadecanoic acid, 15.46 % of octadecanoic acid, and 32.99 % of 9,12-octadecadienoic acid (Z,Z)-. The following section highlights some of the pyrolysis studied of SCG (Krause et al., 2019). indicated that, despite lipid extraction, the main components of bio-oil derived from DSCG are dominated by palmitic acids (13.96 %), linoleic acid (9.4 %), and stearic acid (4.94 %), respectively. Additionally, relatively high levels of hydrocarbons (tetradecane and pentadecane) have been identified. Additionally, the bio-oil possesses a significant phenolic content including 3.72 % of phenols, 2.16 % of catechol and finally 2.32 % *p*-cresol. Additionally, increased accumulation of N-compounds, together with compounds such as indole, pyridine, amides, caffeine, and amines were found.

It has been reported that the quality of bio-oil from SCG as fuel has some drawbacks as it has a high water and oxygen content (Bedmutha et al., 2011; Elmously et al., 2019). This limits the use of bio-oil as a fuel. Thus, some other applications, such as for pesticide, polymers, pharmaceutical and agrochemical industries, have been suggested in the literature (Bedmutha et al., 2011). On the other hand, some current studies have concentrated on catalytic innovations to upgrade the thermal competence of pyrolysis and enhance the overall quality of bio-oil from SCG (Cho et al., 2016; Elmously et al., 2019; Kan et al., 2014). (Kim et al., 2019) investigated the use of CO₂ as a reaction intermediate to develop the thermo-chemical methods of SCG (Elmously et al., 2019). specified that the quality of the bio-oil produced by the

thermo-catalytic reforming system (TCR®) is significantly better than the oil product produced by the technique of fast pyrolysis.

4.1. Pyrolysis of SCG

The influence of operating parameters such as residence time (5, 10, 15, 20, and 25 min), holding temperature (200, 225, 250, 275, and 300 °C), water to SCG mass ratio (5:1, 10:1, 15:1 and 20:1) and initial nitrogen gas pressures (2.0 MPa and 0.5 MPa) via hydrothermal liquefaction (HTL) in a stainless-steel autoclave reactor was studied by (Yang et al., 2016) on the bio-oil yield. The highest amount of bio-oil (47.28 wt %) was achieved at a retention time of 10 min at 275 °C with water to SCG mass ratio of 20:1 with an initial pressure of 2.0 MPa.

(Bok et al., 2012) conducted fast pyrolysis on SCG where nitrogen was used as a fluidization gas in a fluidized bed reactor and in the absence of oxygen (O₂). The authors performed a comprehensive analysis of the effect of temperature (673–873 K) on bio-oil yield and quality. The vapor residence time was 1.07 s, and the heating rate was (1000–10,000 K/s). The yield was also compared with that from other biomasses such as mallee and sweet sorghum. It was observed that the highest yield of bio-oil of 54.85 % was obtained at 823 K in comparison to the 36.75 wt% yields obtained at 673 K, which was followed by a reduction at 873 K. The highest bio-oil yield from mallee and sweet sorghum was >60 wt% at temperature range 723–773 K. From Table 7,

it was concluded that the oil generated from SCG has a higher carbon content than that of bio-oil from mallee. The authors indicated that it is even much higher than bio-oil attained of woody biomass. However, the N content is higher as SCG has numerous organic groups that include N like caffeine of roughly around 6.61 %, dodecanamide of approximately 0.13 %, and 2-methyl-pyridine of around 0.24 %. This has been further validated by GC analysis. Table 8 portrays the physio-chemical properties of bio-oil from SCG obtained at diverse range reaction temperatures. The highest HHV of 23.19 MJ/kg was obtained at 723 K.

(Bedmutha et al., 2011) conducted the pyrolysis of SCG using a fluidized bed reactor at 5 dissimilar temperatures of 400 followed by 450 then 500, 550, and finally 600 °C with a vapor retention time of 5 s. Similar to (Bok et al., 2012; Kelkar et al., 2015), the consequence of the different temperatures on the overall yield of the products via pyrolysis on the bio-oil yield was clear. The most favorable yield of 43.8 % was acquired at a temperature of 500 °C. The authors also indicated that yield of gas increased from 17.6 % at 400 °C to 32.1 % at 600 °C with the increase in HHV from 575.5 J/g at temperature of 400 °C–3445.8 J/g at a temperature of 600 °C due to increase in both hydrogen and methane concentrations. Biochar yield dropped from 35.2 % at a temperature of 400 °C to 19.6 % at a temperature of 600 °C.

(Primaz et al., 2018) examined the effect of reaction temperatures (400, 450, 500, 550, and 600 °C) on bio-oil yield from SCG in a fixed bed reactor. Similar to what was observed in other studies (Bedmutha et al., 2011; Kelkar et al., 2015; Luz et al., 2018a), the highest bio-oil yield of 30.51 % was attained at 500 °C. Including the aqueous part, the crude bio-oil yield was 51.61 %. The highest yield of the non-condensable gases at 550 °C was almost 30.86 %. When the temperature was raised from 400 °C to the highest point of 600 °C, however, the yield of biochar decreased from 35.61 % to 21.92 %. This decrease indicates that the yield of the non-condensable gases increases. This is attributed to the further disintegration of the organic functional groups at elevated temperatures, associated with the secondary cracking of the produced biochar.

The process of fast pyrolysis of SCG using a screw-conveyor pyrolysis reactor was introduced by (Kelkar et al., 2015) and (Luz et al., 2018a). This technology has many advantages as it does not use sand to transmit heat or nitrogen (inert) gas for its fluidization (Kelkar et al., 2015). assessed the effects of reactor temperature (429–550 °C) and retention time (23–42 s) on the final bio-oil, char, and yield of the gases from SCG (Table 9). As it can be seen, the highest oil yield of 61.7 wt% was attained at 500 °C with a retention time of 23 s, while the maximum bio-char yield of 20.6 wt% was acquired at 429 °C with a retention time of 23 s. The maximum gas yield was obtained at 550 °C (27.4 %). The authors also reported the elemental analysis of bio-oil with a carbon composition of 44.97 %. The authors specified that bio-oil yield was much higher, and the char yields were slightly lower than those obtained with the fluidized-bed reactors. For instance, bio-oil yield in this work was higher than some of the other work reported by (Bok et al., 2012) (54.85 wt% at 600 °C) (Bedmutha et al., 2011), (43.8 wt% at 500 °C) (Primaz et al., 2018), (30.51 % mass fraction at 500 °C) and (Luz et al., 2018a) (56.09 ± 0.22 wt% at 500 °C). The authors also used the central composite rotatable design (CCCRD) and response surface methodology (RSM) (a quadratic polynomial response surface model) to examine the experimental statistics by least-squares regression. Prediction of the

Table 8

Chemical & physical characteristics of bio-oil derived from SCG (Bok et al., 2012).

Reaction temperature (K)	HHV (MJ/kg)	Viscosity ^a (cP)	Water content (wt.%)	Solid residue (wt.%)	pH	Ash (wt.%)	Density (kg/m ³)
673	12.04	51.20	28.88	0.07	2.90	0.12	1.05
723	23.19	197.50	23.96	0.10	3.10	0.08	1.06
773	22.46	163	29.82	0.06	3.20	0.19	1.10
823	20.38	87.70	31.11	0.25	3.10	0.17	1.15
873	20.03	32.93	32.93	0.13	3.50	0.06	1.10

^a ≡ at 293 K.

Table 9

Bio-oil & char yields (% w/w biomass) (Kelkar et al., 2015).

Temperature (°C)	Retention time (s)	Bio-oil (wt.%)	Char (wt.%)	Gas
429	32	59.6	20.6	22.3
450	27	57.3	19.9	20.2
450	28	60.7	18.9	25.6
500	42	55.5	18.6	19.7
500	32	61.5	18.3	25.9
500	32	60.0	17.7	20.4
500	32	59.8	18.2	22.0
500	23	61.7	18.6	22.9
550	37	54.5	18.1	19.8
550	28	60.8	13.6	27.4
571	32	57.8	17.3	24.9

bio-oil yields was found to be done with reasonable accuracy ($p < 0.05$). However, char yield prediction was less precise ($p < 0.11$, $R^2 = 0.77$). According to the developed model, the maximum bio-oil yield is obtainable at 505 °C. The quality of bio-oil from SCG has been found to be quite excellent. In addition to containing oxygenated organic molecules typical of bio-oils, SCG bio-oil also has more hydrophobic composites (>20 % peak area) such as fatty acids and esters, medium-chain paraffins, caffeine, and olefins (Luz et al., 2018a). experimentally assessed the effects of reactor temperature (450, 500, and 550 °C) on char, bio-oil, and gas yields from SCG. As it can be seen, the utmost bio-oil yield of 56.09 ± 0.22 (wt.%) was obtained at 500 °C. At this temperature, the syngas yield was 21.98 (wt.%), while bio-char was 21.93 ± 0.19 % (wt.%). The authors also aimed at predicting bio-oil yield by developing a mono-dimensional model. As can be seen from Table 10, the developed model was validated and showed low errors, especially for bio-oil yield.

(Ktori et al., 2018) pyrolyzed SCG on the laboratory pilot scale using a wire mesh captive model type reactor at temperatures ranging from 400 to 700 °C while keeping the heating rate at 50 °C/s under an inert atmosphere at atmospheric pressure. The utmost yield of bio-oil of 36 wt % was obtained at 540 °C, while gas and char yields were 9 wt% and 29 wt%, respectively. The bio-char yields decreased with increasing pyrolysis temperature from 43 wt% at 400 °C to 26 wt% at 700 °C. On the other hand, gas yields increased with increasing temperature, reaching the highest value of 28 wt% at 700 °C. Matrapazi and Zabaniotou (2020) also denoted that the highest bio-oil yield of ~41 % was acquired at 600 °C (Li et al., 2014). achieved a maximum bio-oil yield of 66 wt% at around 627 °C (900 K).

(Cho et al., 2016) examined the catalytic effect and pretreatment of SCG with FeCl₃ (Fe-SCG) prior to pyrolysis utilizing carbon dioxide (CO₂) as a reaction medium. This was done to enhance syngas' generation while reducing condensable hydrocarbons (e.g., tar) via the CO₂-induced thermal cracking of volatile organic compounds (VOCs) and the reaction between CO₂ and VOCs. This resulted in the subsequent reduction of tar. These identified effects on pyrolysis of SCG were more pronounced in the pyrolysis of Fe-SCG, which could be attributable to the Fe mineral's catalytic effect, which resulted from the phase transition of FeCl₃ during pyrolysis. The generation of CO during the pyrolysis of Fe-SCG in the presence of CO₂ increased by 8000 % as compared to the pyrolysis of SCG in N₂.

(Matrapazi and Zabaniotou, 2020) conducted slow pyrolysis of SCG

Table 10

Contrast of experimental and numerical data of fast pyrolysis of SCG at reaction temperatures (450, 500, and 550 °C) (Luz et al., 2018a).

Temp (°C)	Bio-oil (w.%)			Gas (w.%)			Char (w.%)		
	Exp	Model	Error	Exp	Model	Error	Exp	Model	Error
450	54.01 ± 0.23	53.33	-1.26	22.03	18.88	14.23	23.95 ± 0.20	27.79	16.03
500	56.09 ± 0.22	56.58	+0.87	21.98	20.60	6.21	21.93 ± 0.19	22.82	4.06
550	54.95 ± 0.24	54.15	-1.45	23.07	23.77	3.03	21.98 ± 0.18	22.08	0.058

under various pyrolysis temperatures (450–750 °C) with a heating rate of 50 °C/s under helium atmosphere in a laboratory-scale wire mesh captive sample type reactor. The pyrolysis gas and bio-oil production augmented with the rise of the pyrolysis temperature. The overall yield of pyrolysis gas approached a maximum at 700 °C (20 %) while the quantity yield of bio-oil achieved the highest 600 °C (~20 %). On the other hand, biochar yield diminished with the increase in temperature. The optimum pyrolysis temperature denoted by the authors was in the range of 500–600 °C.

The effect of carbon dioxide on the pyrolysis of SCG was reported by (Kim et al., 2019). The flow rates of N₂ or CO₂ were 500 mL/min, respectively. The process was conducted in two stages. The first stage includes a temperature-ramping zone with 10 °C/min as the heating rate while the second stage involves an isothermal zone. The authors indicated that the division of the resulting products is dissimilar. For instance, fewer aromatic compounds were formed in the pyrolysis with CO₂ than N₂. The authors attributed that to CO₂ accelerating the thermal cracking of SCG during pyrolysis.

(Elmously et al., 2019) evaluated the conversion of SCG through the TCR® system. It is a batch system containing a screw-conveyor reactor for moderate pyrolysis and catalytic reforming. For the catalytic reformer, its temperature was assorted between 500 and 700 °C to attain the greatest bio-oil quantity and quality. The hydrogen content percentage was maximized around the temperature of reforming at 700 °C, and a gas yield of around 52 wt% is accomplished. The thermal constant bio-oil produced at 700 °C had a maximum calorific value of 36.8 MJ/kg with considerably lower O₂ and water content, lower viscosity, and overall lower total acid number (TAN). Moreover, the highest bio-oil and bio-char yields were acquired at 500 °C, which is the lowest reforming temperature.

4.2. Pyrolysis of DSCG

(Krause et al., 2019) studied the fast pyrolysis of DSCG in a stainless steel fixed bed reactor with a vertical furnace. It was detected that the yield of bio-oil mass was 30 % in liquid products, being around 6 % bio-oil. This outcome is lesser than the bio-oil attained via SCG. The authors attributed it to the extraction of lipids from SGC. Moreover, the authors indicated that bio-oil derived from DSCG is also not suitable as a biofuel due to its high viscosity and acidity. Additionally, the quantity of nitrogenated molecules is much more than that usually discovered in bio-oil from other waste organic matter and is excluded for application as biofuel. Therefore, the authors recommended utilizing the bio-oil produced from DSCG for the production of polymers in the pharmaceutical and agrochemical industries.

(Vardon et al., 2013) reported the slow pyrolysis of the DSCG. Slow (conventional) pyrolysis was carried out using a Thermolyne 79,400 tube furnace, as discussed in detail previously. The reaction was conducted up to 450 °C while the heating rate was kept at 50 °C/min and a residence time of 2 h using nitrogen as the inert gas. Similar to (Krause et al., 2019), its yield from DSCG was much lower (13.7 %). The authors supposed that the bio-oil yield from DSCG was approximately part of the yield of bio-oil produced from SCG (27.2 %). The authors attributed that to the extraction of lipids from SGC. Lipids are renowned to quickly break during the process of pyrolysis into bio-oil organic products, which include compounds such as ketones, fatty acids, alkanes, and acrolein. The authors indicated that biochar's energy density can let it

be co-fired as a rock-solid fuel while comparing its energy density to conventional fossil fuels. On the other hand, the utilization of biochar as a soil adjustment in blend with fertilizer showed an important enrichment in the biomass yield of Sorghum-Sudangrass over a span of the 4-day period. The authors indicated the advantage of biochar from DSCG over the non-pyrolyzed SCG and DSCG. This is due to the high nutrient profile (S, P, K, Ca, Mg, and Na) and micronutrients (Zn, Fe, Mn, Cu, and B) in biochar. This is in agreement with (Matrapazi and Zabaniotou, 2020), who indicated that biochar from SCG doesn't display phytotoxicity since the organic matter was already eliminated from SCG during the process of pyrolysis.

From Table 4, it can be determined that bio-oils obtained from both SCG and DSCG have higher HHV compared to many other woody biomasses. Due to lipids extraction, bio-oil from SCG has higher HHV than DSCG (Vardon et al., 2013). Moreover, the combustion of bio-oil from DSCG might lead to higher NO_x releases since it has a relatively increased nitrogen percentage than SCG. Therefore, this factor has to be considered before burning bio-oil from DSCG. It can also be blended with bio-oils from other biomasses that have a lower nitrogen content.

4.3. Reactors

To untap the perspective of the use of SCG for energy, the spent coffee grounds waste can be converted to energy-rich gases, bio-oil and biochar through pyrolysis. Different reactors and arrangements (Battista and Barampouti, 2020; Matrapazi and Zabaniotou, 2020), have been employed by various researchers for the pyrolytic conversion of SCG. The SCG reactors can be identified as classical fixed-bed reactors, fluidized-bed reactors, screw conveyor reactors, tubular reactors, and others based on different studies. A description of the reactors used for SCG pyrolysis with a simplified schematic is provided below.

4.3.1. Fixed bed reactors

They are mostly used on smaller scales and rarely scaled up in the industry. Non-uniform heating caused by the lower heat transfer coefficients, absence of mixing, and relatively slower heating rates are the main factors that restrict their upscaling as a continuous system for bio-oil production. A simplified diagram of a typical vertical fixed bed reactor is shown in Fig. 4(a). The reactor is composed of a vertical cylinder. The volatiles are generally transported out of the SCG bed by a carrier gas. Fixed bed pyrolysis reactors are simple in design, easy to manage and require the least maintenance. These set-ups are common among the scientific community. Several researchers used similar configurations of fixed bed reactors for SCG pyrolysis (Krause et al., 2019; Ktori et al., 2018; Primaz et al., 2018). (Primaz et al., 2018) used a fixed bed reactor with a nitrogen flow of 150 mL/min, heating at 100 °C/min to reach isothermal temperatures ranging from 400 to 600 °C with a residence time of 15 min. They were able to produce 22–31 % non-condensable gases, 17–30 % bio-oil, 19.75–25.4 % aqueous phase, and 22–35 % biochar from SCG pyrolysis. Krause et al. (2019), performed the pyrolytic conversion of SCG using a fixed bed reactor at 600 °C with a nitrogen flow of 100 mL/min, achieving yields of 45.4% gases, 6.08 % bio-oil, and 25.1 % each of aqueous and solid biochar. Horizontal tube reactors are fixed-bed reactors; the reactor is placed horizontally in the tube furnace, as shown in Fig. 4(b) (Vakalis and Moustakas, 2019). utilized a tubular reactor to perform SCG pyrolysis at 500 and 800 °C. With a residence time of 30 min at the final temperature, they were able

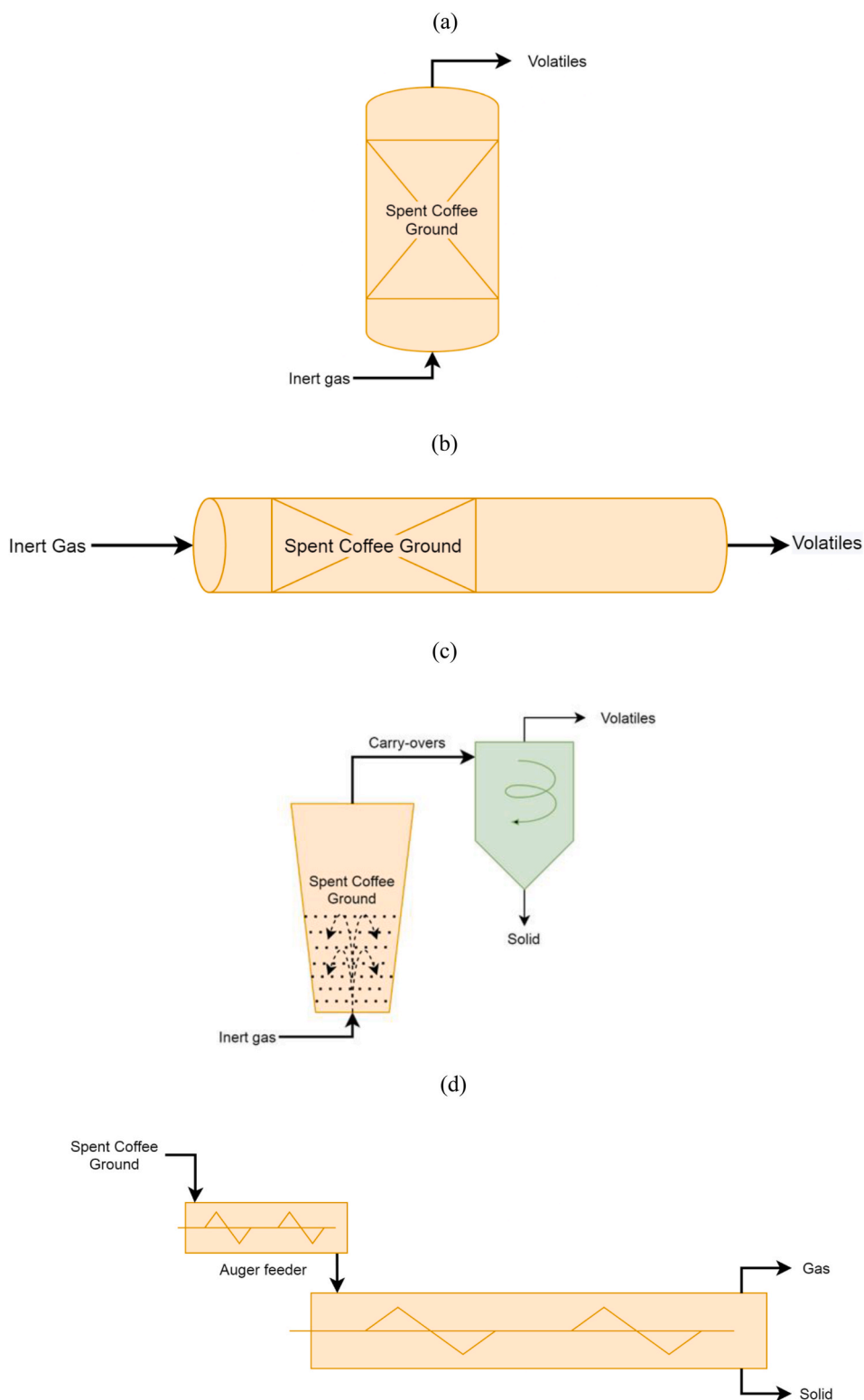


Fig. 4. Reactors for the pyrolytic conversion of spent coffee ground.

to produce 28.2% of biochar at 800 °C and 10.1% at 500 °C.

4.3.2. Fluidized bed reactor

Fluidized-bed reactors are suited for continuous operation, large contact area, and higher efficiency of heat transfer, allowing for shorter residence time. The inert gas is injected through a perforated distributor to fluidize the bed of sand. A sufficient empty space above the bed is

provided to retain the sand. A cyclone at the downstream settles down-solid biochar from the volatiles. An illustration of a typical fluidized bed reactor is shown in Fig. 4(c). Fluidized bed reactors owing to complex design, are usually difficult to control because of moving media and erosion of the inner walls, which poses another issue (Bedmutha et al., 2011). used a fluidized bed for the pyrolytic conversion of SCG at 400, 500, and 600 °C at a retention time of 0.083 min. Increasing temperature

resulted in an increase in the gas yield from 17.6 to 32.1 %, with a corresponding decrease of biochar from 35.2 % to 19.6 %. However, they reported the highest bio-oil yield (43.8 %) at a moderate temperature of 500 °C (Bok et al., 2012). also used a similar arrangement to examine the quality and yield of the valuable products from SCG pyrolysis. A similar trend was reported for biogas and biochar, however contrary to (Bedmutha et al., 2011), the highest yield of bio-oil (54.85%) was obtained at 600 °C.

4.3.3. Screw-conveyor reactor

Screw-conveyor reactors are used on small and large scales alike. The reactor's construction is tubular with a screw-conveyor to move the feedstock forward in the reactor tube. A simplified illustration of the screw-conveyor reactor is portrayed in Fig. 4 (d). The arrangement is continuous with respect to feed, volatiles, and char. Although the design is simple, control of the system is complicated to maintain a uniform temperature. For this reactor, pre-dried SCG is required to avoid clogging (Kelkar et al., 2015). studied different temperatures and speeds of the screw-conveyor. They showed that liquid yield could be obtained by operating the screw-conveyor reactor at a faster speed and higher temperatures.

Table 11 lists pros and cons of different reactors used for SCG pyrolysis whereas their operating parameters and product yields are mentioned in Table 13.

4.4. Kinetics of SCG pyrolysis

Kinetic studies of SCG pyrolysis are vital to design an appropriate reactor, upscale, and process downstream. When subjected to heating in the absence of air, SCG degrades, and the rate of its degradation under such conditions is described by the differential rate equation as below.

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (1)$$

where the rate $\frac{d\alpha}{dt}$ is proportional to the reaction model $f(\alpha)$, and the constant of proportionality from Arrhenius law, $k(T) = A \exp\left(\frac{-E_a}{RT}\right)$, depends on the absolute temperature T, frequency factor A and activation energy E_a .

As per the authors' information, the research on kinetic investigations of SCG pyrolysis were not enough to predict the mechanism and its applicability to various applications. Table 12 shows the research work conducted on the kinetics of SCG pyrolysis. Some of the authors

Table 11
Advantages and disadvantages of different reactor types used for SCG pyrolysis.

SCG reactor type	Benefits	Drawbacks
Fixed bed	Simple design Easy operation Biomass size independent Mature technology	Small scale batch operation Longer residence time Difficult to remove char Non-uniform heating Lower heat transfer
Fluidized bed	Easier temperature control (uniform heating) Large contact area Lower residence time Higher heat transfer Suitable for large scale continuous operation Mature technology	Small particle sizes are needed Complex hydrodynamics Complex design Char is finer
Screw-conveyer	Compact construction No carrier gas required Lower process temperature Higher heat transfer	Complex process Moving parts in hot zone Small scale continuous operation Not mature enough

Table 12

Research work conducted on the kinetics of SCG pyrolysis.

Feedstock	TGA Operating conditions			Activation Energy (kJ/mol) [Kinetic model]	Ref
	Final Temperature (°C)	Heating rate (°C/min)	Inert gas flow rate (ml/min)		
Spent Coffee ground	850	20	5000	Zone I: 41.93 and Zone II: 7.09 [Coats Redfern F ₁]	Saeed and Shafeeq (2020)
Spent Coffee ground	800	5, 10, 20, 30, 40	30	101.8 [FWO], 96.7 [KAS], 97.1 [Starink], 154.2 at 5 °C/min, 166.7 at 10 °C/min, 173.1 at 20 °C, and 163.5 at 30 °C/min [Coats Redfern F ₂]	Polat and Sayan (2020)
Spent coffee ground pellets	900	5	200	56.9 [F _{1/2} model fitting]	Jeguirim and Limousy (2014)
Coffee ground residue	500	5, 10, 15, 20, 25, 50, 100	100	212.4 [Kissinger], 243.6 [KAS], and 241.3 [FWO]	Fermoso and Mašek (2018)
Coffee silver skin	750	5, 7, 10, 15	3500	268 (FWO), 285 [Starink]	Pinzi and Buratti (2020)

used the model-fitting approach to conduct kinetic analysis, for example (Saeed and Shafeeq, 2020) used the chemical reaction model (first order) Coats-Redfern model-fitting integral method to estimate the kinetics.

$$\text{Coats - Redfern: } \ln\left[\frac{g(\alpha)}{T^2}\right] = \text{const} - \frac{E_a}{RT} \quad (2)$$

where $g(\alpha)$ is the integral inverse of model function, $f(\alpha)$. For first order, F₁, $f(\alpha) = (1 - \alpha)$ and thus $g(\alpha) = -\ln(1 - \alpha)$.

(Jeguirim and Limousy, 2014) linearized the rate equation containing nth order reaction model $f(\alpha) = (1 - \alpha)^n$, to estimate the kinetic parameters.

$$\ln\left(\frac{d\alpha}{dt}\right) = \text{const} - \frac{E_a}{RT} + n \ln(1 - \alpha) \quad (3)$$

On the other hand, model-free approaches (Kissinger, KAS, FWO, and Starink) were also utilized to predict its pyrolysis behavior (Fermoso and Mašek, 2018; Pinzi and Buratti, 2020; Polat and Sayan, 2020).

$$\text{Kissinger: } \ln\left(\frac{\beta}{T_m}\right) = \text{const} - \frac{E_a}{RT_m} \quad (4)$$

$$\text{KAS: } \ln\left(\frac{\beta}{T^2}\right) = \text{const} - \frac{E_a}{RT} \quad (5)$$

$$\text{FWO: } \ln \beta = \text{const} - 1.052 \frac{E_a}{RT} \quad (6)$$

$$\text{Starink: } \ln\left(\frac{\beta}{T^{1.92}}\right) = \text{const} - 1.008 \frac{E_a}{RT} \quad (7)$$

where T_m corresponds to the absolute temperature (T) at maximum

Table 13
Comparison of SCG pyrolysis with DSCG and other feedstocks at different temperatures.

Raw material	Pyrolysis type	Reactor type	Temperature (°C)	Bio-oil (w t %)	Char (wt %)	Gas (wt %)	Ref			
Agricultural Waste										
Rice husks	Fast	—	500	36	48	16	Kahhat et al. (2017)			
Hazelnut shell	Slow	Fixed-bed tubular reactor	400	20	48	19	Pittin et al. (1999)			
			700	45	38	27				
Rapeseed	Flash	—	500	71	16	8	Kockar and Onay (2003)			
			600	73	15	8				
			700	67	13	15				
Rice straw	Intermediate	Heat-carrier-free-rotating bed reactor	400	33	40	25	Ba et al. (2017)			
			500	38	39	27				
			600	35	38	28				
Maize straw			400	32	40	27				
			500	36	35	29				
			600	34	33	31				
Wheat straw			400	35	39	24				
			500	37	32	26				
			600	38	31	25				
Olive kernel	Intermediate	Batch	350	30	60	10	Antoniou and Zabaniotou (2018)			
			450	37	34	29				
			550	51	31	18				
Mallee	Fast	Fluidized-bed-reactor	700	62	21	12	Bok et al. (2012)			
			800	57	14	17				
Food Waste										
Sweet sorghum	Fast	Fluidized-bed-reactor	700	59	25	13	Bok et al. (2012)			
			800	55	18	22				
Orange bagasse	Intermediate	Semi-batch	400	16	50	25	Bhattacharjee and Biswas (2019)			
			500	25	35	30				
			600	26	28	39				
SCG										
SCG	Fast	Fluidized-bed-reactor	700	44	34	11	Bok et al. (2012)			
			800	53	20	15				
SCG	Intermediate	Batch	450	33	38	8	(Ktori et al., 2018)			
			550	38	30	10				
			650	27	25	16				
			450	30	33	9		Matrapazi and Zabaniotou (2020)		
			550	40	23	13				
			650	43	20	16				
			750	39	19	29				
			Fast	screw-conveyor pyrolysis reactor	450	54.01 ± 0.23			23.95 ± 0.20	22.03
					500	56.09 ± 0.22		21.93 ± 0.19	21.98	
					550	54.95 ± 0.24		21.98 ± 0.18	23.07	
450	57.3	19.9			20.2	Kelkar et al. (2015)				
500	61.5	18.3			25.9					
Batch TCR® system with screw-conveyor reactor	550	60.8	13.6	27.4	Elmously et al. (2019)					
	500	54.08 ^a	10.80	35.12						
	600	54.87 ^b	8.26	36.87						
700	41.56 ^c	6.28	41.56							
SCG	Slow	Thermolyne 79,400 tube furnace	450	27.2	28.0	24.0	Vardon et al. (2013)			
DSCG				13.7	27.0	21.0				

^a ≡ Condensate having 7.33 % bio-oil and 46.75 % aqueous phase.

^b ≡ Condensate having 6.22 % bio-oil and 48.65 % aqueous phase.

^c ≡ Condensate having 5.23 % bio-oil and 36.33 % aqueous phase.

degradation rate, $\left(\frac{da}{dt}\right)_{max}$

However, a piece of detailed knowledge on the kinetics of SCG thermal decomposition is required for process optimization and reactor design. Beyond chemical reactions, other possible mechanisms such as diffusion, power, and growth methods could also be utilized to predict complex kinetics. DAEM has also emerged as a powerful technique to predict the kinetics of complex compounds during the pyrolysis process.

4.5. Reactor modeling

The pyrolysis process can be modeled for various reactor configurations using different techniques such as CFD (Computational fluid dynamics), ANN (Artificial neural networks), or any other process simulation software (HYSYS, UniSim etc). Depending on the chosen technique, the input may require extensive biomass properties and reaction kinetics described earlier. A detailed description of the merits and demerits of the techniques employed by researchers for modeling the pyrolysis of diverse feedstock under different operating conditions using

various reactor configurations can be found elsewhere (Vikram et al., 2021) and is beyond the scope of this review. However, as per authors information, not a single study was found where these techniques were used to model SCG pyrolysis.

5. Comparison of SCG pyrolysis with DSCG, other food waste & agricultural waste

Table 13 compares various pyrolysis studies for SCG, DSCG and other food waste and agricultural waste. An experimental results on both the SCG and DSCG pyrolysis were conducted by (Vardon et al., 2013). The study revealed a lower bio-oil yield for the DSCG (13.7 %) compared to 27.2 % for the SCG. This was approximately half of the bio-oil yield as that of the SCG. Authors attributed this lower yield to the lipid extraction process, consistent with their previous findings for the raw and defatted algal biomass. Lipids are known to rapidly break down during pyrolysis into bio-oil organics, including alkanes, fatty acids, esters, ketones, and acrolein. The biochar yield (27.0–28.0 %) and gas-phase yield (21.0–24.0 %) were comparable for both the DSCG and SCG. However, the pyrolysis aqueous-phase yield from the DSCG was found much higher (33.3 %) compared to the SCG (23.8 %). This was attributed to the higher content of cellulose and hemicellulose in the DSCG. Cellulose and hemicellulose can degrade into water-soluble organics. Additionally, the authors indicated that energy recovery from pyrolysis aqueous-phase organics is of interest for a potential source of hydrogen, alkanes, and polyols production.

6. Future perspectives and challenges

Anything that can enhance economic gains further would be much appreciated, especially in the current global scenario. However, extracting more from any bio waste requires additional equipment that puts a burden (Matrapazi and Zabaniotou, 2020) when it comes to valorizing many of the bio waste. Since the availability of SCG is huge due to its global demand, it tends to be a cheap feedstock having higher heating value (HHV), thus making it an attractive candidate for further economic gains (Bok et al., 2012) as compared to its other counterpart waste. It is estimated that the pyrolysis of SCG could generate about 47€/t, making it highly attractive cumulative revenue due to massively available SCG. The pyrolysis technology required to decompose the SCG is a proven, simple, and well established, with almost all kinds of its reactors that can be employed to extract additional benefits from SCG.

Though the availability of SCG has a great potential for economic benefit, there are certain challenges that need to be addressed to optimally use this bio waste. It is noted that the bio-oil extracted by pyrolysis of SCG contains a substantial amount of water (Bedmutha et al., 2011; Elmously et al., 2019) that puts a limitation on its use as biofuel. Furthermore, the yield of bio-oil is highest when the pyrolysis temperature is around 600 °C, requiring a lot of input energy and robust reactor design to sustain such temperature. There are some efforts being made to use catalytic intervention to improve the overall quality of bio-oil from SCG (Cho et al., 2016; Elmously et al., 2019; Kan et al., 2014).

7. Conclusions and recommendations

The present article provides a comprehensive review of the research being carried out in the field of SCG. The following concluding remarks were drawn after going through the articles published in the field of SCG.

- There is a mounting attention in adopting the valorization of SCG to gain multifold benefits.
- Temporal evolution subject categories of the WoS showed that the subject category for SCG pyrolysis belongs mostly to Energy & Fuels sectors

- Fuel and Bioresource Technology are the top journals covering the research work related to SCG pyrolysis.
- It was estimated that 2566 t/yr of SCG pyrolysis could bring profits of 47€/t of SCG, showing some positive financial results and a return on investment (ROI) and payout time (POT) of just 0.24 and 2.6, respectively.
- Due to its excellent characteristics, pyrolysis technology has one of the most promising valorization potentials of SCG.
- In most cases, a temperature of 500–600 °C was found to be a reasonable choice to get better output.
- It was observed that the quality of bio-oil produced by the thermo-catalytic reforming system (TCR®) is significantly better than the bio-oil produced by fast pyrolysis.
- It was reported that the HHVs of bio-oil produced from SCG was much higher than that of bio-oil produced from woody biomass.
- It was found that the SCG bio-oil is more uniform and did not split into aqueous and organic parts in contrast to most bio-oils.
- SCG bio-oil is unattractive as a fuel due to a higher amount of water content, but it can be used as a pesticide.
- The key molecules in the bio-oil from SCG samples are *n*-hexadecanoic acid (palmitic acid), 9-octadecenoic acid (oleic acid), octadecanoic acid (stearic acid).
- The bio-oil derived from SCG has much higher carbon composition than that of bio-oil from mallee.

Our current review also revealed that, only 2 studies been conducted so far to examine the pyrolysis technology on the DSCG. Such conclusion may help the scientific community to propose some pathways to valorize the SCG in a more economical way through the biorefinery in which the extracted oil from the SCG can be valorized for either biofuels or value-added products while the DSCG can be pyrolyzed.

Credit author statement

The contributions of each author to this manuscript were as follow: A.E. Atabani: Pre-writing, Conceptualization, Discussion, Tables preparation, Figures preparation, Writing, Reviewing and Editing. Imtiaz Ali: Conceptualization, Discussion, Figures preparation, Tables preparation, Writing, Reviewing and Editing. Salman Raza Naqvi: Tables preparation, Writing, Reviewing and Editing. Irfan Anjum Badruddin: Discussion, Writing, Reviewing and Editing. Muhammad Aslam; Figures preparation, Writing, Reviewing and Editing. Eyas Mahmoud: Pre-writing, Writing, Reviewing and Editing. Fares Almoani: Tables preparation, Figures preparation, Writing, Reviewing and Editing. Dagmar Juchelková; : Pre-Writing-, Tables preparation, Writing, Reviewing and Editing. M.R. Atelge: Pre-Writing, Tables preparation, Writing, Reviewing and Editing. T.M. Yunus Khan: Pre-Writing, Tables preparation, Writing, Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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