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Enhanced catalytic activity of Sm/CeO$_2$ to produce gasoline-range hydrocarbons from pyrolysis of spent coffee grounds

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ABSTRACT

This study investigated the application of Sm/CeO$_2$ catalyst for hydrocarbon production in catalytic pyrolysis (CP) of spent coffee grounds (SCGs). A temperature range of 450–750 °C and catalyst/biomass (C/B) ratios of 0.5–4 were employed in the CP. The results showed that an increase in pyrolysis temperature consistently increased the quantity of hydrocarbons and considerably decreased the oxygenated compounds like acids and phenols. At temperatures of 450 and 550 °C, C/B ratios of 2 or 1 generated the maximum amount of hydrocarbons. At 650 and 750 °C temperatures, C/B ratios of 0.5 and 1 were capable to achieve a higher content of hydrocarbons in bio-oils, suggesting the synergistic effect of temperature and catalyst activity. The hydrocarbons in bio-oils were found in the gasoline range, mainly containing benzene, toluene, ethylbenzene, xylene (BTEX), olefins, and cycloalkenes. Primary reactions involved to convert oxygenated compounds into hydrocarbons were dehydration, decarboxylation, decarbonylation, dehydrogenation, isomerization, and aromatization reactions.

1. Introduction

Approximately 18 million tonnes of wet waste spent coffee grounds (SCGs) are estimated to be produced annually around the world [1]. SCGs are a sustainable source of renewable energy. SCGs contain 30-40 wt% of cellulose, 8–20 % of hemicellulose, 20–30 % of lignin, 13–17 % of proteins, and 7–12 % of lipids [2]. The pyrolysis process can convert SCGs into valuable energy-rich liquid products like bio-oil [3]. A bio-oil yield of 61.80 % can be obtained with the pyrolysis of SCGs at 500 °C [4]. However, the bio-oil contains nearly 59.5 wt% of oxygen, mainly due to the occurrence of oxygen-containing compounds such as acids like palmitic acid, linoleic acid, ester, ketone and phenol, consequently, exhibiting a low higher heating value (HHV) of 17.23 MJ/kg [5]. The calorific value of bio-oil can be substantially improved with the application of acidic or basic catalysts since the catalysts can convert low-energy oxygen-containing compounds into high-energy aromatic hydrocarbons [6,7].

A well-recognized process known as catalytic pyrolysis (CP) has been widely employed to produce high-quality bio-oil or other value-added products from SCGs. For example, a study carried out CP of SCGs in the presence of a ZSM-5 catalyst and showed that the catalyst promoted decarboxylation and decarbonylation reactions to convert fatty acids into alkanes and alkenes, respectively [8]. ZSM-5 also favoured oligomerization, cyclization, and aromatization reactions to transform saturated aliphatics into monocyclic-aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX) and polycyclic aromatics like naphthalene [8]. The selectivity of aromatics was increased ten times in CP compared to non-catalytic pyrolysis [8]. Though acidic catalysts could prove advantageous to achieve high aromatic yield they are prone to significant coke deposition [9]. In contrast, basic catalysts are competitive to generate aromatic hydrocarbons via several reactions such as hydrogenation, ketonization and aldol condensation [10,11], and have shown remarkable resistance to coke deposition [11], making them valuable catalysts for CP of SCGs. For example, a study employed a basic CaO catalyst for thermo-catalytic pyrolysis of *Azadirachta indica* and showed that the application of CaO catalysts resulted in a considerable decline in the proportion of oxygenated compounds, and an increase in the proportion of hydrocarbons [12].

CeO$_2$ is a rare earth metal, an ideal basic catalyst which exhibits excellent ketonization activity to convert oxygenated compounds into

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valuable monofunctional molecules, such as ketones and aldehydes [13]. Cerium oxide's excellent ketonization activity can be attributed to its several characteristics such as high oxygen exchange, Lewis basicity, and outstanding active redox characteristics that involves the exchange of Ce^{3+} and Ce^{4+} ions [13,14]. CeO_2 exhibits a number of surface-bound defects that usually are oxygen vacancies and contain Ce^{3+} that acts as key catalytic active sites [15]. CeO_2 has been shown to convert pyrolytic vapours of biomass into high yields of ketones [13]. For instance, the results from CeO_2-catalyzed pyrolysis of biomass like poplar and rape straw showed the abundance of acetone, 2-pentanone, cyclopentanone in the bio-oil. CeO_2 also promotes deoxygenation and dehydration reactions to transform oxygenated compounds like phenol into benzene [16]. The addition of an active metal to a support material generally increases its catalytic activity by creating new active sites that may carry out additional catalytic reactions such as hydrogenation and aromatization. For instance, introducing Ce onto ZSM-5 significantly enhanced the formation of BTEX from cellulose pyrolysis [17]. Ce increased the quantity of Lewis acid sites and decreased Brønsted acid sites, generating a favourable balance of acid sites that carried out Diels-Alder and dehydrogenation-aromatization reactions to first convert olefins into cycloalkanes and then transforming cycloalkane intermediates into BTEX [17]. Similarly, the incorporation of an active metal into CeO_2 can further improve its overall catalytic activity. The combined catalytic active sites on metal/CeO_2 catalyst can carry out an additional number of reactions and produce a variety of hydrocarbons from SCGs.

Samarium (Sm) is a rare earth metal that has been used as a catalyst in the production of aromatic hydrocarbons like benzene. The catalytic mechanism of Sm may involve several reactions. Sm promotes the dehydrogenation of cycloalkanes which can remove hydrogen atoms and convert the cycloalkanes into aromatic compounds, and the aromatization of paraffins to produce aromatics [18]. Sm also catalyses the isomerization of cycloalkanes, which can convert a cycloalkane into a different isomer with an aromatic structure [19]. Sm has shown to promote the cracking of large molecular weight compounds, which can increase the yield of smaller hydrocarbons such as benzene [20].

Literature suggests that Sm has the ability to carry out several reactions which can also be important in pyrolysis process to convert the oxygen-containing compounds into aromatic hydrocarbons. To the best of our knowledge, the application of Sm-based catalysts has not been reported for CP of any biomass feedstock including SCGs. Therefore, the primary objective of this study was to investigate the performance of Sm/CeO_2 catalyst in *in-situ* CP of SCGs for enhanced hydrocarbon yield. This study hypothesizes the formation of oxygenated compounds from SCGs constituents like cellulose, hemicellulose, and lignin, and converting them into gasoline range hydrocarbons like BTEX, paraffins, olefins and other aliphatic and aromatic hydrocarbons using the combined catalytic activities of Sm/CeO_2 such as ketonization, dehydrogenation, isomerization, aromatization, dehydration, and deoxygenation reactions. Other objectives of the study were to examine the optimized pyrolysis temperature and catalyst to biomass ratio to obtain the highest proportion of hydrocarbons. Thus, the catalytic and non-catalytic pyrolysis experiments were carried out at four temperatures, 450, 550, 650, and 750 °C. Further, the effect of catalyst to biomass (C/B) ratio (0.5, 1, 2, and 4) was investigated on the selectivity of hydrocarbons.

2. Materials and methods

2.1. Materials

SCGs were chosen as the feedstock in the study based on several purposes. SCGs are carbon rich, contains cellulose, hemicellulose, lignin and offers a major proportion of nearly 71.5 % volatile compounds. These characteristics make coffee grounds highly suitable for pyrolysis process for the formation of energy products like bio-oil with a high yield. In addition, utilizing SCGs for pyrolysis offers a sustainable solution to waste management while generating valuable energy products.

SCGs were gathered from a coffee shop at James Cook University, Townsville Campus, Queensland, Australia. SCGs were dried overnight at a temperature of 105 °C in an oven to eliminate the moisture content.

Sm/CeO_2 was purchased from Sigma-Aldrich (product no. 734624, 0.5 μm particle size). The concentration of Sm in the catalyst was 20 %. The catalyst was used in Py-GC/MS experiments as received without any modification.

2.2. Characterization of SCGs and catalyst

SCGs were characterized by ultimate and proximate analyses to examine the elemental composition, volatiles, fixed carbon, and ash contents. The ultimate analysis was carried out in a Costech Analytical Elemental Analyser 4010 (Valencia, CA, USA). The equipment utilizes dumas combustion to generate CO_2 and N_2 which are detected by a thermal conductivity detector. The weight percentages (wt%) of C, H, and N were calculated from a calibration curve formulated from standards. O content was determined from the mass difference of the combined elements and a total mass of 100. Proximate analysis of SCGs was carried out in a Thermogravimetric analysis (TGA) study using the 'Discovery TA/SDT650' analyser as mentioned in our previous study [21].

TGA/DTG – Thermal degradation behaviour of SCGs was studied in TGA. Approximately 25 mg of SCGs sample placed in a crucible was kept in the furnace of the analyser. A temperature range of 25–1000 °C was applied. The heating rate for the analysis was kept 10 °C/min, while the N_2 flow rate was 50 mL/min. The rate of change of mass with respect to temperature was determined by plotting a derivative thermogravimetric (DTG) curve.

X-ray diffraction (XRD) – The crystalline phases of Sm and CeO_2 were examined using the XRD. The instrument used for XRD was A Rigaku Ultima IV. A Cu-Kα radiation source at 40 KV and 40 mA was used for the analysis. The spectra were achieved by scanning diffraction angle 2θ range of 5–60° and a step size of 0.05°.

BET/BJH analysis – The textural properties of Sm/CeO2 catalyst such as surface area and pore volume were evaluated using N_2 adsorption-desorption isotherms and Brunauer-Emmett-Teller on Autosorb iQ station 2 instrument at −196 °C. Prior to the analysis, the catalyst sample was degassed at 300 °C for 6 h under a vacuum.

TPD-CO_2 – The basic site characteristics of the catalyst were analysed through CO_2-temperature programmed desorption (CO_2-TPD), utilizing a Micromeritics Autochem II instrument. For this process, the catalyst sample underwent an initial preparation phase where it was exposed to a nitrogen flow of 20 mL/min at a temperature of 150 °C. This pre-treatment lasted for 30 min, with the temperature rising steadily at a rate of 10 °C/min. After this step, the sample was allowed to cool down to 30 °C. Subsequently, a CO_2 flow of 10 mL/min was directed over the sample for a duration of 60 min. Afte the CO_2 treatment, the sample was purged with helium at a flow rate of 20 mL/min for another 30 min. The final phase involved a gradual temperature increase to 950 °C at a heating rate of 10 °C/min.

FESEM-EDS – The catalyst morphology and elemental composition (Sm, Ce and O) were determined using FESEM/EDS. The analysis was carried out on a Field Emission Scanning Electron Microscope (FESEM, SU5000, Hitachi), measured at Vac = 5.0 kV, EC = 115 nA, WD = 7.5 mm.

X-ray photoelectron spectroscopy (XPS) – The Kratos Axis Supra instrument with a monochromated Al Kα X-ray source was utilized in an X-ray photoelectron spectroscopy (XPS) analysis to identify the elemental composition and oxidation states of Ce and Sm in the catalyst. The peaks were deconvoluted using Origin software.

2.3. Py-GCMS of SCGs

Py-GC/MS (Shimadzu (QP2020NX EI) coupled with Multi-Shot Pyrolyzer (EGA/PY-3030D) was used for pyrolysis of sole SCGs and SCGs mixed with the catalyst at four temperatures, 450, 550, 650, and 750 °C with holding time of 1 min and heating rate of 10 °C/ms. An Ultra-Alloy+5 column was used to perform GC separation at a consistent helium flow rate of 1.0 mL/min, while the injector temperature was maintained at 300 °C. The MS was operated at typical conditions, including an ionization energy of 70 eV and *m/z* scanning mode over a range of 25–550 amu. The percentage of chromatograph peak area was utilized to identify the relative content of liquid products, which has been employed in previous studies [6]. The catalyst-to-biomass ratios of 0.5, 1, 2, and 4 were used for CP experiments. A schematic diagram of Py-GC/MS is shown in Fig. S7 (see supplementary file).

3. Results and discussion

A detailed characterization of the catalyst Sm/CeO$_2$ is available in supplementary information.

3.1. Feedstock properties

Table 1 presents the findings of ultimate and proximate analyses of SCGs. The ultimate analysis data showed that SCGs consisted of 47.5 wt % elemental carbon and 6.4 wt% hydrogen, indicating the feasibility of the biomass to be utilized to produce energy-rich hydrocarbons composed of carbon and hydrogen. The nitrogen and oxygen contents were 2.5 and 43.7 wt% which suggests pyrolysis of SCGs can generate some nitrogen-containing compounds and oxygenated compounds which could serve as ideal target compounds in catalytic pyrolysis to be converted into high-energy-density hydrocarbons [22]. Additionally, the proximate analysis suggested that SCGs have a high volatile content of 71.5 wt% and a low ash content of 2.5 wt%, which could be favourable for producing high yields of bio-oil using SCGs as feedstock. The biomass contained 18.8 wt% of fixed carbon and 7.2 wt% of moisture content. Overall, these analyses recommend that SCGs contain an adequate amount of carbon which can be a renewable source to generate high-value-added fuels in the pyrolysis process.

SCGs are generally composed of a variety of organic and inorganic compounds such as cellulose, hemicellulose, lignin, proteins, phenolic compounds and minerals like potassium, magnesium, calcium, and various acids such as chlorogenic acid, quinic acid, and citric acid [22]. These compounds undergo various chemical and physical transformations when subjected to thermal treatment. Fig. 1 displays the thermal decomposition behaviour of SCGs biomass and the rate of weight reduction with respect to temperature as determined by TGA and DTGA analyses. The thermal decomposition of SCGs can be divided into three stages. The first stage is generally termed dehydration which occurs between room temperature and 200 °C. In this stage, a small weight loss of 7.2 wt% was noticed, which can be attributed to the loss of moisture and other volatile organic compounds such as aldehydes, ketones, and alcohols, which are commonly found in biomass feedstocks. Stage 2 is termed devolatilization, which is considered the main stage and occurs between 200 and 520 °C. During this stage, a significant weight loss of 72.4 wt% was observed. A study by Ref. [5] showed similar results for SCGs, achieving nearly 75 wt% of mass loss between 180 and 600 °C temperature range. The highest weight loss rate of 6.1 wt %/°C was achieved in this stage at 300 °C, while the lowest weight loss rate of 3.4 wt%/°C was observed at 390 °C. A weight loss rate of 4.7 wt %/°C was noticed at 320 °C. These results are in-line with a previous study by Ref. [23] that also achieved similar weight loss rates for TGA analysis of SCGs. These variable weight loss rates in stage 2 suggest the depolymerization of different chemical compounds of SCGs carried out by several intensive reactions. SCGs contain hemicellulose of nearly 8–20 % [2]. The thermal decomposition of hemicellulose occurs between 180 and 300 °C to produce smaller molecules such as sugars and furans and completely depolymerized up to 350 °C, generating volatile organic compounds, carbon dioxide, carbon monoxide, and other gases [24]. The proportion of cellulose can vary from 30 to 40 % in SCGs [2]. Cellulose degradation starts above 180 °C and is completely depolymerized up to 400 °C to form a complex mixture of organic compounds, including furans, phenols, aldehydes, ketones, acids and gaseous products such as carbon dioxide, carbon monoxide, methane, and hydrogen [25]. SCGs contain 20–30 % of lignin [2]. Lignin is a complex macromolecular structure which depolymerizes between 200 and 500 °C into smaller molecules such as phenols, aromatic compounds, and aldehydes [25]. Lipids and proteins present in SCGs also degrade in the temperature range of 200–500 °C to produce fatty acids, aldehydes, and nitrogen-containing compounds [4]. The last stage is termed carbonization which occurs between 500 and 700 °C. In this stage, a weight loss of 1.9 % was detected, which can be ascribed to the decomposition of remaining organic compounds and the formation of carbonaceous materials. At temperature above 700 °C, oxidation and combustion of carbonaceous materials can take place, resulting in the release of carbon dioxide and other gases which can be marked by a mere weight loss of 0.1 wt%.

Table 1
Proximate and ultimate analysis of SCGs.

Proximate analysis (dry wt%)				Ultimate analysis (%)			
Moisture	Volatiles	Ash	Fixed carbon	C	H	N	O[a]
7.2	71.5	2.5	18.8	47.5	6.4	2.5	43.6

Note.
[a] Calculated by weight difference.

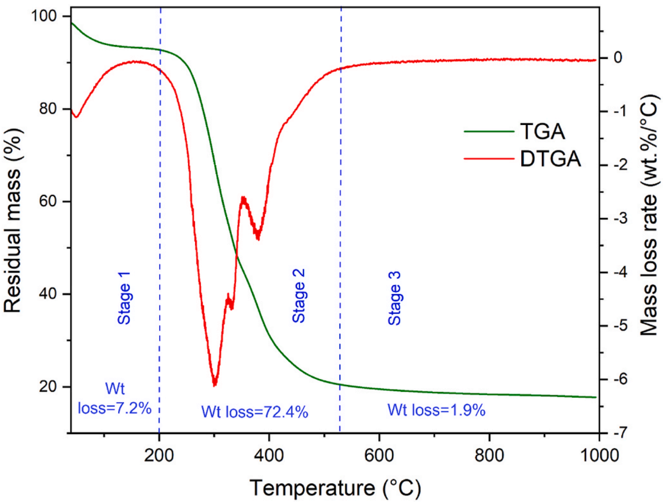

Fig. 1. TGA and DTGA analyses of SCGs, varying the temperature from room temperature to 1000 °C with a heating rate of 10 °C/min.

3.2. Py-GCMS results

3.2.1. Effect of temperature on product distribution

Fig. 2a–d shows the results for the distribution of all classes of chemical compounds in the bio-oil obtained at varying temperatures of 450–750 °C and C/B ratios of 0.5–4 in catalytic and non-catalytic pyrolysis modes. In addition, Fig. 3 shows the effect of temperature and C/B ratio on the quantities of acids, phenols, and hydrocarbons. For the non-catalytic pyrolysis of SCGs, increasing the pyrolysis temperature from 450 to 750 °C consistently increased the total hydrocarbon quantity, and a total increase of 52.4 % was obtained. This is primarily because high temperatures advance the breakdown of complex and larger organic molecules into smaller molecules [8]. Secondary reactions such as cracking and isomerization reactions become prevalent at high temperatures, which can result in the generation of extra hydrocarbons [26]. In addition, the rate of secondary reactions increases with a rise in temperature, which may increase the content of

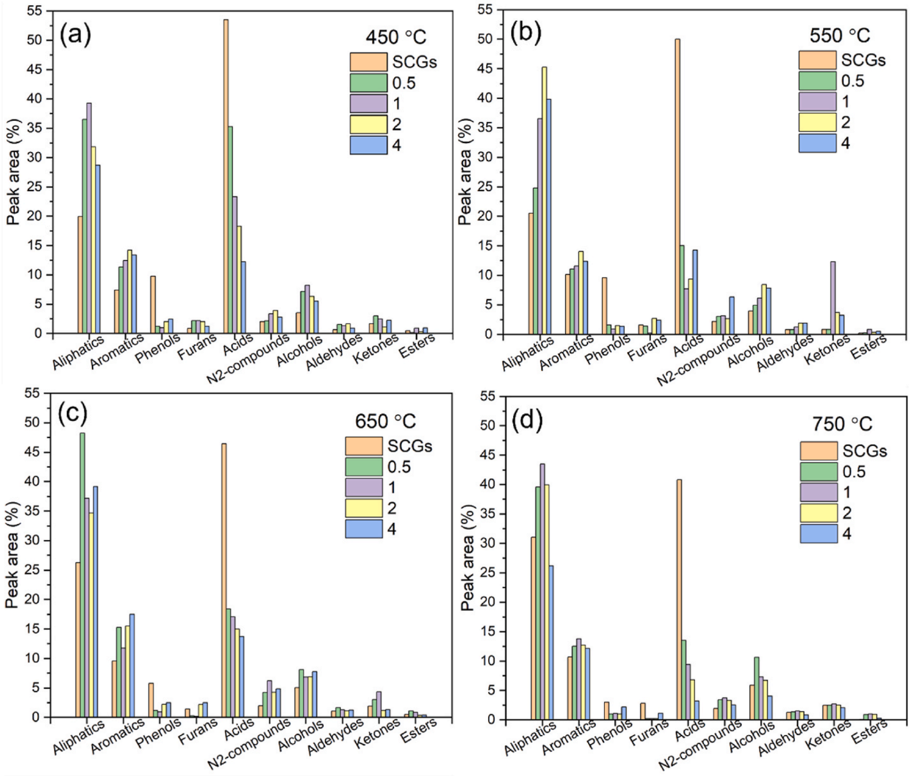

Fig. 2. Effect of temperature and C/B ratio (0.5, 1, 2, and 4) on the distribution of chemical categories in bio-oils at (a) 450 °C, (b) 550 °C, (c) 650 °C, and (d) 750 °C with and without Sm/CeO_2 catalyst.

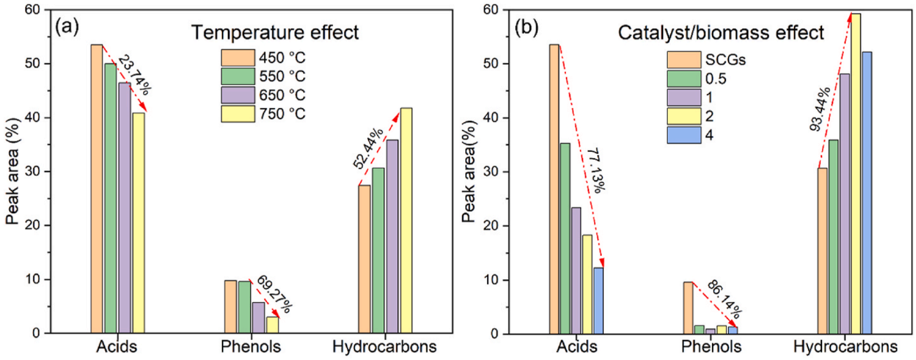

Fig. 3. (a) Effect of temperature on the production of acids, phenols, and total hydrocarbons in non-catalytic pyrolysis of SCGs and (b) effect of C/B ratio (0.5, 1, 2, and 4) on the production of acids at 450 °C; and phenols and hydrocarbons at 550 °C.

hydrocarbons [27]. On the other hand, a significant decrease was noticed for undesirable low-energy density oxygenated compounds like acids and phenols with the increase in temperature. For instance, increasing the temperature from 450 to 750 °C, a significant decrease of 23.7 % and 69.3 % was observed in the proportions of acids and phenols, respectively (Fig. 3a). The decrease in oxygenated compounds can be attributed to the breaking of these compounds and the removal of oxygen atoms via dehydration, decarboxylation, and decarbonylation reactions [28]. High temperatures promote these reactions, which results in enhanced removal of the oxygen and consequently, reduces the proportion of oxygenated compounds in bio-oil [25]. Moreover, high temperatures fasten the reaction kinetics which decreases the residence time for organic compounds to break down in a pyrolysis reactor, subsequently, provides less time for the generation of oxygenated compounds [27]. These results are also consistent with previous studies with other types of biomass feedstocks, which showed that high temperatures (500–600 °C) promote deoxygenation reactions and hydrocarbon formation [28,29].

For other classes of chemical compounds, the surge in temperature marginally increased the proportion of alcohols, ketones, and furans in bio-oils. This marginal increase in these oxygenated compounds can be attributed to secondary cracking reactions taking place at high temperatures, which might contribute to the formation of these compounds [26]. Whereas the quantities of esters, aldehydes, and nitrogenous compounds were considerably low (in the range of 0.5–2.5 %) and were trivially affected by the temperature.

3.2.2. Effect of catalyst/biomass ratio on product distribution

A variety of trends were observed for the distribution of chemical compounds under applied C/B ratios at different temperatures, probably due to the synergistic effect of the temperature and catalyst loading. As shown in Figs. 2 and 3b, increasing the C/B ratio from 0.5 to 4 substantially decreased the quantity of major oxygenated compounds like acids and phenols at all the studied temperatures, while the quantities of most desirable chemicals-aromatic hydrocarbons were considerably enhanced. For instance, at 450 °C, non-catalytic pyrolysis produced a maximum amount of acids (53.5 %), which reduced to 12.2 % when the highest C/B ratio of 4 was applied. Similarly, at 750 °C, the proportion of acids was 40.8 % which decreased to a minimum of 3.2 % with a C/B of 4. However, at 650 °C and 750 °C, even a low C/B ratio of 0.5 was able to generate substantial fractions of hydrocarbons (63.5 % and 52.0 %), indicating the high catalytic activity of the Sm/CeO_2 catalyst at these temperatures. It can be explained by the fact that the metal ions (Sm^{2+}-Sm^{3+}/Ce^{3+}-Ce^{4+}) in the catalyst may act as the active sites and catalyse multiple reactions such as dehydration, decarboxylation, and decarbonylation to remove oxygen from oxygenated compounds and reactions such as dehydrogenation, aromatization, isomerization, and hydrogen transfer reactions to transform oxygenated compounds into hydrocarbons [16,18,30]. Since high temperatures are more conducive to stimulate these reactions, the synergistic effect of temperature-catalyst could also be responsible for reducing the quantity of oxygenated compounds and increasing the proportion of hydrocarbons [31]. In addition, a high C/B ratio indicates a larger amount of the catalyst with a greater number of active sites. Subsequently, the catalyst with additional number of active sites has a substantial potential to react with more oxygenated compounds and carry out different reactions aforementioned to enhance the production of hydrocarbons [32]. At 550 °C, the C/B ratio of 2 produced the maximum amount of total hydrocarbons of 59.3 % in the bio-oil. Therefore, it can be suggested that at a temperature of 550 °C or <550 °C, the formation of hydrocarbons was predominantly dependent on the catalyst volume and moderately on the temperature, whereas >550 °C, the temperature played the central role and the catalyst as a stimulator to enhance the production of hydrocarbons. A previous study also found 500 °C temperature highly advantageous to obtain a high-quality pyrolytic oil in catalytic pyrolysis mode, indicating to lower the proportion of oxygen-rich products and acids, and increase the aromatic yield [33]. Another study optimized the pyrolysis process parameters using various catalysts and found that 525 °C was the most suitable temperature to obtain the bio-oil with highest aromatic yield and calorific value [34].

3.2.3. Effect of temperature and catalyst/biomass ratio on hydrocarbon selectivity

The proportions of hydrocarbons obtained in the bio-oil were further classified into different categories like BTEX (benzene, toluene, ethylene, and xylene), polycyclic aromatic hydrocarbons (PAH), cycloalkenes, cycloalkanes, paraffins, olefins, and alkynes. The results are shown in Fig. 4a–d. As shown in the figures, the dominant categories of hydrocarbons were olefins (14.3–35.5 %), BTEX (5.7–15.1 %), and cycloalkenes (3.0–11.2 %) at all the studied temperatures and C/B ratios. Other categories of hydrocarbons were present in the range of 0.1–3.1 %. The increase in temperature from 450 to 750 °C consistently enhanced the fraction of all hydrocarbons including BTEX, olefins and cycloalkenes during non-catalytic pyrolysis of SCGs, and a maximum proportion of these hydrocarbons was obtained at 750 °C. Noticeably, at 750 °C, the quantities of BTEX, olefins and cycloalkenes were 9.1, 20.3, and 8.9 %, respectively. These hydrocarbons can be originated from different oxygenated compounds like acids, phenols, and ketones through a combination of various reactions [35]. For instance, acids undergo decarboxylation and dehydration reactions to form a pool of alkenes, which further go through dehydrocyclization to produce cyclic intermediate hydrocarbons (cycloalkenes and cycloalkanes) [36]. Cyclic intermediates are converted into aromatics like BTEX via dehydrogenation and aromatization reactions [36]. Direct decarboxylation of ketones and hydrogen transfer reactions of phenols can result in the generation of BTEX and other aromatics as well [37,38].

The addition of Sm/CeO_2 catalyst further increased the fractions of these hydrocarbons at each temperature with a specific C/B ratio. As aforementioned, 650 and 750 °C were the most suitable temperatures to generate hydrocarbons, it required a lower amount of catalyst to convert oxygenated compounds into hydrocarbons. Consequently, a low C/B ratio of 0.5 was sufficient to produce a high fraction of BTEX at 650 °C

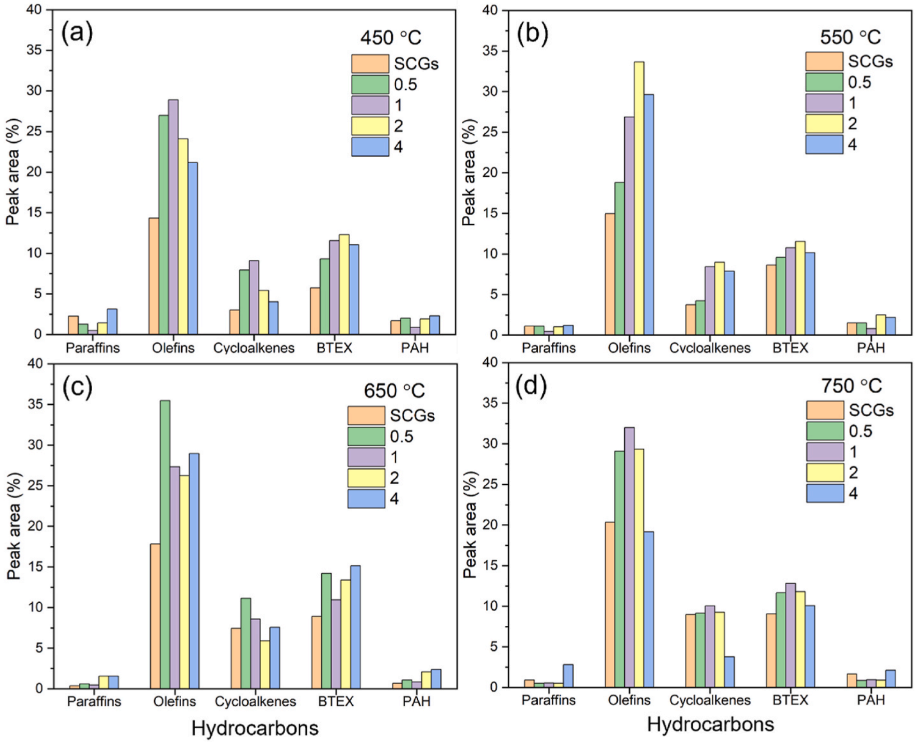

Fig. 4. Effect of temperature, (a) 450 °C, (b) 550 °C, (c) 650 °C, and (d) 750 °C and C/B ratio (0.5, 1, 2, and 4) on the distribution of various aliphatics and aromatics with and without Sm/CeO_2 catalyst.

which was 14.2 % and a further increase in the C/B (of 4) could only increase the BTEX fraction up to 15.1 %. In the presence of Sm/CeO$_2$, BTEX can also be formed via an additional pathway which involves the dehydration of ketones to form enone intermediates that undergo dehydrogenation and aromatization reactions [18]. Whereas phenols first go through dehydration to form cyclohexadiene and then dehydrogenation of cyclohexadiene generates BTEX and other aromatics [37]. A similar trend was observed for olefins and cycloalkenes, a C/B ratio of 0.5 generated the maximum fractions of olefins (35.5 %) and cycloalkenes (11.1 %) at 650 °C. On other hand, low temperatures of 450 and 550 °C were comparatively less conducive for hydrocarbons production, therefore, it required a higher amount of the catalyst. Accordingly, a C/B ratio of 2 produced the maximum quantities of BTEX at 450 and 550 °C, which were 12.3 % and 11.5 %, respectively. Similarly, at 550 °C, a C/B ratio of 2 produced the maximum amounts of olefins and cycloalkenes, which were 33.7 % and 8.9 %, respectively.

PAH are the most undesirable hydrocarbons since they can form coke and cause the deactivation of the catalyst. In this study, the proportion of PAH was found significantly low (in a range of 0.7–2.3 %), indicating that Sm/CeO$_2$ catalyst was comparatively less favourable to produce PAH.

3.2.4. *Carbon number distribution in bio-oil*

Based on the carbon number, the chemical composition of bio-oil samples was classified into four categories, C4–C8, C9–C14, C15–C19, and C20–C29. The results are shown in Fig. 5a–d, which indicate that at all the studied pyrolysis temperatures and C/B ratios, the fraction of C4–C8 hydrocarbons was considerably higher compared to other counterparts. In the C4–C8 category, the majority of hydrocarbons were BTEX; olefins like 2-butene, 1-hexene, and 1-octene; cycloalkenes such as 1,3-cyclopentadiene, cyclopentene, cyclohexene; and cycloalkanes like cyclohexane and cyclopropane. The C9–C14 category contained mainly benzene-derived compounds, naphthalenes, fluorene, and phenanthrene; paraffins like nonane, decane, and tridecane; and olefins such as 1-decene, 1-tridecene, and 1-tetradecene. In the C15–C19 category, major hydrocarbons were paraffins like pentadecane, octadecane and nonadecane and their olefin forms, while > C20 exhibited five hydrocarbons namely eicosane, 3-eicosene, heptadecane, 1-hexacosene, and stigmasta-3,5-diene.

The results further revealed that during non-catalytic pyrolysis of SCGs, an increase in temperature from 450 to 650 °C increased the content of C4–C8 hydrocarbons from 16.6 % to 26.8 % but a further rise of temperature to 750 °C enhanced the quantity to 28.5 %. The fraction of C9–C14 hydrocarbons consistently increased with temperature, as a minimum content of 8.3 % at 450 °C and a maximum content of 11.1 % was obtained at 750 °C. Insignificant changes were observed in the fractions of C15–C19 and C20–C29 hydrocarbons irrespective of the alteration in temperature and amount of catalyst in CP experiments. On contrary, a significant surge was observed in the quantity of C4–C8 and C9–C14 hydrocarbons after the incorporation of the Sm/CeO$_2$ catalyst. Noticeably, at low temperatures of 450 and 550 °C, C/B ratios of 1 and 2 generated the maximum proportions of C4–C8 hydrocarbons, with values of 40.4 % and 40.8 %, respectively. In addition, at high temperatures of 650 and 750 °C, C/B ratios of 0.5 and 1 resulted in the highest proportions of C4–C8 hydrocarbons, 49.6 and 44.7 %, respectively. On the other hand, the maximum quantity of C9–C14 hydrocarbons was produced at 550 °C with a C/B ratio of 2.

Generally, gasoline contains hydrocarbons in the category of C5–C12, with a mixture of different types of hydrocarbons like paraffins (15–25 %), isoparaffins (25–40 %), olefins (1–10 %), cycloalkanes (8–15 %), and aromatics (25–40 %). In this study, it was found that bio-oil samples predominantly contained C4–C12 hydrocarbons with a variety of similar hydrocarbons present in the gasoline. Therefore, it could be suggested that the bio-oils obtained from CP using Sm/CeO$_2$ catalyst were close to the gasoline range. However, the quantity of aromatics was lower in bio-oils and the proportion of olefins was slightly higher compared to gasoline. Hence, there is still a scope to further improve the quality of bio-oil and modifications in the catalyst can help to convert olefins into aromatics and produce bio-oil close to gasoline composition and physicochemical properties.

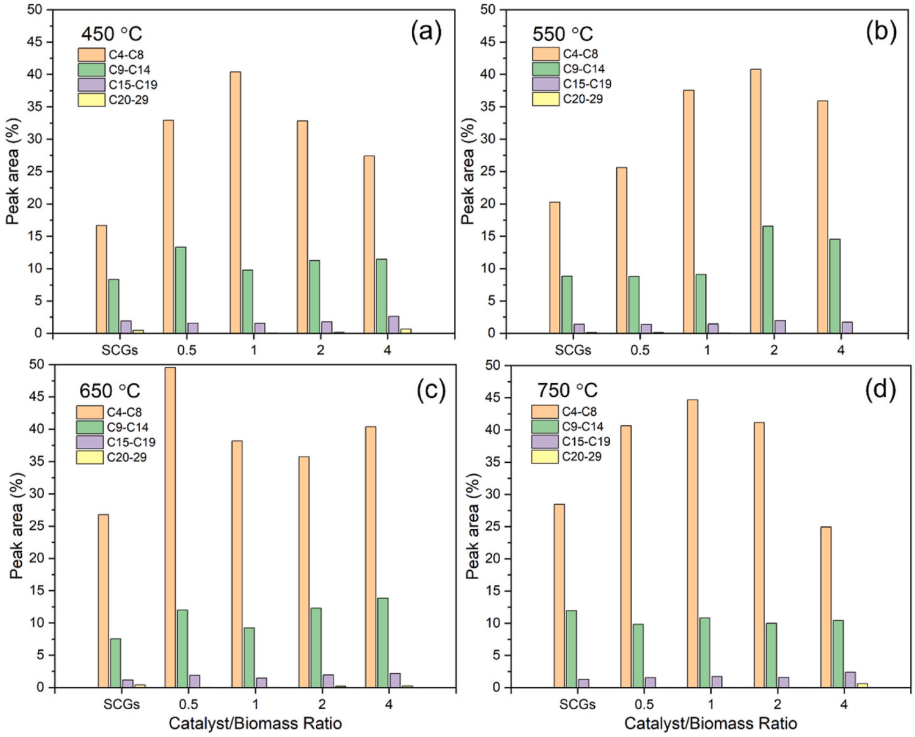

Fig. 5. Carbon number distribution of hydrocarbons under different temperatures, (a) 450 °C, (b) 550 °C, (c) 650 °C, and (d) 750 °C and C/B ratios (0.5, 1, 2, and 4) with and without Sm/CeO$_2$ catalyst.

3.2.5. Mechanism of the catalytic reaction of Sm/CeO_2

Based on the hydrocarbon composition in bio-oil, their formation mechanisms/pathways were developed. SCGs generally contain cellulose, hemicellulose, lignin, proteins, and lipids. Therefore, after thermal treatment, these polymer compounds are depolymerized into a variety of compounds [22]. In this study, the dominant oxygen-containing compounds were acids (palmitic acid, oleic acid), ketones, esters, aldehydes, phenols, alcohols etc. (the mechanisms of their generation are discussed in section 3.2.1). These oxygenated compounds were converted by Sm/CeO_2 catalyst into a variety of hydrocarbons.

The addition of Sm/CeO_2 significantly reduced the quantity of oxygenated compounds, mainly acids, ketones and phenols (other oxygenated compounds were less affected), while the content of gasoline-range hydrocarbons like BTEX, olefins and cycloalkenes was considerably increased in bio-oils. Hence, it can be predicted that the major proportion of dominant oxygenated compounds was converted into hydrocarbons by the active sites (Sm^{2+}-Sm^{3+}/Ce^{3+}-Ce^{4+} ions) of the Sm/CeO_2 catalyst [16,18]. The mechanisms of possible reactions occurring on the surface of the Sm/CeO_2 catalyst to convert oxygenated compounds into different hydrocarbons are shown in Fig. 6. Considering the obtained results, it can be suggested that the large quantity of acids (for example, palmitic acid, oleic acid, and hexadecenoic acid) were firstly converted by CeO_2 into aldehyde intermediates (like palmitaldehyde and hexadecanal) via decarboxylation reaction [36]. These aldehyde intermediates undergo decarbonylation and dehydration reaction to generate long-chain alkenes such as 1-tetradecene, 1-octadecene, 1-heaxcosene [36]. Subsequently, alkenes are transformed into cyclic intermediates like cyclohexene, and cyclopentane via a aromatization and hydrocracking reaction [36]. Sm is well known to carry out dehydrogenation and aromatization reactions [18,30]. Hence, Sm/CeO_2 catalyst promoted Diels-Alder reactions to convert cyclic intermediate compounds to gasoline-range hydrocarbons, such as benzene, toluene, ethylbenzene and xylene, and other benzene derivative compounds (of C8–C12 range).

Sm/CeO_2 catalyst can convert ketones into hydrocarbons mainly via two pathways. In the first pathway, ketones can directly undergo a decarbonylation reaction to form gasoline-range aromatics [38]. In the second pathway, Sm/CeO_2 catalyst may carry out a dehydration reaction to convert ketones into conjugated enone intermediates such as 2-heptadecanone and 2-*n*-heptylcyclopentanone. Further, the enone intermediates can be subjected to dehydrogenation and aromatization reactions to generate a variety of gasoline range aromatic hydrocarbons [35].

Phenolic compounds can be transformed into aromatics via two pathways [37,39]. The first pathway involves hydrogen transfer reactions to directly convert phenols into aromatics [37]. In the second pathway, Sm/CeO_2 catalyst may carry out a dehydration reaction to form cyclohexadiene, which further goes through a dehydrogenation reaction to produce aromatic hydrocarbons [39].

The comparative analysis of product distribution and BTEX yield from various catalyst utilizing the SCGs as a feedstock is shown in Table S2. Multiple experiments employed Py-GC/MS to assess the product distribution and the yield of BTEX directly. These experiments aimed at feedstock deoxygenation to increase selectivity for BTEX. Yet, the aromatic yield derived from different catalysts tends to be low, predominantly generating olefins and aliphatic hydrocarbons. As an example, Yao et al., evaluated Ni/HZSM-5 against Ni/Al_2O_3 to enhance the BTEX yield. The findings revealed that Ni/HZSM-5 exhibited better BTEX production selectivity, with benzene and toluene being notably high. The metallic Ni encapsulated within the zeolite structure is pivotal for improving aromatic selectivity, supporting the oligomerization, cyclization, and aromatization of smaller hydrocarbons within these channels. Conversely, Ni elements on the outer zeolite surface tend to support the hydrocracking and hydrogenolysis of larger pyrolytic fragments. Similarly, Hoanga et al., investigate the effect of dolomite, HZSM-5, hematite, and magnetite as a catalyst on spent coffee. Their findings highlighted a slight increase in selectivity for alkenes and alkanes, while a decrease for acids. Specifically, using magnetite as a catalyst resulted in 14.2 % C5–C11 compounds. However, hematite, which fosters decarboxylation and ketonization reactions, elevated C5–C11 compounds to 28.34 %. In this study, the Sm/CeO_2 catalyst demonstrated superior catalytic efficacy compared to others research,

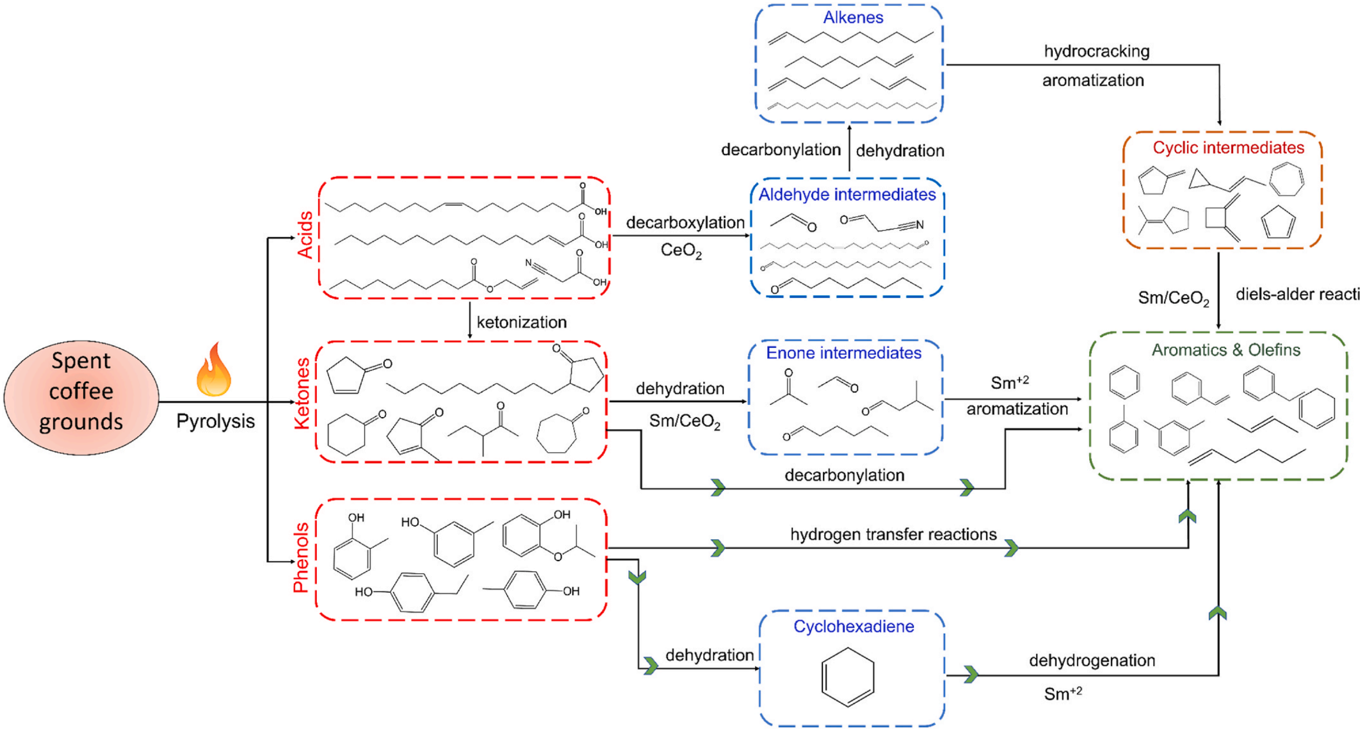

Fig. 6. The mechanism of possible reactions involved in the conversion of oxygenated compounds in gasoline-range hydrocarbons over Sm/CeO_2 catalyst.

confirming this with the highest BTEX yields of 15.2 %. The presence of Sm in Sm/CeO_2 promotes an additional reaction pathway that encompasses ketone dehydration to produce enone intermediates, which subsequently undergo dehydrogenation and aromatization processes.

Overall, Sm/CeO_2 was found highly active to catalyse the necessary reactions discussed above that significantly improved the conversion of low-energy-density oxygenated compounds into valuable gasoline range hydrocarbons. This study was a preliminary demonstration of Sm based catalyst for CP of a biomass feedstock. Therefore, more studies can be carried out in the near future to explore the role of Sm metal incorporated with other catalyst supports for the pyrolysis of different biomass feedstocks.

4. Conclusions

The study demonstrated the potential of Sm/CeO_2 catalyst for CP of SCGs to generate gasoline range hydrocarbons under a temperature range of 450–750 °C and C/B ratios of 0.5–4. Firstly, the prepared catalyst was characterized using different physicochemical techniques to examine its textural properties, crystalline phases, and oxidation states of Sm and Ce in the catalyst. Basic sites in the catalyst were also analysed using CO_2-TPD. The results confirmed that the catalyst had a crystalline structure and contained 17.4 wt% of Sm and 68.15 wt% of Ce in the catalyst. CO_2-TPD analysis demonstrated the presence of Lewis and Brønsted acidic sites, which could facilitate deoxygenation reactions that transform oxygenated compounds into hydrocarbons. The pyrolysis results confirmed that active sites of Sm/CeO_2 carried out various reactions like dehydrogenation, isomerization, and aromatization to convert oxygenated compounds into valuable high-energy-density hydrocarbons. Consequently, the proportion of oxygenated compounds was significantly reduced (up to 77 % for acids and 86 % for phenols), and hydrocarbons were nearly doubled (at 450 and 550 °C) in bio-oils. Overall, the study suggests that pyrolysis temperature and catalyst-to-biomass ratio play a decisive role in influencing the formation of BTEX and the quality of the bio-oil.

CRediT authorship contribution statement

Tewodros Kassa Dada: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft. **Ravinder Kumar:** Writing – review & editing. **Umer Rashid:** Formal analysis, Writing – review & editing. **Murugavelh Somasundaram:** Writing – review & editing. **Elsa Antunes:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & 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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Appendix A. Supplementary data

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