**Valorization of Spent Coffee Grounds into Biofuels and Value-Added Products:
Pathway towards Integrated Bio-refinery**

A.E. Atabani^{1*}, Ala'a H. Al-Muhtaseb^{2*}, Gopalakrishnan Kumar^{3*}, Ganesh Dattatrya Saratale⁴, Muhammad Aslam⁵, Hassnain Abbas Khan⁶, Zafar Said⁷, Eyas Mahmoud⁸

¹Green Processing, Bioremediation, and Alternative Energies Research Group, Faculty of Environment and Labour Safety, Ton Duc Thang University, Ho Chi Minh City, Vietnam

²Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat-Oman

³Institute of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, Box 8600 Forus, 4036 Stavanger, Norway

⁴Department of Food Science and Biotechnology, Dongguk University – Seoul, Ilsandong-gu, Goyang-si, Gyeonggido 10326, Republic of Korea

⁵Department of Chemical Engineering, COMSATS University Islamabad (CUI), Lahore Campus, Defense Road, Off Raiwind Road, Lahore, Pakistan

⁶Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900 Saudi Arabia

⁷Sustainable and Renewable Energy Engineering, College of Engineering, University of Sharjah, PO Box: 27272, Sharjah, United Arab Emirates

⁸Department of Chemical and Petroleum Engineering, College of Engineering, United Arab Emirates University, PO Box: 15551, Al Ain, United Arab Emirates

***Corresponding authors:**

A.E. Atabani

Email: abdulaziz.atabani@tdtu.edu.vn.

Ala'a H. Al-Muhtaseb

Email: muhtaseb@squ.edu.om.

Gopalakrishnan Kumar

Email: gopalakrishnanchml@gmail.com, gopalakrishnan.kumar@uis.no.

Graphical Abstract

Abstract

Coffee is the second largest traded commodity after petroleum and the second most popular beverage after water. This big industry is believed to generate huge amount of waste with spent coffee grounds (SCGs) represents one of the main by-products. Recycling of such waste to fuels and value-added products through bio-refineries is a promising way to solve the problem of many countries that face daily challenges and heavy cost in waste disposal. This review aims to shadow the light on SCGs recycling potential in which over 230 published papers on SCGs recycling topic were gathered and discussed. Various opportunities to produce biofuels such as biodiesel, biogas, bioethanol, bio-oil and fuel pellets besides value-added products such as bioactive compounds, adsorbents, polymers, nanocomposites, and compost were discussed. Moreover, the potential of membrane technology related to various processes of biorefining, separation and purification in the proposed SCG-integrated biorefinery are presented. Based on the presented review, it is obvious that recycling of SCGs offers many worthwhile options to policymakers that can contribute towards huge financial saving on taxpayers of running and maintaining landfills besides saving the environment from harmful emissions. In conclusion, this review emphasizes that SCG-integrated biorefineries to produce different types of biofuels and value-added products are a very promising approach that shall be economically more scrutinized in the foreseen future.

Keywords: *Recycling, Spent coffee grounds, Biofuels, Value-added products, Bio-refinery.*

Nomenclature

AV	Acid value	HDF	Hydrotreated diesel fraction
But	Butanol	HDO	Hydrodeoxygenation
BHD	Bio-hydrogenated diesel	HRT	Hydraulic retention time
CH	Coffee husks	HTL	Hydrothermal liquefaction
CI	Compression ignition	HHV	Higher heating value
CIME	<i>Calophyllum inophyllum</i> methyl ester	IV	Iodine value
CN	Cetane number	KOH	Potassium hydroxide
COD	Chemical oxygen demand	KV	Kinematic viscosity
CP	Cloud point	LHV	Lower heating value
CW	Coffee waste	LCSF	Long chain saturated factor
CS	Coffee silverskin	DME	Dimethyl ether
DSC	Differential scanning calorimetry	MLR	Methanol-lipid ratio (mL-methanol/g-lipid)
DSCG	Defatted spent coffee grounds	NaOH	Sodium hydroxide
D100	Euro diesel	OS	Oxidation stability
DCO	Decarbonylation	Pen	Pentanol
DCO ₂	Decarboxylation	PHAs	polyhydroxyalkanoates
DU	Degree of unsaturation	PMHS	Polymethylhydrosiloxane
FAC	Fatty acid composition	PP	Pour point
FFA	Free fatty acids	SCG	Spent coffee grounds
FAME	Fatty acid methyl esters	SCGO	Spent coffee grounds oil
FAEE	Fatty acid ethyl ester	SCGOME	Spent coffee grounds oil methyl ester
FCG	Fresh coffee grounds	SFE	Supercritical fluid extraction
FP	Flashpoint	SN	Saponification number
FW	Food waste	STW	Spent tea waste
GC	Gas chromatography	TGA	Thermogravimetric analysis
GC-MC	Gas chromatography-mass spectrometry	TG-FTIR	Thermogravimetric analyzer coupled to a Fourier transform infrared spectrometer
H ₂ SO ₄	Sulfuric acid	WCO	Waste cooking oil
HCL	Hydrochloric acid	XRD	X-ray diffraction

1.0 Overview of waste and recycling

The world is producing a huge amount of waste on a daily basis. These mainly include municipal, food, beverage, agricultural, and industrial wastes. Dumping these wastes directly to the landfills is very harmful if not disposed or recycled appropriately as they are toxic and may cause serious environmental problems [1]. This is due to the existence of some organic compounds that demand excessive amounts of oxygen to be degraded [2, 3]. Moreover, direct disposal of waste without assessing its recycling potential may contribute towards huge financial cost on taxpayers who run and maintain landfills [4]. Recycling of waste to energy and value-added products is one effective way to solve the problem of many countries that face a serious challenge in dealing with huge amount of waste generated daily due to their increasing population, industrial growth, and human consumption. Waste recycling offers many environmental, social and financial benefits [5]. It also contributes to producing biofuels and value-added products without the need for growing plants (edible or non-edible) or converting food (edible oils) to fuel [6]. **Fig. 1** highlighted an effective mechanism of recycling waste into products [4]. This pathway can be organized in a sequential, systematic and consistent manner whereby the output of one process becomes the input for another process, thus avoid wasting secondary materials [7].

In this regard, restaurants and beverage shops generate a huge amount of waste such as waste cooking oil (WCO), spent coffee grounds (SCG), food waste (FW), spent tea waste (STW), etc. Among them, SCG is a valuable waste due to its promising characteristics. Direct disposal of SCG to landfills can emit methane, carbon dioxide and greenhouse gases that contribute to global warming [4]. Thus, creating proper waste management plans that are consistent with existing national regulation are much needed [8].

This review article aims to shadow the light on SCG recycling potential. 233 published papers on the topic were gathered to introduce various opportunities to produce biofuels such as biodiesel, biogas, bioethanol, bio-oil and fuel pellets besides value-added products such as bioactive compounds, adsorbents, polymers, nanocomposites, and compost. Moreover, membrane technology for SCG-integrated biorefinery was also introduced in this review. Finally, the current review emphasizes the potential of SCG recycling in which a proposed SCG bio-refinery with many options was presented at the end of the paper. This review article was also enriched with many data that highlighted different important characteristics of SCG.

2.0 Overview of coffee and coffee industry

Coffee was discovered in Ethiopia 1000 years ago [9]. Coffee tree belongs to the family *Rubiaceae*. *Coffea* genus comprises 103 species which are divided into subgenus *Coffea* and subgenus *Baracoffea*. The subgenus *Coffea* includes the species that used in coffee production [10]. *Coffea arabica* (*arabica coffee*) and *Coffea canephora* (*robusta coffee*) have been classified as the most economically and commercially used among others [11, 12]. *Coffea canephora* is less susceptible to disease and can be grown in lower altitude and warmer climate. However, *Coffea Arabica* represents 75-80% of the worldwide coffee production [13, 14]. **Fig. 2** shows coffee fruit(berry/cherry) [15]. The fruit (berry/cherry) can be divided into two main parts, the pericarp and the bean [16]. The pericarp consists of a smooth, tough outer skin usually green in unripe fruits and turns red-violet or deep red when ripe (even yellow or orange in particular genotypes) [17]. The pericarp covers a soft yellowish, fibrous and sweet pulp (outer mesocarp), a highly hydrated layer of mucilage (the pectin layer), and a thin endocarp (the parchment). The bean comprises silver skin, an endosperm, and coffee seed [13, 17]. The fruit (berry/cherry) usually bears two coffee beans [18] (**Fig. 2**). Coffee bean size varies; however, their average size 10 mm long and 6 mm wide [16]. Coffee is grown in about 80 countries [19] with Brazil and Vietnam represent the major coffee producing and exporting countries around the world (35% and 15% respectively) (**Fig. 3**) [20, 21]. The main coffee-brewing methods are boiling (Greek/Turkish, Scandinavian, etc., with caffeine content less than 50 mg cup⁻¹), the filter (filter coffee: caffeine content, 100-150 mg cup⁻¹), the dissolving (instant/soluble coffee: caffeine content, 65-100 mg cup⁻¹), and the pressure method (espresso: caffeine content, 60 mg cup⁻¹). Due to its refreshing properties, millions of cups of coffee are consumed every day worldwide, and thus coffee is the most important food commodity, the second most popular beverage after water and the second largest traded commodity after petroleum [22-25]. Between 2015-2016, more than 9 million tons of coffee products were consumed worldwide (according to International Coffee Organization) resulted in an estimated 3.6 million tons of SCG [26, 27]. In South Korea, a total of 118.8 million kg of coffee were consumed in 2015-2016 compared to 104.9 million kg in 2012-2013 representing annual growth of 4.2% [28]. In Malaysia, a total of 650 thousand bags (60 kg each) were consumed in 2013/14 increasing by 30% from the previous year [29]. Australians consume 6 billion cups of coffee every year [4]. Most of the world's developed countries have the highest per capita coffee consumption with Finland leading the world (11.9 kg per capita) followed by Norway (8.63 kg per capita), Denmark (8.6 kg per capita) and Austria (8.58 kg

per capita) [26, 30]. Coffee beverage has proven to offer many health benefits [3] such as reducing the risk of cancer (liver, kidney, oral, breast and colorectal), cell protection from damage, Neurodegenerative diseases (Parkinson, Alzheimer, and Amyotrophic lateral sclerosis) and cardiovascular disorders [31].

Coffee industry generates large quantities of waste that are either directly disposed in landfills or used as compost [7]. Therefore, proper waste management is needed [23] with SCG, coffee silverskin (CS) and coffee husks (CH) represent the main by-products [32]. According to Kourmentza *et al.*, [9], SCG are available at low-cost of 0.061 USD/kg in Colombia. SCG is considered as the key culprit for contaminating other waste streams [33]. According to [4], coffee industry generates around 6 Mt of waste per year. The UK produces 500,000 tons of SCG each year [34]. As a result, large amounts of dark-coloured waste are generated as 650 kg of SCG are generated from 1 ton of green coffee [23, 32]. Moreover, coffee wastewater generated from this industry contains dissolved and suspended organic carbon with average chemical oxygen demand (COD) between 18,000-30,000 milligrams per litre that can also be valorized in many useful ways among which anaerobic digestion (AD) to produce biogas is the most viable approach [35, 36]. According to Tucker [36], wastewater treatment strategy has resulted in generating 200,000 kW at the CISA pilot site, Diriamba, Nicaragua using biogas plant with annual savings of \$40,000.

3.0 Overview of SCG recycling potential

SCG is the solid residue that is left over after the preparation of an instant coffee beverage with fine particle size, high organic load, and humidity [37]. It represents one of the largest by-products of soluble coffee processing industries representing 40-45% of the fresh weight of coffee cherry [38-41]. **Fig. 4** shows the images of freshly brewed SCG, dried SCG and defatted spent coffee grounds (DSCG) (after lipids removal/extraction) [42].

SCG has been reported to contain large amounts of organic compounds (more than 1000 individual compounds) such as proteins, carbohydrates, tannins, fibres, caffeine, cellulose, non-protein nitrogenous, fatty acids, amino acids, polyphenols, minerals lignin and polysaccharides [43, 44] namely; galactomannans and arabinogalactans [45-47]. Besides more than 700 volatile compounds that remain insoluble and unextractable in SCG during the thermal water extraction process and thus can be valorized in different ways. These components have been proven to possess high quality, organic content and energy content and superior physical properties that must be exploited in an appropriate manner. SCG can be

recycled in different ways to produce various types of biofuels such as biohydrogen [6], biobutanol [1], biodiesel [5, 6, 20, 21, 28, 30, 48-82], fuel pellets [5-7, 51, 65, 66, 79, 83-89], bio-oil [62, 90-100], bioethanol [53, 59, 79, 101, 102], biogas [103-111] and hydrocarbon fuels [112, 113] or value-added products such as bioactive compounds for food, pharmaceutical, cosmetic and chemical industries [2, 29, 40, 114-130] and antioxidants and anti-tumor activities [3, 14, 26, 45, 131-152], adsorbents [7, 32, 153-166], composting [167, 168], co-composting [169-171], vermicomposting [172, 173], nanocomposites [174], biopolymers [175-178], creams-scrubs, soaps and detergents [7], odor control [7], textile [41], facile preparation of pyrolytic carbon as anode in sodium-ion battery [179], inks and screen painting [7], yarn [7] and pulp and paper production [1, 7]. SCG has also been reported to possess functional properties such as water holding capacity (WHC ~ 5.7 g water/g dry SCGs), oil holding capacity (OHC ~ 5.2 g oil/g dry SCGs), emulsifying activity (54.7%) and emulsion stability (92.4%) [25]. An early study conducted by Givens and Barber [180], indicated that SCGs are worthless as a ruminant feed. Simões and Nunes [43] reported that polysaccharides; galactomannans and arabinogalactans are polymers that can be used as dietary fibre and present immune-stimulatory activity. This is also a useful resource for the food industry [40]. An interesting study conducted by Go *et al.*, [181] proposed a way to valorize SCG in which it was first hydrolyzed with sulfuric acid to obtain sugar that can be fermented to bioethanol followed by extracting the lipids from the hydrolyzed SCG known as spent coffee grounds oil (SCGO) to produce biodiesel and glycerin. The DSCG was then proposed for the use either as fuel pellet or soil amendment agent. Alternatively, Kondamudi *et al.*, [6] proposed to extract SCGO followed by converting it to spent coffee grounds oil methyl ester (SCGOME) (biodiesel) while glycerin can be further processed into biohydrogen. DSCG can be then hydrolyzed to produce bioethanol while the remained solid residue can be utilized as fuel pellets. Another pathway proposed by [52, 53, 66] suggested the utilization of glycerin and the solid residue of DSCG after hydrolysis process as fuel pellets instead of biohydrogen production from glycerin. Preliminary calculations conducted by Kondamudi *et al.*, [6] indicated that converting SCGO to SCGOME beside utilizing SCG left after oil extraction (DSCG) as fuel pellets can yield an annual profit of more than \$8 million in the United States alone (considering only the waste generated by Starbucks stores). **Fig. 5** shows the growing number of publications on the coffee industry recycling potential since 1983. Although this figure does not cover all published work on this topic. However, it is obvious that SCG recycling has got much attention especially in the past 8 years (2011

onwards). The following chapters will highlight all recycling potentials of SCG to both biofuels and value-added products with emphasize on biofuels production opportunities.

4.0 Valorization of SCG into biofuels

4.1 Biodiesel

Coffee produces more oil per unit of land area than other traditional biodiesel crops with 386 kg/ha compared to 375 kg/ha for soybean [37]. It has been reported that 90.2% of lipids remain in SCG [8]. Processing the oil extracted from SCGs known as SCGO (brownish colour with concentrated coffee smell) to biodiesel (SCGOME) has been recently investigated in many publications [5, 6, 20, 21, 28, 30, 48-82]. Table 1 shows the advantages and disadvantages of biodiesel production from SCGO compared to other wastes [5, 6, 75]. SCGO has higher stability and cost-effective than other waste sources available to date [5, 6]. SCGO (represented as triolein) ($C_{57}H_{104}O_6$) can be transesterified to methyl oleate ($C_{19}H_{36}O_2$) and glycerol ($C_3H_8O_3$) by the following reaction [30]:

Compared to fresh coffee grounds (FCG), biodiesel from SCG does not contain caffeine that may increase NO_x emissions. For instance, addition of 130 mg of caffeine to 100 g of coffee sample produces around 150 mg/kg of NO_x upon fuel combustion. This value is almost double the Euro 6 standard [20]. Production of biodiesel from SCG could add approximately 340 million gallons of biodiesel to the world's fuel supply per annum [49]. Another pathway proposed that SCGO to be converted either into fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) via non-catalytic transesterification process which shows high tolerance to both FFA moisture content followed by converting DSCG to bioethanol. Following this pathway, the production of FAEE from bioethanol may increases the renewability of SCG industry [6, 53, 59]. On the other hand, DSCG has been also proposed as purification material (activated carbon) to purify SCGOME [78] or to be further processed into bio-oil and bio-char by slow pyrolysis [62]. DSCG can be also used as fuel pellets in pure form [6] or mixed with glycerin (a by-product of biodiesel reaction) as addition of glycerin may enhance the combination of biomass particles besides increasing its heating value [66]. DSCG can be also used as compost as it has excellent C/N ratio (Table 9).

Different types of non-polar solvents such as hexane [5, 6, 21, 27, 28, 42, 48, 50, 52, 53, 59, 62, 64-66, 71, 78, 80, 151, 182-185], toluene, chloroform and n-pentane [64, 186], ethyl

acetate [27], n-octane and n-heptane [50], dichloromethane and diethyl ether [6] and dimethyl ether (DME) [70] and polar solvents such as iso-propanol, 1-butanol, ethanol, and acetone [42, 50, 64, 101, 151, 185, 186] have been employed to extract SCGO. The antioxidant activities of SCGO extracted by polar solvents were reported to be higher than that of SCGO extracted by non-polar solvents. However, these values decreased by one third during biodiesel production process [151].

Other extraction methods of two-phase oil extraction have been reported in [187], ultrasound-assisted solvent extraction has been reported in [59], and supercritical fluid extraction (SFE) using CO₂ has been reported in [44, 184, 188-190] achieving 0.61-0.81 of n-hexane soxhlet extraction value [189]. A comparison among these methods revealed some drawbacks of soxhlet extraction and SFE along with some advantages of ultrasound-assisted solvent extraction method. Soxhlet oil extraction method is a relatively time-consuming process that requires a larger amount of solvent and energy to complete the extraction besides having low productivity. Moreover, SFE requires feedstock with very low water content besides the process requires high temperature and pressure and thus high energy demand. SFE also requires highly qualified labour [7].

On the other hand, ultrasound-assisted solvent extraction has been effectively applied in the extraction of some oils with the ability to enhance the oil extraction from feedstocks having either low or high moisture contents and at a low energy cost [59]. Moreover, some solvents such as hexane are classified as hazardous air pollutants as they cause ozone formation at the ground level which consequently forms smog [191]. Sakuragi *et al.*, [70] reported the use of liquefied dimethyl ether (DME) as environmentally friendly, energy saving and low boiling solvent for oil extraction. The oil content of SCG was satisfactory (16.8±1%). The study also indicated that SCG has a higher oil content than other wastes such as soybean cake (0.97±0.05%) and rapeseed cake (2.6±0.2) respectively. Couto *et al.*, [190] reported that utilization of ethanol as a co-solvent at ethanol:CO₂ mass ratio of 6.5:93.5 (w/w), 20 MPa and 323 K achieved oil yield of 19.4% higher than without ethanol (13.1%) at the same pressure and temperature and higher than soxhlet extraction with n-hexane (18.3%). Mechanical extraction using hydraulic ram pressing and screw press has been reported in [192] and applying pressure with minimum quantities of solvents (ether or ethyl alcohol) that can be recycled back has been reported in [7]. This method has been developed at Università di Napoli Federico II, Italy. **Table 2** highlights the oil content of SCG obtained from various resources [5, 6, 20, 21, 28, 42, 44, 48, 50, 52, 54, 56, 59, 61, 64-70, 77, 78, 80, 82, 113, 151,

176, 183, 184, 188-190]. Variations in oil content are attributed to the type of extraction process, solvent used, time, temperature, liquid-solid ratio (LSR) and conditions of SCG. Liquid-solid ratio (LSR) has been reported to be the main parameter that affects the lipid extraction from SCG [28].

The results of acid value (AV) (mg KOH/ g oil) of SCGO reported in literature are tabulated in **Table 3 [5, 21, 50, 52-54, 56, 59, 61, 62, 64-67, 74, 80, 82, 113, 151]**. The variations in AV can be attributed to the prolonged storage duration of SCG especially at high storage temperature (25-40 °C) and moisture content (11.8%) which increase the AV of SCGO [183]. Since SCGO has been reported to have relatively high AV (**Table 3**) and as SCG has good HHV (**Table 7**), it has been proposed that SCG to be directly combusted in boilers or processed into other value-added products such as fertilizer as its rich in nitrogen (**Table 8**) [51]. Another recent study suggested the concept of pre-blending in which SCGO can be blended with other oils that have low AV to reduce its high acidity prior to biodiesel production [81].

SCGO has been proposed to improve the oxidation stability of biodiesel obtained from other feedstocks by three main approaches namely, blending SCGO with other oils at different percentages [81, 151], soaking powder of SCG in the reaction mixture during biodiesel production process or adding methanol extracts from SCG. All approaches were reported to remarkably improve the oxidation stability of biodiesel obtained from waste rapeseed from 1 to 3 h, besides methods 2) and 3) being simple [151].

The main feature in SCGOME is that it has a low degree of unsaturation (DU) with high long-chain saturated factor (LCSF) [5]. According to [6, 20, 28, 37, 44, 50, 52-54, 57, 59, 61, 62, 65, 66, 69, 71, 77, 182, 183, 186, 188-190, 192], fatty acids composition (FAC) of SCGOME is mainly dominated by linoleic and palmitic acids followed by oleic, stearic and arachidic acids. This FAC structure yields a biodiesel with high cetane number (CN) and oxidation stability (OS), lower iodine value (IV), acceptable higher heating value (HHV) and flash point (FP) besides higher cloud point (CP), pour point (PP), cold filter plugging point (CFPP) and kinematic viscosity (KV) higher than 5 mm²/s at 40 °C. Linoleic acid has excellent emollient properties that can be utilized as a component for the prolongation of skin barrier while palmitic acid can protect skin from ultraviolet ray affection [130]. **Tables 4-6** show a comparison of SCGO properties, FAC and SCGOME properties collected from various resources. The properties of SCGOME and its blends with Euro diesel (D100) and butanol

have been reported in [5], SCGOME and its blends with butanol, pentanol, hexanol and Euro diesel (D100) have been reported in [81] while the properties of SCGOME and its blends with diesel (B5 and B20) has been reported in [62].

Oil content and some fuel properties of SCGOME from 8 different geographical locations including; Costa Rica, Honduras, Ethiopia, Indonesia, Kenya, Columbia, Brazil, and Vietnam has been reported by [20]. Analyses of all samples indicated that SCG contains in average 7-14% lipids. FAC of all samples contains high percentages of linolenic acid (44-50%), palmitic acid (35-40%) with low percentages of stearic (7-8%) and oleic (7-8%) acids. Analyses of fuel properties of SCGOME indicated that KV ranges between 3.5-5.5 mm²/s, density between 841-927 kg/m³ and PP between -1 to 16 °C. SCGOME has been reported to have similar KV, HHV and flash point but higher density compared to *Calophyllum inophyllum* methyl ester (CIME) (Table 6) [193].

From literature, SCGOME can be produced by four main pathways:

- 1- Direct transesterification with catalytic alkaline-based transesterification or acid-catalyzed esterification [6, 20, 28, 53, 56, 60, 64, 65, 70, 82, 182], methanol/carbon dioxide mixtures [68] and enzymatic catalysis/biocatalyst such as *Candida rugose*, *Porcine pancreas*, *Pseudomonas fluorescens*, *Candida Antarctica* lipase-B *Mucor miehei*, *Pseudomonas cepacia*, *Rhizopus delemar*, *Thermomyces lanuginosus*, *Geotrichum candidum* and *Candida rugosa* [48, 60, 71, 80, 194].
- 2- Catalytic reaction of two steps of acid-catalyzed esterification followed by alkaline-based transesterification [5, 21, 50, 52, 59, 62, 64, 66, 78].
- 3- Non-catalytic transesterification [53].
- 4- *In-situ* transesterification [54, 57, 61, 69, 72-74, 77].

4.1.1 Insight into in-situ transesterification as a promising biodiesel production method from SCG

Liu *et al.*, [54] proposed an alternative pathway to obtain SCGOME directly from SCG (in-situ) without the need for the solvent extraction process. Before that, the oil content of SCG was determined to be 17.32±0.93 wt.%. The process was conducted in a Soxhlet apparatus in which SCG were impregnated with H₂SO₄ at various concentrations (5-20% of dry SCGs weight) for esterification process since the AV of SCGO was in the range 6.18-6.94 mg KOH/g oil. The optimum reaction condition was 70 °C and 12 h with 20 wt.% H₂SO₄. This was

followed by adding deionized water and heating the slurry at 70 °C with stirring for 3 h and then dried in an oven for 24 h at 105 °C. The dried impregnated SCGs were load in cellulosic thimble where methanol was placed in the distillation flask to perform the transesterification process. The results of the FAC of SCGOME showed that it has 44.3% palmitic acid (C16:0) followed by 30.8% linoleic acid (C18:2), 9.7% stearic acid (C18:0), 6.1% oleic acid (C18:1), 3.3% arachidic acid (C20:0) and small fractions of linolenic acid (C18:3) and behenic acid (C22:0) of 0.8 and 0.3% respectively. Biodiesel yield was 17.08 ± 0.70 wt.% based on SCG. This was equivalent to oil to biodiesel conversion of 98.61 wt.%. Under the optimal reaction condition of 12 h, the KV of biodiesel was $5.36 \text{ mm}^2/\text{s}$ with OS of 6.62 h which met ASTM D6751 standards. However, AV of biodiesel was 0.8 mg KOH/ g which failed to satisfy ASTM D6751 standards. Thus, SCGOME was washed with 1% NaOH, and the AV of the final product was reduced to 0.31 mg KOH/g to meet ASTM D6751 standards of maximum 0.5 mg KOH/ g.

Park *et al.*, [57] conducted in-situ transesterification in which 0.6 g of SCG was mixed with methanol, chloroform as a solvent and H_2SO_4 . Different reaction parameters to optimize the production of SCGOME were set as follow, methanol (0.25-3 ml), chloroform (0-2 ml) and H_2SO_4 (0-0.3 ml). The effect of moist content was also studied besides some other acid catalysts such as nitric acid, HCl and acetic acid. It has been found the maximum FAME yield was over 16.75 wt.% at 95 °C. H_2SO_4 and HCl were found the best catalysts. FAC of SCGOME was dominated by linoleic acid (C18:2) (41.88%) and palmitic acid (C16:0) (35.4%) followed by oleic acid (C18:1) (9.22%) and stearic acid (C18:0) (6.72%) respectively.

Tuntiwiwattanapun *et al.*, [61] studied in-situ transesterification process for SCG into SCGOME. After sun drying, five different sizes of SCG were fractionated using US sieve sizes No. 12 (1.68 mm), 16 (1.19 mm), 18 (1.00 mm), 40 (0.42 mm) and 60 (0.25 mm). AV was calculated as 5.93 ± 0.02 mg KOH/g oil, and oil content was 18.8 ± 0.5 . To reduce the AV, 36 g of each SCG fraction was deacidified by washing with 120 ml methanol and mixed at 15.7 rad/s for 1 h at 45 °C. The slurry was filtered and rinsed with 15ml methanol followed by drying in an oven at 75 °C overnight. Afterwards, a solution containing 2.225 NaOH was dissolved in 250 ml methanol followed by suspending 30 g of deacidified SCG in 105 ml methanol in the reactor while mixing at 15.7 rad/s for 3 h at a temperature between 30 and 60°C. A calculated amount of H_2SO_4 then neutralized the catalyst. The slurry was then filtered and rinsed with methanol. Methanol was then removed by rotary evaporator. The

product was then transferred to a separation funnel in which n-hexane was added to separate SCGOME from glycerol. The mixture of SCGOME-hexane was then washed 2 times with deionized water. The product was finally incubated for 2 h in a water bath at 50 °C to remove hexane. Finally, SCGOME was incubated in an oven at 105 °C for 1 hour to remove moisture. FAC was mainly comprised of 42% linoleic acid (C18:2), 34% palmitic acid (C16:0), 11% oleic acid (C18:1), 7% stearic acid (C18:0), 3% arachidonic acid (C20:4) and 3% other fatty acids. The KV of SCGOME was $4.18 \pm 0.03 \text{ mm}^2/\text{s}$ which satisfies ASTM D 6751 standards. However, AV ($1.4 \pm 0.18 \text{ mg KOH/g}$) did not satisfy ASTM D6751 standards of maximum 0.5 mg KOH/g. In another study, Tuntiwiwattanapun *et al.*, [77] proposed an optimized methanol washing pretreatment process of SCG (3.7 ml methanol/1 g SCG, 30 °C, 1h) that successfully reduce its acid value from 10.28 mg KOH/g oil to 0.78 mg KOH/g oil. This was followed by in-situ transesterification of SCG. Optimized parameters of 2.5 g of KOH in 100 cm³ methanol with 25% isopropanol (by volume) to 1g of SCG at 30 °C for 1h achieved a biodiesel yield of 10.2% SCGOME/SCG. FAC of the extracted oil was mainly comprised of 45% linoleic acid (C18:2), 35% palmitic acid (C16:0), 9% oleic acid (C18:1), 6% stearic acid (C18:0), 3% arachidonic acid (C20:4)

Son *et al.*, [72] applied in-situ transesterification process for wet SCG with supercritical methanol. Optimized biodiesel yield of 10.17 wt.% of dry SCG mass was obtained at reaction conditions of 270 °C, 90 bars, space loading 58.4 ml/g, methanol to wet SCG ratio 5:1 and reaction time 20 min. Park *et al.*, [73] attempt to investigate the solvothermal effect of 1,2-dichloroethane (DCE) for in-situ transesterification of SCG with ethanol over 160 °C. An optimized yield of biodiesel (fatty acid ethyl ester) of 11.8 wt.% (mass of dried SCG) was obtained with 3.36 ml ethanol and 3.16 ml DCE at 196.8 °C. In both studies, authors indicated that this process eliminates the need for the drying process, extraction process and acid catalyst providing not only economic feasibility but also the environmental advantage of recycling waste.

Calixto *et al.*, [68] indicated that 89.4% of SCOME yield is obtained when using supercritical methanol in-situ transesterification process of SCG (473-603 K, 10-30 MPa). Carbon dioxide (CO₂) was then added to methanol to reduce the temperature and pressure. It has been found that at a reaction temperature of 573 K, the pressure of 10.0 MPa and a CO₂/MeOH molar ratio of 0.11 yielded 93.4% of SCGOME.

4.2 Fuel pellet

Several studies examined and highlighted the potential of SCG as fuel pellets [5-7, 51, 65, 66, 79, 83-89]. Table 7 conducts a comparison between the calorific values of SCG, DSCG and other biomass residues [5, 14, 51, 52, 62, 65, 70, 80, 83, 84, 88-90, 181, 192]. The results of SCG range between (19.3-24.913 MJ/kg) while for DSCG range between (19-21.54 MJ/kg). The heat of combustion of SCG (kg/kg dry) at different degrees of humidity (w.b.) has been reported and compared with different biomass in [84]. Authors indicated that, SCG compared to other biomass is considered as an excellent fuel as it has a higher heat of combustion indicating that coffee industry could become self-sufficient in thermal energy with some technological advancements and investment to improve the performance of boilers. Energy, emissions and combustion characteristics of agro-pellets from pure SCG and SCG mixed with pine sawdust in a residential pellet boiler has been investigated by [87]. It was found that the use of pure SCG lowered boiler efficiency along with an increase in particle and gas emissions. However, when SCG was mixed with pine sawdust (50/50 wt.%), combustion parameters (emissions and boiler efficiency) were very close to wood pellets and satisfied the NF agro-pellets standard (French standards) which are essential to selling before commercializing it. The same conclusion was confirmed by Jeguirim *et al.*, [86].

Addition of 10% and 25% of SCG to beech wood increased its calorific values from 18.77 MJ/kg to 19.12 MJ/kg and 20.32 MJ/kg respectively [88]. The effect of mixing DSCG with glycerin (content from 20-40%) has been reported in [66] in which glycerin was obtained as a by-product of biodiesel production from SCGO. It has been found that mixing DSCG with 40% glycerin yield a heating value of 21.6 MJ/kg compared to 19.3 MJ/kg (20% glycerin). Similar work has been reported by Potip and Wongwuttanasatian [89] who examined the effect of mixing SCG with crude glycerol at different ratios of 100:0, 95:5 and 90:10 and different theoretical air supply of 550%, 700%, 850%, and 1000%. Both parameters have been found to affect the combustion of SCG briquettes. The combustion equation of 100% theoretical air for 100g SCG and 1-mole crude glycerol can be written as follow:

Increasing the percentage of glycerol in the briquettes from 5-10% increased the heating value to 21.21 and 21.55 MJ/kg respectively compared to 21.14 MJ/kg of SCG with increasing the burning rate up to 53.8% and 10% higher combustion temperatures. Results showed that the briquette ratio of 90(SCG):10(glycerol) and 850% theoretical air gave the maximum temperature and combustion rate of 533.4 °C and 0.20 g/s respectively. Compositions of the exhaust gases, namely carbon monoxide, nitrogen dioxide, sulfur dioxide) and acrolein gas were all satisfying the international standards.

4.3 Bio-oil

Pyrolysis is a physicochemical process of thermal decomposition of organic substances, occurring under inert atmosphere (Nitrogen), limited oxygen and high temperatures between 500-1000 °C. Pyrolysis degradation yields liquid (bio-oil and water phase), biochar and syngas [91, 96, 99]. These proportions depend on pyrolysis technique and reaction parameters (slow or fast pyrolysis) [99]. Bio-oil can be utilized as fuel or chemical [96] while bio-char can be used as an energy source, adsorbent, soil amendment or land applied for carbon sequestration [94]. Several studies examined the pyrolysis potential of both SCG and DSCG as a source for bio-oil and biochar [62, 90, 92-96, 98-100] while the co-pyrolysis (co-liquefaction) of SCG with polypropylene (plastic) has been reported in [91] and paper filter, corn stalk, and white pine have been reported in [97]. Co-pyrolysis causes improvement in both oil yield and crude oil quality. Improvement in KV and molecular weight was obtained following this concept. The optimum conditions were the temperature of 250 °C and a mixing ratio of 1:1.

The effects of different operating parameters such as retention times (5 min, 10 min, 15 min, 20 min and 25 min), reaction temperatures (200, 225, 250, 275 and 300 °C), water/feedstock mass ratios (5:1, 10:1, 15:1 and 20:1) and initial pressure of process gas (2.0 MPa and 0.5 MPa) on bio-oil yield from SCG via hydrothermal liquefaction (HTL) in a stainless-steel autoclave reactor under Nitrogen was investigated by [90]. The highest bio-oil yield of 47.28% (mass fraction) was obtained at optimized conditions of 275 °C, 10 min retention time and water/feedstock mass ratio of 20:1 with an initial pressure of 2.0 MPa.

The effect of temperature on bio-oil yield has been studied by [93]. The highest yield of bio-oil was obtained 823 K (54.85 wt.%) compared to 36.75 wt.% at 673 K and then decreased at 873 K. In contrast to that, the highest bio-oil yield of 61.8% of was obtained at 773 K [94]. Similar to [99] who achieved a maximum bio-oil yield of 56.09±0.22 (wt.%), 21.98 (wt.%)

syngas and $21.93 \pm 0.19\%$ (wt.%) bio-char through fast pyrolysis of SCG, [96] who achieved a maximum bio-oil yield of 30.51% (mass fraction) at the same temperature (773 K), 66 wt.% at around 627 °C (900 K) [95] and 36 wt% at 813 K [100].

A detailed comparison of HHV and elemental composition (ultimate analysis) of SCG, DSCG and bio-oils derived from SCG and DSCG and other biomass are shown in **Table 8** [5, 42, 50, 51, 62, 65, 70, 86-88, 90, 92-95, 97, 100, 105, 106, 110, 111].

From **Table 8**, it can be seen that conversion of both SCG and DSCG to bio-oil seems to be more practical compared to many other woody biomass which have lower energy content (19-21 MJ/kg). It can be also concluded that bio-oil from SCG has higher HHV than DSCG due to lower carbon and hydrogen contents and higher oxygen content in bio-oil from DSCG caused by lipids extraction [62]. Moreover, combustion of bio-oil from DSCG may cause higher NO_x emissions as it has relatively higher Nitrogen content than SCG.

4.4 Bioethanol

The potential of producing bioethanol from SCG has been highlighted in [53, 59, 79, 101, 102]. Nevertheless, direct conversion of SCG to bioethanol (without oil extraction) has been reported to be not feasible due to the existence of triglyceride and FFA which inhibits the activity of enzymatic saccharification process [53]. This indicates that lipid extraction from the SCG is vital to produce bioethanol where lipids can be utilized to produce biodiesel. Such strategy would set the initial stage of bio-refinery from SCG industry as SCGO can be reacted with bioethanol to produce FAEE [53, 59]. Another practical pathway for SCG bio-refinery in which phenolic extraction with ethanol was applied to obtain chlorogenic acid prior to produce bioethanol was proposed by [101]. This pathway increased the percentage of sugars in the solids and the sugar release efficiency. This is because of the extraction of phenolic enhanced the breakdown of polymers with no loss of soluble sugars. The yield of bioethanol from DSCG has been reported to be 0.43 g/g [53] and 0.50 g/g [59] compared to 39 g/L phenolic extracted and 22 g/L non-extracted phenolic SCG [101].

4.5 Biogas

The potential of producing biogas from SCG through anaerobic digestion and co-digestion has been recently investigated in [103-111]. SCG is a valuable material for fermentation process due to its excellent elemental composition and C/N ratio (**Table 8**), chemical composition, and existence of polysaccharides, proteins, and minerals [104]. **Table 9** shows

the composition of SCG collected from literature [1, 7, 80, 97, 103, 104, 106, 108-111, 127, 163, 195]. Mineral composition of SCG has been reported in [103, 163]. Composition varies from one study to another. This is attributed to the different varieties of coffee used in production [84]. Anaerobic digestion of coffee waste (CW) [196, 197] and generated coffee wastewater [35, 36, 198] has also been described earlier. Anaerobic digestion of SCG under mesophilic conditions have been reported in [104, 111] while thermophilic conditions have been reported in [106, 110]. Biogas yields has been reported to range from 0.500-0.598 m³/kg dry organic matter with methane concentration 55-61% [104], in agreement with [107] (0.54 m³/kg). The methane production ranged from 0.271-0.325 m³/kg dry organic matter [104], in agreement with [197] (0.25-0.28 m³/kg), [196] (0.24-0.28 m³CH₄/kg VS_{initial}), [105] 296 ml.CH₄/g-VS, and [111, 197] (0.36 m³ CH₄/kg VS).

According to Lus *et al.*, [105], anaerobic co-digestion of SCG with cow manure achieved a 48% increase in biogas yield with 53.7% methane (CH₄) and 37.8% CO₂ yield. The output of CH₄ was 296ml.CH₄/g-VS. Kim *et al.*, [103] have evaluated the feasibility of anaerobic co-digestion of SCG with various organic wastes, i.e., FW, Ulva biomass, waste activated sludge, and whey. Co-digestion of SCG with the other co-substrates showed similar or higher methane production than pure SCG. Among all substrates, the highest cumulative methane production of 0.355±0.09 L CH₄/g VS_{in} was reported for FW75SCG25 which was 13.1% higher than pure SCG. Similar improvement pattern was reported by authors when co-digesting SCG with Ulva biomass (2.5% COD basis) achieving 51.8% of CH₄ [109].

4.6 Hydrocarbon fuels

Most of the published work on SCGO indicated that single alkaline-catalyzed transesterification reaction is impossible to directly convert it to biodiesel due to its high AV value besides the high saturation level in SCGO yields biodiesel with high CP, PP, and CFPP which causes many problems in fuel tank especially in cold regions. Therefore, production of hydrocarbon fuels from SCGO has been suggested in [112, 113] as another option to produce biofuels from SCGO. It has been reported that in every 1kg SCG, 77g of hydrocarbons is produced allowing a driving distance of ~2.4km (AudiA31. 6TDIULTRA, ~3.2L/100km) [112].

Hydrotreating process of SCGO to produce hydrotreated diesel fraction (HDF) using catalysts such as NiMo/γ-Al₂O₃ and Pd/C has been reported by [113] while polymethylhydrosiloxane (PMHS) has been reported by [112]. **Table 10** shows a comparison of HDF and commercial

bio-hydrogenated diesel (BHD) properties. It can be seen that the HDF catalyzed by NiMo/ γ -Al₂O₃ exhibits lower density and KV and higher cetane index compared to HDF catalyzed by Pd/C. These results support that NiMo/ γ -Al₂O₃ has higher catalytic activity over Pd/C. These results also show that BHD has lower density and kinematic viscosity than SCGOME.

5.0 Valorization of SCG into value-added products

SCG contains large amounts of organic compounds (more than 1000 individual compounds) such as proteins, carbohydrates, tannins, fibers, cellulose, non-protein nitrogenous, fatty acids, amino acids, polyphenols, minerals lignin and polysaccharides [8, 38, 41, 43, 44, 63, 80, 124] namely; galactomannans and arabinogalactans [43, 45-47] besides more than 700 volatile compounds that remain insoluble in SCG and thus can be toxic to the environment. SCG retain approximately 70% of the polysaccharides present in the roasted coffee beans [124]. SCG contains various bioactive compounds such as polyphenols, flavonoids, sugars, proteins, and Millard reaction products. It has been reported to contain a considerable amount of protein (8.97-17.44%), carbohydrates (78.5%), ash (1.3-2.77%), tannins (30.36%), nitrogen content (2.03-3.97%) and cellulose (8.6-24.3%) (Tables 8 & 9) making it a promising material for bioactive compounds and compost besides its huge potential as adsorbent and nanocomposite. These compounds can be used as antioxidants and antimicrobial agents in food, cosmetics and pharmaceutical industries [38, 124]. Polysaccharides; galactomannans and arabinogalactans are polymers that can be used as dietary fibre and present immune-stimulatory activity [43]. This is also a useful resource for the food industry [40]. Moreover, SCG has a high potential as an adsorbent with environmental and economic benefits [160]. SCG and DSCG are ideal compost for the soil since they C/N ratio higher than 20:1 [52]. DSCG have vital applications in cosmetic products due to its high levels of linoleic acid and palmitic acid [29]. SCG, SCGO and DSCG have been found to be excellent substrate for polyhydroxyalkanoates (PHAs) production due to the higher number of carbon atoms per weight. This indicates the high potential of coffee industry to produce biopolymers [175-178] and thus eliminates the need of using edible oil plants. However, it was concluded that additional work is required to increase biopolymers yield (for instance only 8wt% of residue per total mass of polyol obtained from SCG) [178]. A summary of SCG recycling potential to produce value-added products is highlighted in Table 11.

6.0 Membrane technology for SCG-integrated biorefinery

Membrane technology has the potential to play an anchor role in process intensification, biofuels or other value-added products separation and purification in the SCG-integrated biorefinery production process. Among the different separation techniques, membrane technology facilitates a highly selective separation and fractionation capabilities, reduced chemical consumption and labour costs, fewer requirements of floor space, wide flexibility in operation and energy saving separation [199, 200]. Membrane technology is associated to various processes of SCG-integrated biorefinery such as separation and purification of distinct molecules, removal and/or recovery of process inhibitors and enzymes from hydrolysis, biogas upgrading; and production of bioethanol, biodiesel, bio-oil, hydrocarbon fuels, hydrogen and bioethanol dehydration. The membrane is an ultra-thin semipermeable barrier which is placed between two fluids to separate them by permitting transport of one or more components from one fluid to other. It is a mass transfer unit operation employed for separation of gas and liquid streams in an SCG-integrated biorefinery. Membranes utilized in bioseparation are semi-permeable and porous in nature to separate a variety of process streams and composed of organic polymers, ceramics, metals as well as gas and liquid membranes. In recent years, inorganic and hybrid membranes are commonly used. The fluid that passes through the membrane is called permeate and the fluid which is left behind is called retentate [201, 202]. A variety of specific membrane processes are of particular interest for SCG-integrated biorefinery such as microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), membrane distillation (MD), vacuum filtration, pervaporation (PV), diafiltration (DF), dialysis and hyperfiltration (reverse osmosis). PV membrane is non-porous and separation driving force is a chemical potential gradient, whereas MD is equipped with porous hydrophobic membrane driven by a thermal gradient. On the other hand, membranes of UF, MF and NF processes are also porous, but the driving force is hydrostatic pressure. The flat sheet/plate and frame, hollow fibre and spiral-wound modules are the commonly used configurations [203]. The characteristics and applications of various membrane processes for SCG-integrated biorefinery are presented in **Table 12**.

In SCG-integrated biorefinery, membranes would be employed in upstream and downstream separation and purification to concentrate and recover the biofuels and value-added products. Pervaporation, hyperfiltration and gas/ vapour permeation have been suggested for producing bioethanol. Hyperfiltration membranes are required which can primary reject water in the presence of bioethanol. Mehta [204] firstly conducted a preliminary evaluation of bioethanol

dehydration by employing a hypothetical hyperfiltration membrane. After that, Leeper and Tsao [205] adapted two ways of hyperfiltration for recovery and purification of bioethanol, which resulted in a significant reduction in energy demand for bioethanol recovery. Vapour permeation is a membrane process in which components pass through the membrane entirely in the vapour phase. Pervaporation is a new development in membrane separations, which includes phase change and potential for bioethanol production. Since, it does not depend on vapour-liquid equilibrium, azeotropes and close boiling liquid can be separated efficiently. LURGI pervaporator integrated with a special plate type membranes and permeate condenser has been proposed for effective bioethanol recovery in biorefinery concept at commercial scale. About three decades earlier, Sander and Soukup [206] presented the operation and design of pervaporation plant for bioethanol dehydration, which revealed the potential of membrane technology for biofuel separation and purification.

Bio-oil produced is contaminated with finer particles ($<10\ \mu\text{m}$), leading to problems with end-use, storage and necessitating further treatment. Conventional techniques such as cyclone filtration and hot gas filtration only remove the larger particles ($>10\ \mu\text{m}$) [207]. Javaid *et al.*, [208] applied microfiltration to explore the feasibility of removing finer particles. The results demonstrated that microfiltration decreased the overall finer ash contents in bio-oil significantly. Moreover, the concentration of critical constituents associated with bio-oils energy content was not affected by microfiltration process. Similarly, biodiesel also contains some intermediates and residual compounds produced in the reaction in addition to the main product of fatty acid alkyl esters (FAAE) and byproduct glycerol. These contaminants will negatively influence both environment and engine at end-user [209]. Currently, membrane separation is new to biodiesel production but recent studies have revealed the promising potential for enhanced efficiency. Membranes can be installed in either membrane reactor for transesterification or as a final separation and purification to refine biodiesel. Membrane reactors combined the reaction and membrane filtration into a single process, leading to enhanced conversion for equilibrium limited reactions by taking out reaction products from the reactor through membranes. The glycerol from the crude biodiesel and enzymatic reaction was removed using membrane extraction, while membrane separation processes are employed to remove glycerol during biodiesel refinement [210]. Mostly, inorganic membrane reactors were used and high oil to FAME conversion was observed. Baroutian *et al.*, [211] compared the chemical and physical properties of biodiesel produced by membrane reactors with standard specifications. The produced biodiesel was of high efficiency and fulfil ASTM

standard limits of all the properties. However, performance and economic aspects of large-scale membrane systems have not been examined for the treatment of bio-oil and biodiesel at industrial scale.

Biohydrogen and biogas produced in SCG-integrated biorefinery also required upgrading and enhancement to utilize as a substitute for natural gas or its exploration as a transport fuel. Apart from methane, other gases (such as CO₂, H₂S or N₂) in biogas are not required and are pondered as biogas pollutants because higher contents of these gases lower the lower calorific value (CLV) in biogas. Presently, different chemical/physical/biological technologies are available at a commercial level to separate/transform to upgrade biogas and biohydrogen, including adsorption, absorption and membrane separation [212]. However, conventional technologies are cost-intensive. In contrast, membrane technology is a promising cost-effective technique for biogas and biohydrogen upgrading and enhancement [213]. The selective permeability characteristics of membranes permit the separation of the biogas and hydrogen components. The rate of permeation depends on the sorption coefficient of gases and the membrane materials, affecting the selectivity [214]. Presently, four main manufacturing configurations exist for gas-gas membrane cascades including single-stage, two-stage with a recirculation circle, two stage with a stream of biogas sweeping and three stage with sweep biogas stream [215, 216]. In SCG-integrated biorefinery, the role of produced biogas and hydrogen in the energy system creates an environmental and economic incentive for graduation and enhancement.

One of the key challenges in the use of membrane technology for SCG-integrated biorefinery is membrane fouling. The solidify solutes/contaminants accumulate on the membrane surface and/or within the pore matrix, as a result, increase the filtration resistance and decrease the membrane performance [217]. Membrane fouling mechanism varied depending on the process such as the cake layer and gel layer formation, pore-clogging/plugging and adsorption/desorption [218]. This would lead to frequent cleaning and/or subsequent membrane replacement, resulting in higher operating and capital costs. Most of the studies focused on the process efficiency and limited attention paid to address the membrane fouling problems, wherever membrane technology is applied for bioenergy production and biorefinery [201]. Membrane fouling would be organic, inorganic, reversible/irreversible, microorganism fouling during the separation and purification of bioethanol, bio-oil, biodiesel, glycerol, biogas, biohydrogen, enzymes and inhibitors depending on the compositions of feed and system characteristics. Recently, energy efficient fouling mitigation strategies have been

developed including new membrane material developments; control the properties of the bulk fluid in the system, optimization of operating conditions, addition biocarriers, chemical enhanced backwash and different biological ways to reduce fouling in an effective way [219, 220].

7.0 Proposed SCG bio-refinery

Characteristics of SCG are a determinant factor in deciding the bio-refinery design of SCG industry. In this review, several important characteristics such as elemental composition (SCG and DSCG), chemical compositions (SCG), calorific value (SCG and DSCG), oil content (SCG), fatty acid composition (SCGOME), physical and chemical properties (SCGO and SCGOME), etc. were presented. Moreover, several opportunities to produce biofuels and value-added products were presented in **Sections 4 and 5**. Some earlier studies have proposed some pathways to recycle SCG such as [6, 52, 53, 66, 181]. Based on the presented review, a complete SCG bio-refinery is presented in **Fig. 6 (a)**. Based on the evaluation of about 233 published research work on SCG recycling, the best pathway of SCG recycling is to extract the oil to obtain SCGO and the remaining cake (DSCG). As can be seen in **Fig. 6 (b)** following this pathway allows to produce 7 different biofuels namely; bioethanol, bio-oil, biodiesel, hydrocarbon fuel, biogas, biohydrogen, and fuel pellets and 5 valuable added value products namely; bioactive compounds, adsorbents, compost, biochar, and glycerin. Therefore, 12 useful products can be obtained from SCG refineries. This opens the gates to protect the environment from harmful emissions caused by the organic compounds presented in SCG, create new jobs, produce biofuels and value-added products and alleviate the tax on landfills.

8.0 Valorization of other coffee industry by-products

Although coffee husks (CH), peel and pulp comprise nearly 45% of the cherry are the main residue of coffee agro-industry [8, 17], most of research done on coffee industry by-products focused on SCG while others valuable residual such as its exocarp (skin), mesocarp (mucilage), and endocarp (parchment), CS and pulp which are produced during the manufacturing process have been relatively rarely investigated [221].

Caffeine content, total polyphenol content and total antioxidant capacity of CS has been reported in [3, 13, 22, 222, 223]. The caffeine content in CS was 10 ± 1.1 mg/g of CS, 3.5 times lower than most coffee brews, Total polyphenol content and total antioxidant capacity

of CS was equal to 16.1 ± 1.2 mg/g of CS and 138.8 ± 14.8 mmol of reduced iron per kg of CS respectively. This is similar to other sources of food antioxidants such as dark chocolate, herbs, and spices. Therefore, CS can be used as an excellent food supplement as it can increase the total antioxidant capacity of various food products. Moreover, it can serve as a good source for phenolic compounds (chlorogenic acids) that can be used as a useful medicine against several chronic diseases. Similarly, CH, skin, and pulp can be a source of phytochemicals for the food and pharmaceutical industries since four major classes of polyphenols (viz., flavan-3-ols, hydroxycinnamic acids, flavonols, and anthocyanidins) exist. Moreover, they are rich in carbohydrates (35%), proteins (5.2%), fibers (30.8%) and minerals (10.7%) [17]. The production of low-cost adsorbents from CH has been reported by [224]. The potential of coffee pulp and CH to produce enzymes, aroma compounds, mushrooms, compost and vermicomposting have been reported by [225]. Authors also indicated the potential of CH hydrolysate to be used as a substrate for bioprocesses. Valorization of CH to produce biogas [18, 19], bioethanol, solid biofuels besides composting and vermicomposting [18] has also been reported. Bioethanol production from coffee mucilage [221, 226] and coffee pulp [227], coffee residue [228] using *Saccharomyces cerevisiae* as yeast has been reported. CS has been reported to be a valuable source of soluble dietary fibre [3, 222].

Biohydrogen production through co-digestion of coffee mucilage and swine manure at a C/N ratio 53.4 and increase in organic load to improve hydrogen production has been reported by [229]. Biogas production from a mixture of coffee seed skin, seed refuse and coffee product refuse has been reported in [230], coffee pulp has been reported in [231], while improving biogas yield through co-digestion of coffee-pulp and cow-dung in mesophilic conditions has been reported in [232, 233].

9.0 Concluding remarks and future perspectives

In this review, the opportunities for recycling SCG into biofuels and value-added products were presented. Moreover, other wastes generated from this industry such as coffee husk, coffee pulp, and coffee silverskin have also been highlighted. SCG contains large amounts of organic compounds (more than 1000 individual compounds) such as proteins, carbohydrates, cellulose, non-protein nitrogenous, fatty acids, amino acids, polyphenols, minerals lignin and polysaccharides namely; galactomannans and arabinogalactans that remain insoluble and unextractable in SCG during the thermal water extraction process and thus can be valorized in different ways. Based on the evaluation of 233 published papers, SCG has been proven to be a

potential feedstock to produce biodiesel, biogas, bioethanol, fuel pellets and bio-oil besides its promising potential to produce bioactive compounds, adsorbents, compost and polymers the milestone for bio-refineries from this industry as very promising environmental and feasible solution to save the environment, create jobs, produce biofuels and value-added products and offer many solutions to landfills. Coffee produces more oil per unit of land area than other traditional biodiesel crops with 386 kg/ha compared to 375/kg ha for soybean. Oil content of SCG has been reported to range between 7-21.5% while acid value was reported to be extremely low 0.62 mg KOH/ g oil to extremely high 118.4 mg KOH/ g oil all of which depending on the storage duration, storage temperature, geographical location, type of coffee, moisture content, extraction process, and solvent used. Fatty acids composition of SCGOME is mainly dominated by linoleic and palmitic acids followed by oleic, stearic and arachidic acids. This structure yields biodiesel with high cetane number and oxidation stability, lower iodine value, acceptable higher heating value and flash point besides higher cloud point, pour point, cold filter plugging point, and kinematic viscosity higher than 5 mm²/s at 40 °C. The results of the higher heating value of SCG range between (19.3-24.913 MJ/kg) while for DSCG range between (19-21.54 MJ/kg). These results are higher than other conventional biomass used as fuel pellets.

Moreover, glycerin which is produced as a by-product of the transesterification process can be mixed with DSCG to increase further its calorific value. The yield of bioethanol from DSCG has been reported to be 0.43-0.5(g/g). C/N of SCG has been reported to range between 16.91-23.7, VS/TS between 96.5-99 and biogas yield from SCG has been reported to be 0.500-0.598 m³/kg while methane yield ranged from 0.25-0.325 m³/kg. The higher heating value of bio-oils derived from SCG and DSCG was also found to be higher than other biomass. SCG has been also reported to contain considerable amount of protein (8.97-17.44%), carbohydrates (78.5%), ash (1.3-2.77%), tannins (30.36%), nitrogen content (2.03-3.97%) and cellulose (8.6-24.3%) making it a promising material for bioactive compounds and compost besides its huge potential as adsorbent and nanocomposite. Moreover, membrane processes in SCG-integrated biorefinery would show a great potential and present suitable performance criteria for biorefining and biofuels productions. Once implemented in an SCG-integrated biorefinery, membrane hybrid processes have the potential to further improve productivity by decreasing costs through the reduction of energy demands, processing steps and produce high-quality final products. A refinery proposal has been suggested in this paper (**Fig. 6**).

Following this figure, authors suggest some future perspectives of SCG industry as follow:

- (1) Oil extraction from SCG is an important factor to improve the economics of SCG recycling industry as the direct use of SCG as fuel pellets seems not economical for the long run.
- (2) Conversion of SCGO to biodiesel seems to be not economical due to the high acidity of SCGO. Therefore, pre-blending with lower acid value oils may seem to be one solution to cut down the cost of biodiesel production from SCG. *In-situ* transesterification process of SCG is another suggested approach. However, it has to be further inspected in the foreseen future.
- (3) It appears that utilizing SCGO as an input raw material for producing value-added products such as polymers or in textile industry is an effective way to improve the economics of this industry rather than biofuel production.
- (4) DSCG can be utilized in many different ways such as producing biofuels (biogas, bioethanol and fuel pellets) and value-added products. Producing bioethanol from DSCG followed by producing fatty acid ethyl ester (FAEE/biodiesel) by reacting bioethanol with SCGO may add to the economics of this industry. However, utilizing DSCG either to produce biogas or as raw material to produce adsorbents/active carbon material or bioactive compounds for food, pharmaceutical, cosmetic and chemical industries seems the most economical pathway so far.
- (5) Some studies also recommended direct hydrolysis of SCG to firstly obtain sugar that is fermented to produce bioethanol followed by extracting the lipids from SCG and then further utilize the DSCG for other applications.

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