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Biochar

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Use of defatted cottonseed-derived biochar for biodiesel production: a closed-loop approach

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Abstract

This study aimed to enhance the economic viability and sustainability of the cotton industry by converting cottonseed into energy. Cottonseed was subjected to lipid extraction for biodiesel production, and a pyrolysis test was conducted under N_2 and CO_2 conditions to valorise defatted cottonseed. Under CO_2 conditions, the increase in CO concentration was due to homogeneous reaction of CO_2 with volatile matters. Biochar, a pyrolytic product of defatted cottonseed, was used as a catalyst for thermally induced transesterification, and showed high performance in biodiesel conversion efficiency due to its abundant alkaline earth metals and meso-/macro-pores. For example, transesterification using silica at 250 ˚C yielded only 1.6 wt.% biodiesel, whereas using biochar at the same temperature resulted in a significantly higher biodiesel yield of 83.5 wt.%. This study experimentally proved that 7,900 tons (304 million MJ) of biodiesel could be produced annually, surpassing the diesel fuel requirement (145 million MJ) for cotton cultivation. These results indicate the potential to fully replace fossil fuels in the cotton industry.

Article highlights

- Oil was extracted from cottonseed, and the defatted cottonseed was used in pyrolysis to produce syngas and biochar.
- Biochar demonstrated catalytic properties in thermally induced transesterification of cottonseed extracts into biodiesel.
- Biochar outperformed conventional silica, providing a biodiesel yield of 83.5 wt.% at 250 ˚C (silica: 1.6 wt.%).

Keywords Circular economy, Waste valorisation, Pyrolysis, Biodiesel, Biochar

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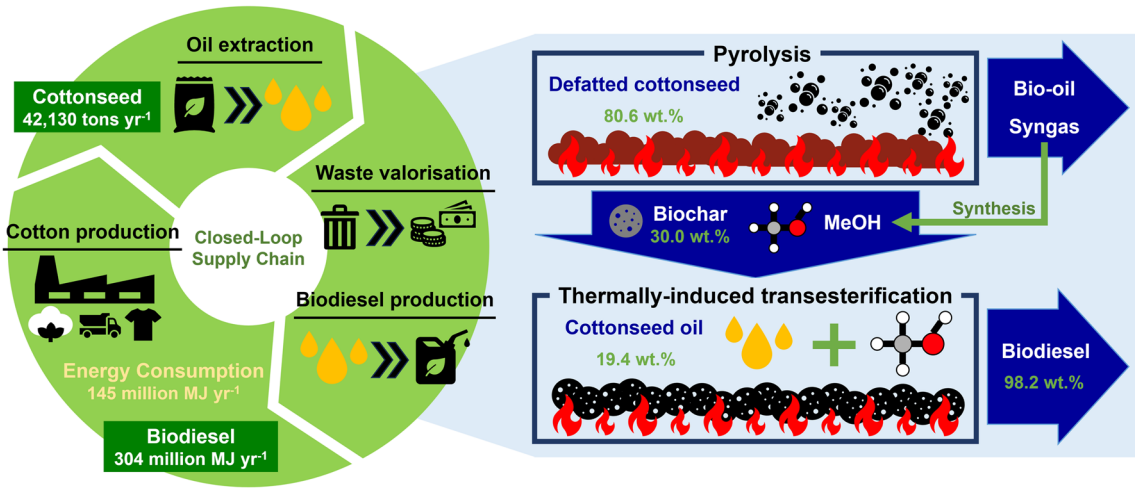
Graphical Abstract



1 Introduction

Transportation is an essential element of human life, as it overcomes limitations in physical accessibility and expands social activities (Kelobonye et al. 2020). The increased global population density has driven the development of transportation infrastructure and escalated energy demands, particularly for road transportation (Adams et al. 2020; Li and Lin 2015). In 2023, the International Energy Agency reported that 90% of road transport energy came from fossil fuels such as gasoline and diesel (IE Agency 2023). The combustion of fossil fuels increases atmospheric CO_2 levels (Paraschiv and Paraschiv 2020). Therefore, the transportation sector is responsible for environmental problems such as global warming (Yoro and Daramola 2020). To address this, biofuels such as bioethanol and biodiesel are being promoted because they are compatible with existing transportation systems and can reduce fossil fuel dependency (Bonenkamp et al. 2020; Solaymani 2019).

Commercial bioethanol is produced through fermentation, a biological process, whereas commercial biodiesel is synthesised via transesterification, a chemical reaction (Awogbemi and Kallon 2024). Because biological processes such as respiration and growth consume carbon for microbial metabolism, biodiesel production does not involve carbon uptake by microorganisms (Jiang et al. 2024). Lipids extracted from biomass feedstock react with alcohols to produce biodiesel (Oliva et al. 2024). Nevertheless, some carbon in the feedstock, called oil cake or defatted biomass, is discarded as a byproduct (Ceriani et al. 2024). The defatted biomass (approximately 65% of raw feedstock) may threaten the environmentally friendly characteristics of biodiesel (Sudalai et al. 2024). In general, defatted biomass is utilised as animal feed because of its high protein content (15–50%) (Mahbub et al. 2019; Sudalai et al. 2024). However, this is not the case for defatted cottonseed, which requires more technical processing because of the presence of toxic compounds such as gossypol (Carbonell-Verdu et al. 2020). Thus, pyrolysis may be an alternative for defatted cottonseed treatment (Wang et al. 2021). Defatted cottonseed can be converted into value-added products such as syngas, bio-oil, and biochar through pyrolysis, which have various applications in the fuel and chemical industries (K N et al. 2022). Therefore, the pyrolysis of defatted cottonseed can be used to enhance the sustainability and economic value of biodiesel production.

In this study, pyrolysis of defatted cottonseed was conducted in N_2 and CO_2 environments to explore greenhouse gas reduction and utilisation strategies by examining the effect of CO_2 on pyrolysis. In addition, thermally induced transesterification was employed to overcome the long reaction times of catalytic methods commonly used for commercial biodiesel production (Maleki et al. 2022). This method, completing the reaction within 1 min, could enhance economic viability by reducing process costs and eliminating the need for catalyst removal (Kim et al. 2024; Velvizhi et al. 2022). Furthermore, this method avoids the need for a washing process to remove catalysts, thus reducing wastewater treatment costs and mitigating the environmental impact associated with wastewater (Kim et al. 2022).

Initiating the reaction solely with heat, without a catalyst, can be an energy-intensive method. Huang et al.

proposed a photothermal process using sunlight as an energy-saving strategy (Huang et al. 2023, 2024). This method successfully reduced the global warming potential (GWP) while achieving a high biodiesel yield (over 95%). However, it required a prolonged reaction time of approximately two hours. In response, this study sought to reduce thermal energy consumption by utilising the catalytic properties of biochar while securing a short reaction time for transesterification. The biochar generated from the pyrolysis of defatted cottonseed was repurposed as a porous catalytic material for thermally induced transesterification. This approach can achieve a closed-loop supply chain in which defatted cottonseeds are processed through pyrolysis to produce biochar, which is then utilised for biodiesel production. The resulting biodiesel can serve as fuel for the cotton industry. This sustainable model efficiently utilises waste products and reduces reliance on fossil fuels, thereby enhancing both environmental sustainability and economic viability within the cotton industry.

2 Materials and methods

2.1 Chemical reagents

n-Hexane (≥ 95.0%), methanol (≥ 99.9%), sulfuric acid (H_2SO_4, ≥ 97.5%), dichloromethane (≥ 99.8%), and silica (pore size 60 Å) were purchased from Sigma-Aldrich (USA). For acid value measurement, potassium hydroxide (95.0%, SAMCHUN Chemicals, Korea), barium hydroxide (95.0%, Sigma-Aldrich, USA), a phenolphthalein solution (0.5 wt.% in ethanol and water [1:1], Sigma-Aldrich, USA), toluene (≥ 99.5%, DAEJUNG Chemicals, Korea), and isopropanol (≥ 99.5%, DAEJUNG Chemicals, Korea) were used. Cottonseed and refined soybean oil were sourced from a local Korean market.

2.2 Sample preparation

The cottonseed was dried at 105 ˚C for 24 h to remove moisture and then milled. Lipids in the cottonseed were obtained via Soxhlet extraction. A thimble filter (25-mm ID and 100-mm L, Whatman, UK) was filled with 100 ± 0.5 g of samples, and extraction was conducted at 100 ˚C for 48 h using 800 mL of n-hexane. Following extraction, the solvent was evaporated using a rotary evaporator (WiseVapor™ Ev-1001 V, SciLab, Korea) to recover the extract (i.e., crude lipid), with a yield of 19.38 ± 1.04 wt.%. In addition, defatted cottonseed was dried at 100 ˚C for 24 h to remove the solvent. The yield (wt.%) of the extract was determined by dividing the weight of the extract by the weight of the sample.

2.3 Characterization of defatted cottonseed

The elemental composition, including that of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) was determined using an elemental analyser (EA3100, EUROVECTOR, Italy). Sulphanilamide was used as the standard sample, and data were recalculated on a dry ash-free basis. Proximate analysis of defatted cottonseed was conducted according to a standard protocol (ASTM D7582). The results of the ultimate and proximate analyses are listed in Table 1.

2.4 Thermogravimetric analysis (TGA)

The thermal degradation characteristics of the cottonseed, defatted cottonseed, extract, and soybean oil were investigated using a TGA instrument (STA 449 F5 Jupiter, NETZSCH, Germany). Approximately 10 mg of each sample was loaded into an aluminium crucible and subjected to heating at a rate of 10 ˚C min^{-1} from 35 to 900 ˚C. Experiments were conducted under a flow of high-purity nitrogen or carbon dioxide (Green Gas, Korea) at 100 mL min^{-1}.

2.5 Pyrolysis of defatted cottonseed

One-stage, two-stage, and catalytic pyrolysis of defatted cottonseed were performed. Each experiment was conducted in two different environments: under nitrogen (100 vol.% N_2) and carbon dioxide (80 vol.% CO_2 and 20 vol.% N_2) conditions. The total gas flow under both conditions was maintained at 800 mL min^{-1}. For one-stage pyrolysis, a sample (10 ± 0.1 g) was loaded in a quartz tube (ID: 22 mm, OD: 25 mm, L: 600 mm) and heated using a single tube furnace (FT-830, DAIHAN Scientific, Korea) from 100 to 600 ˚C at a rate of 10 ˚C min^{-1}. Defatted cottonseed biochar produced via one-stage pyrolysis was collected and used for biodiesel production. For two-stage/catalytic pyrolysis, a longer quartz tube (L: 1,200 mm) and two tube furnaces were used. First tube furnace increased the temperature from 100 to 600 ˚C at a rate of 10 ˚C min^{-1}, while the second tube furnace maintained an isothermal temperature of 600 ˚C. When

Table 1 Ultimate and proximate analyses of defatted cottonseed

	Ultimate analysis				Proximate analysis			
	C	H	O	N	Moisture	Volatile matter	Fixed carbon	Ash
	wt.% on dry ash-free basis				wt.% on dry basis			
Defatted cottonseed	47.16	6.55	39.91	6.38	1.58	71.33	18.91	8.18

loading the sample and catalysts in the quartz tube, the sample was placed at the centre of the heating furnace (first), while the catalysts were positioned at the centre of the isothermal furnace (second). Ni/SiO_2 catalysts were synthesised using the wetness impregnation method described in the literature (Xu et al. 2021). Chemicals in oil condensed at − 40 ˚C were identified using gas chromatography/mass spectrometry (GC/MS 5977B, Agilent, USA) (Table S1), while non-condensable compounds (i.e., gaseous products) were measured using a micro-gas chromatograph (3000A, INFICON, Switzerland). A calibration gas mixture containing H_2, CO_2, CH_4, and C_2-hydrocarbons was procured from INFICON GmbH (Germany).

2.6 Characterization of biochar

The surface morphology and elemental distribution of biochar were examined using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (Cube-II, EMCRAFTS, Korea). Additionally, the surface properties, including surface area, pore volume, and pore size, were measured using a volumetric adsorption measurement instrument (BELSORP-mini II instrument) and the Brunauer–Emmett–Teller method. To determine the inorganic-matter content of the biochar, an inductively coupled plasma-optical emission spectrometer (ICP-OES) (5800 ICP-OES, Agilent, USA) was used, and ICP multi-element standard solution IV (Sigma-Aldrich, USA) was used as the standard solution. The inorganic-matter contents of the cottonseed and defatted cottonseed were also analysed for comparison with that of biochar.

2.7 Transesterification with homogeneous catalyst

The free fatty acid content of the cottonseed extract was measured according to ASTM D974-12. Cottonseed extract reacted with methanol in presence of a heterogeneous acid (H_2SO_4) or alkaline (KOH) catalyst to produce fatty acid methyl esters (FAMEs), which was biodiesel. Details of each transesterification method are presented in Table 2.

2.8 Transesterification with porous materials

To exclude the use of homogeneous catalysts, transesterification of cottonseed extract was conducted using porous materials such as silica and biochar. A bulkhead union (SS-400–61, Swagelok, USA) and two stoppers (SS-400-P, Swagelok, USA) served as batch reactors. The reactor, containing 320 ± 0.5 mg of silica or biochar, 8 µL of extract, and 200 µL of methanol, was placed at the centre of a tube furnace set at 450 ˚C. The reaction temperature was selected from 150 to 380 ˚C based on the TGA results of the extract. The internal temperature of the reactor was monitored using k-type thermocouples (OMEGA, USA). Once the designated reaction temperature was reached, the reactor was allowed to cool to room temperature and then washed with dichloromethane to recover FAMEs. A GC/flame ionisation detector (GC/FID 8890, Agilent, USA) and GC/MS (GC/MS 5977B, Agilent, USA) were employed for calculating FAME yield. A Supelco 37 Component FAME Mix (Sigma-Aldrich) was used as the external standard solution.

3 Results and discussion

3.1 TGA of cottonseed and defatted cottonseed

Understanding the temperature-dependent changes in the chemical composition of feedstock is crucial for improving the efficiency of thermochemical processes. TGA was conducted to investigate the thermal decomposition characteristics of the cottonseed and defatted cottonseed. As depicted in Fig. 1(a), moisture and highly volatile compounds were evaporated at temperatures below 180 ˚C. Continuous thermal degradation of cottonseed and defatted cottonseed was observed at ≤ 550 ˚C. This process involved devolatilisation, and light hydrocarbons, H_2, CH_4, H_2O, CO_2 and CO were released (Janković et al. 2020). Heavy molecules in the biochar decomposed as the temperature increased, resulting in gradual mass loss. This corresponded to the carbonisation of biomass, which included dehydrogenation and demethylation (Janković et al. 2020). Peaks in the differential thermogram (DTG) of cottonseed emerged at 252, 332, and 394 ˚C. A previous study reported that hemicellulose was degraded at 180–340 ˚C, while cellulose was degraded at 250–400 ˚C (Lee et al. 2024). This indicates that the first (252 ˚C) and second (332 ˚C) DTG peaks of cottonseed represent the thermal decomposition of hemicellulose and cellulose, respectively. Although the peak at 394 ˚C was within the temperature range of cellulose thermal degradation,

Table 2 Reaction parameters of acid- or alkali-catalysed transesterification

Catalyst	Molar ratio of methanol to extract	Concentration of catalyst (wt.%)	Reaction temperature (˚C)	Reaction time (hour)	Ref
H_2SO_4	6:1	3	60	24	(Ataya et al. 2007)
KOH	6:1	1.5	60	2	(Azcan and Danisman 2007)

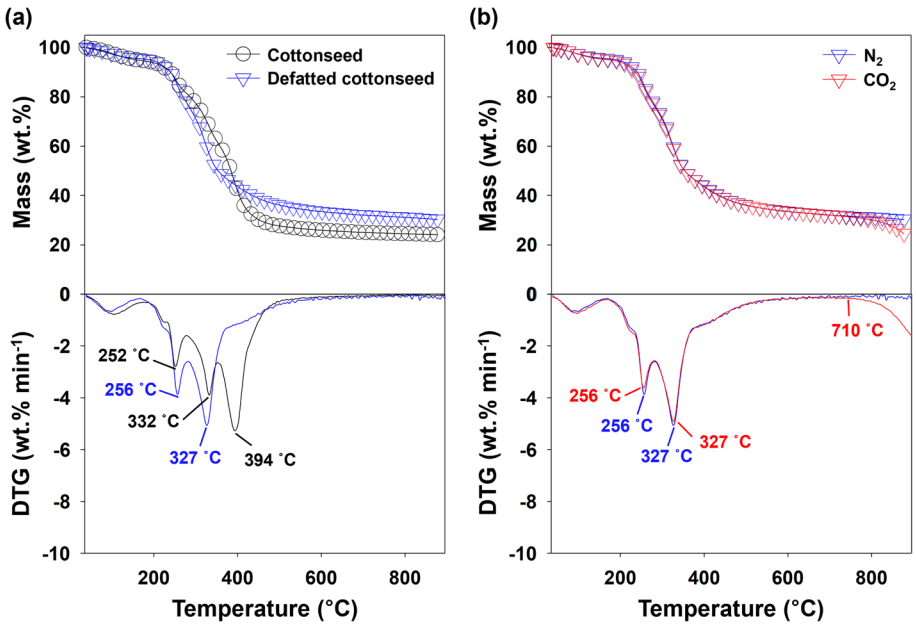


Fig. 1 TGA results of **a** cottonseed and defatted cottonseed under N_2 conditions, and **b** defatted cottonseed under N_2 and CO_2 conditions

it was likely not attributable to cellulose degradation because this peak was not observed in defatted cottonseed. This suggests that other components of the cottonseed may have contributed to this thermal event. Because the difference between cottonseed and defatted cottonseed was the lipid content, it was plausible to conclude that the peak at 394 °C was a result of the mass reduction of lipid compounds in the cottonseed.

To investigate the potential role of CO_2 in the pyrolysis of defatted cottonseed, TGA was conducted in a CO_2 environment and the results were compared with those in the N_2 environment (Fig. 1(b)). The thermolytic patterns of defatted cottonseed in the N_2 and CO_2 environments were identical at ≤ 710 °C. Therefore, CO_2 remained non-reactive with solid samples at ≤ 710 °C. However, additional mass loss of defatted cottonseed was observed above 710 °C in the CO_2 environment. The final residual mass of defatted cottonseed differed between the N_2 (30.01%) and CO_2 (22.09%) environments. These results were ascribed to the Boudouard reaction (heterogeneous gas–solid reaction), in which CO_2 reacts with solid carbon (biochar) at high temperatures (exceeding 700 °C) (Lahijani et al. 2015). Because TGA only measures the weight loss of a sample as the temperature increases, it could be confirmed whether CO_2 reacted with volatile matter before the Boudouard reaction. As such, the pyrolysis temperature was set to 600 °C to ensure sufficient carbonisation of the biochar and to observe the reaction between CO_2 and volatile matter.

3.2 Pyrolysis of defatted cottonseed

The use of CO_2 as a gaseous medium for pyrolysis could provide environmental benefits by serving as a greenhouse gas mitigation strategy. To investigate the homogeneous reaction of CO_2 with volatile matter, pyrolysis of defatted cottonseed was conducted at 600 °C under N_2 and CO_2 conditions, employing the same heating rate (10 °C min^{-1}) as that under TGA conditions. The concentration profiles of the main gaseous products of pyrolysis, namely syngas and CH_4, are shown in Fig. 2a. The generation of CO was initiated at a lower temperature than that of H_2 or CH_4. The highest amount of CO was produced at 280 °C. This might be attributed to the thermal decomposition of cellulosic compounds through deoxygenation processes such as decarboxylation and decarbonylation (Zong et al. 2020). H_2 was produced from 400 °C, and its concentration increased proportionately with the temperature. The temperature at which H_2 was generated was in line with the carbonisation temperature of defatted cottonseed, which is caused by dehydrogenation and demethylation (Liang et al. 2018). Given that the CH_4 concentration decreased from 500 °C, it could be assumed that carbonisation mainly proceeded through dehydrogenation. The contribution of CO_2 to pyrolytic products was confirmed at ≥ 400 °C. Indeed, CO concentration continuously increased at ≥ 400 °C under CO_2 conditions but decreased under N_2 conditions. Considering that the Boudouard reaction of defatted cottonseed was initiated at 710 °C, it was inferred that the increase in CO generation resulted from the CO_2 reaction with

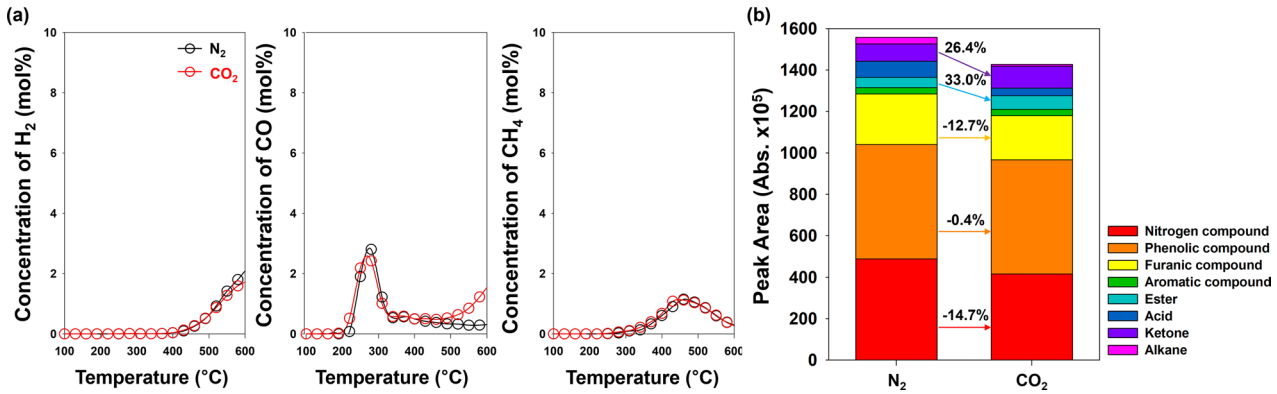


Fig. 2 **a** Concentration of gaseous products and **b** peak area of pyrolytic oil from one-stage pyrolysis of defatted cottonseed

volatile matter. To confirm this hypothesis, another pyrogenic product (pyrolytic oil) produced under N_2 and CO_2 atmospheres was analysed using GC/MS.

As illustrated in Fig. 2(b), the pyrolytic oil produced from defatted cottonseed mainly consisted of nitrogen, phenolic, and furanic compounds. Given that defatted cottonseed is a nitrogen-rich biomass (nitrogen content of 6.38 wt.%), it is understandable that the pyrolytic oil of defatted cottonseed contained a considerable amount of nitrogen-containing oil. The phenolic and furanic compounds might have originated from the decomposition of lignocellulosic materials (Borrero-López et al. 2018; Liu et al. 2022). The pyrolytic oil obtained under CO_2 conditions exhibited a decrease in the peak area of ring-structure substances (nitrogen-containing, phenolic, and furanic compounds) and an increase in that of ketones and esters. The alteration in the chemical composition of the pyrolytic oil indicated that CO_2 served as an oxidising agent, causing additional reactions with volatile matter. In addition, the lower total peak area of the pyrolytic oil under CO_2 suggested that the carbon of the volatile matter was converted into more CO.

The oxygen content of the pyrolytic oil could limit its practical application. For instance, in fuel applications, oxygen compounds are undesirable because of their high reactivity, which leads to alterations in the fuel characteristics during storage and transportation (Kay Lup et al. 2017). For the practical application of pyrolytic oil, further upgrading processes which are energy-intensive and expensive, such as deoxygenation, are required (da Costa et al. 2022). Given that the pyrolytic oil derived from defatted cottonseed contained a high amount of oxygen, additional upgrading processes are necessary for its application. Thus, the production of gas, rather than oil, from defatted cottonseed pyrolysis may be economically beneficial. To achieve this, the pyrolysis design was modified to maximise the ability of CO_2. Notably, the use of CO_2 enhanced gas production by reducing pyrolytic oil generation through the reaction between CO_2 and volatile matter (Fig. 2).

3.3 Two-stage/catalytic pyrolysis of defatted cottonseed under CO_2 conditions

The TGA results showed that approximately 64% of the total mass of defatted cottonseed was lost at < 500 ˚C as a result of volatile matter release. However, it was confirmed that a homogeneous reaction with CO_2 commenced at 500 ˚C (Fig. 2(a)). It was hypothesised that aligning these different temperature windows might be the key to enhancing CO_2 reactivity. Therefore, two-stage pyrolysis was conducted to crack volatile matter generated below 500 ˚C and expedite a homogeneous reaction with CO_2. Nickel-based catalysts were used in a two-stage pyrolysis setup for catalytic pyrolysis. The concentrations of the gaseous products generated from the two-stage and catalytic pyrolysis are shown in Fig. 3(a) and (b). Compared to one-stage pyrolysis, the initiated temperatures of H_2 and CH_4 generation were lower (200 ˚C), while the concentrations of syngas and CH_4 increased. It is plausible to state that the volatile matter thermally cracked into lighter hydrocarbons or gaseous products (H_2, CO, and CH_4) in the second heating zone, which was maintained at 600 ˚C (Jung et al. 2023). In addition, a homogeneous reaction between CO_2 and volatiles might be promoted in two-stage pyrolysis. The total CO concentration under CO_2 conditions increased by 3.2 times and 5.7 times for catalytic and two-stage pyrolysis, respectively, compared to that for one-stage pyrolysis. However, an effect of CO_2 on improving the H_2 concentration was not observed, and the formation of H_2 was suppressed. This could be attributed to the stabilisation of light hydrocarbons generated during the homogeneous reaction (Gao et al. 2018). The free radicals of hydrogen were

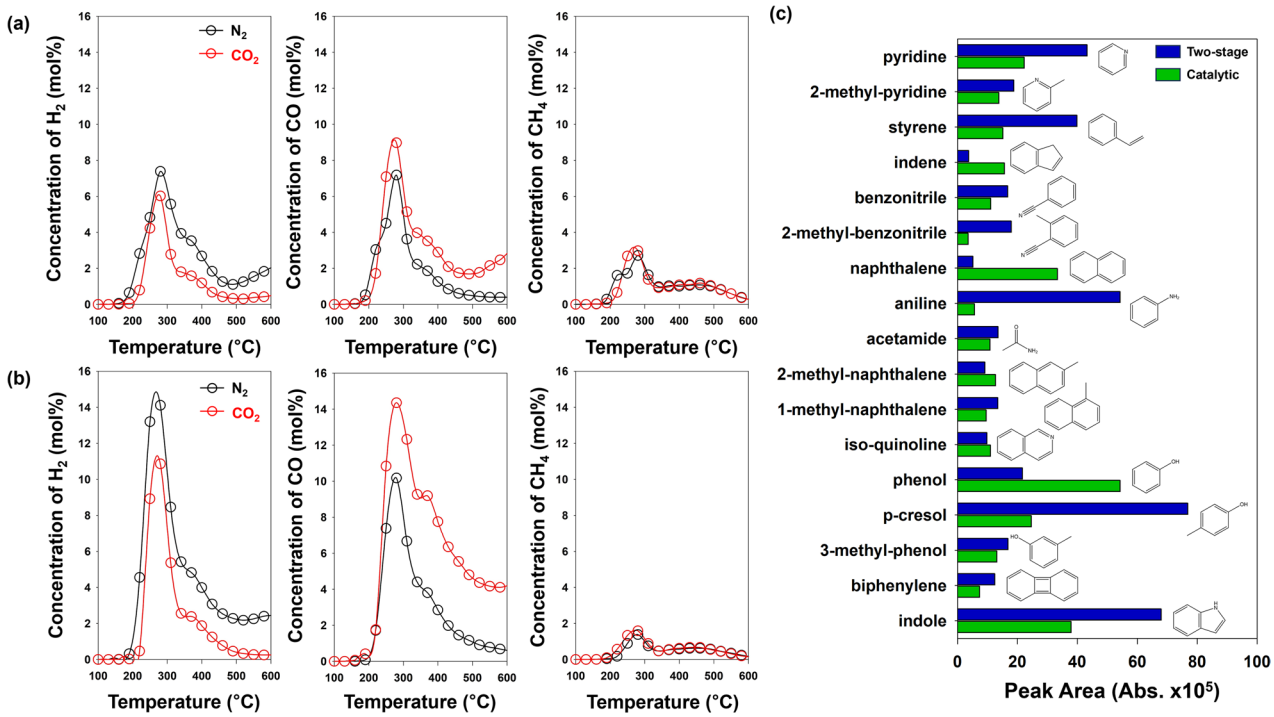


Fig. 3 Concentration of gaseous products from **a** two-stage and **b** catalytic pyrolysis of defatted cottonseed, and **c** peak area of pyrolytic oil from two-stage and catalytic pyrolysis of defatted cottonseed in a CO_2 environment

consumed to stabilise the free radicals of light hydrocarbons with a high H/C ratio before hydrogen was released in the form of H_2 (Luo et al. 2022).

As illustrated in Fig. 3(b), the catalytic pyrolysis of defatted cottonseed resulted in an enhanced syngas (H_2 and CO) concentration and a reduced CH_4 concentration. Compared to two-stage pyrolysis, the H_2 and CO concentrations increased by 1.8 and 2.5 times, respectively, under CO_2 conditions. Nickel-based catalysts are commonly utilised in tar cracking and syngas production because of their excellent catalytic performance and cost-effectiveness (Dong et al. 2019). A catalytic effect was also confirmed through GC/MS analysis of the pyrolytic oil under a CO_2 atmosphere (Fig. 3(c)). Cyclic compounds were predominant in the two-stage pyrolysis regardless of the presence of a catalyst, suggesting that the deoxygenation and dehydrogenation of volatile matter advanced further in the second heating zone (Park et al. 2024). In catalytic pyrolysis, there was a decrease in the peak area of nitrogen compounds, especially aniline, whereas the peak area of polycyclic aromatic hydrocarbons, such as indene and naphthalene, increased. Additionally, decomposition of the methyl group of p-cresol was promoted, leading to an increase in the concentration of phenol. These results suggested that CO_2 was effective in increasing syngas yield.

3.4 Thermally induced transesterification of cottonseed extract

Commercial biodiesel has been produced using homogeneous catalysts such as acid and alkaline catalysts (Mukhtar et al. 2022). The limitations associated with homogeneous catalysts, such as long reaction times and significant wastewater generation, have prompted attempts to develop heterogeneous catalysts or catalyst-free processes (Kant Bhatia et al. 2021). In our previous studies, we developed a transesterification process using thermal energy without a catalyst (Jung et al. 2020). Given that heat is an energy source that activates the biodiesel production reaction, it is crucial to determine the thermal cracking characteristics of lipids, which are key reactants. Therefore, TGA of cottonseed extract was performed, and refined soybean oil was used as a reference (Fig. 4).

The DTG profile of the cottonseed extract was similar to that of refined soybean oil. Specifically, a distinct DTG peak emerged at 420 ˚C, and triglycerides, the main component of lipids, were decomposed from 300 ˚C to 500 ˚C. Therefore, the weight loss of the cottonseed extract from 300 ˚C to 500 ˚C was attributed to the volatilisation of fatty acids after the bond dissociation between the glyceride backbone and carboxyl group in the liquid triglycerides. Considering that transesterification involves the exchange of alkyl groups between an ester

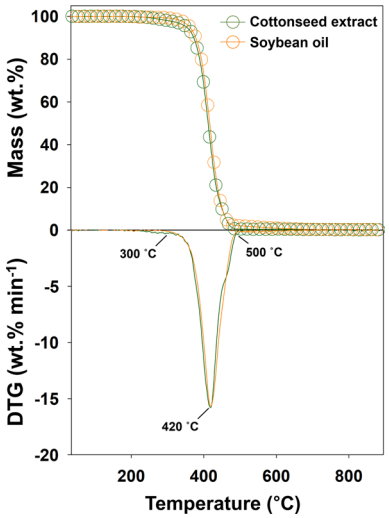


Fig. 4 TGA results of cottonseed extract and refined soybean oil

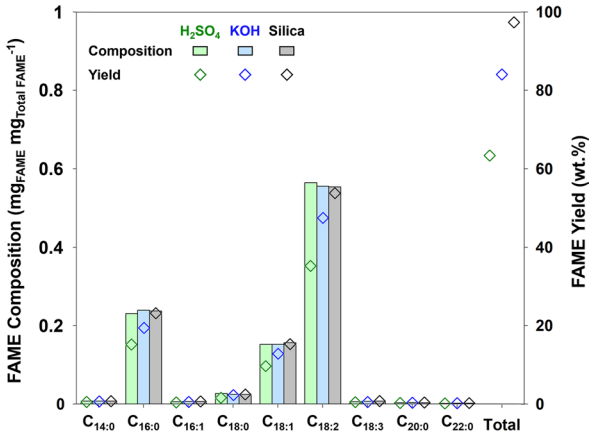


Fig. 5 Yield and composition of FAME converted from cottonseed extract through acid- or alkali-catalysed transesterification and thermally induced transesterification

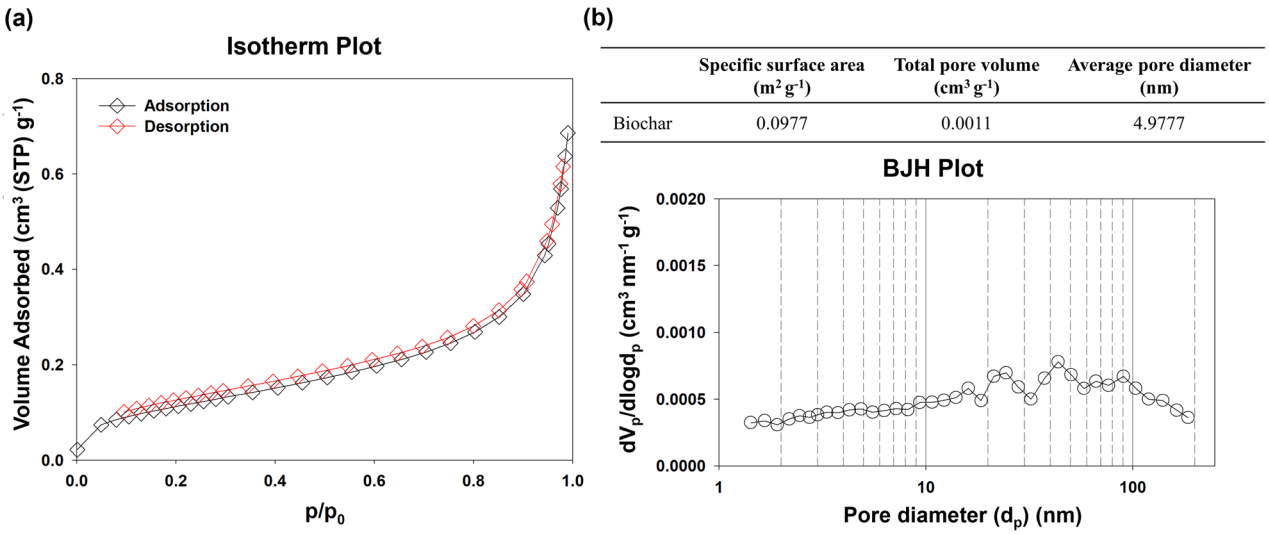
and methanol, it can be expected that thermally induced transesterification of cottonseed extract would be initiated at 300 ˚C. At ≥ 300 ˚C, thermally induced transesterification is a heterogeneous reaction between gaseous methanol and liquid triglyceride. The heterogeneous reaction rate is slower than the homogeneous reaction rate because the reactants collide only at the interface between phases (Huang et al. 2021). To expedite the rate of thermally induced transesterification, a porous material was employed. The limited space for transesterification within the pores increases the frequency of collisions between triglycerides and methanol, resulting in a complete reaction with 1 min.

The biodiesel conversion efficiency of thermally induced transesterification was confirmed by comparison with that of a conventional method using acid/alkaline catalysts. Thermally induced transesterification using silica resulted in the highest FAME yield of 97.4 wt.%, followed by alkaline-catalysed (84.1 wt.%) and acid-catalysed (63.4 wt.%) transesterification. The low yield of conventional transesterification was attributed to the reverse reaction of FAME with glycerol (Mandari and Devarai 2022). To avoid the reverse reaction, separation of glycerol might be necessary. In contrast, thermally induced transesterification reached a FAME yield of 97.4 wt.% at 380 ˚C without glycerol separation. This indicated that a reverse reaction induced by glycerol did not occur during the thermally induced transesterification.

Figure 5 illustrates the FAME composition ratios for three biodiesel production methods. The FAME composition ratio of the thermally induced method was similar to that of conventional methods using catalysts. These results suggest that no cracking of multiple bonds occurred (Jung et al. 2016). Biodiesel derived from cottonseed extract exhibited the highest proportion of linoleic acid ($C_{18:2}$), followed by that of palmitic acid ($C_{16:0}$) and oleic acid ($C_{18:1}$). Large amounts of linoleic acid can positively affect the properties of biodiesel. Indeed, biodiesel with a higher degree of unsaturation has a lower melting point, which enhances engine performance in colder climates (Folayan et al. 2019). Moreover, the low kinematic viscosity of unsaturated fatty acids contributes to better fuel–air mixing (Li et al. 2018).

3.5 Utilization of biochar as a catalyst for biodiesel production

Biochar is commonly used as an adsorbent and catalyst because of its thermal and chemical stability, sufficient porosity, and inorganic-matter content (Patra et al. 2021). In this study, the feasibility of using biochar as a pore source and catalyst to expedite thermally induced transesterification was examined. Defatted cottonseed-derived biochar was produced via pyrolysis. The hysteresis loop in the isotherm plot of Fig. 6(a) indicates that the biochar was mainly composed of meso- and macro-pores. Additionally, in the BJH plot (Fig. 6(b)) showing the pore size distribution, the position of the highest peak was between 40 and 50 nm, which corresponds to the mesopore range. For thermally induced transesterification to occur within pores, biochar must have sufficiently large pores to accommodate triglyceride molecules. This ensures that the reactants can access the active sites within the biochar structure, thus facilitating transesterification. The average pore diameter of the biochar was approximately 5 nm, which was larger than the average molecular size of the triglycerides (2 nm) (Zulkepli et al.



	Specific surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)
Biochar	0.0977	0.0011	4.9777

Fig. 6 **a** Adsorption and desorption isotherms and **b** surficial properties and BJH plot of biochar

2022). Therefore, the biochar had sufficient porosity for thermally induced transesterification.

Figure 7(a) illustrates that, as the cottonseed was subjected to lipid extraction and pyrolysis, the proportion of organic matter decreased, whereas the concentration of alkaline earth metals in the resulting biochar increased. This suggested that extraction and pyrolysis led to both a reduction in organic-matter content and a relative enrichment of inorganic components, particularly alkaline earth metals, in the biochar. The SEM image shows that a porous structure formed as volatile matter was released during pyrolysis (Fig. 7(b)). Indeed, defatted cottonseed-derived biochar mainly contains calcium (Ca), potassium (K), and magnesium (Mg). Particularly, K had the highest content. Zhao et al. reported that basicity increased as the content of alkaline metals in biochar increased, which enhanced the biodiesel yield (Zhao et al. 2018). As such, it was hypothesised that defatted cottonseed-derived biochar could be used as a porous catalyst in thermally induced transesterification because of the presence of alkaline earth metals in the biochar.

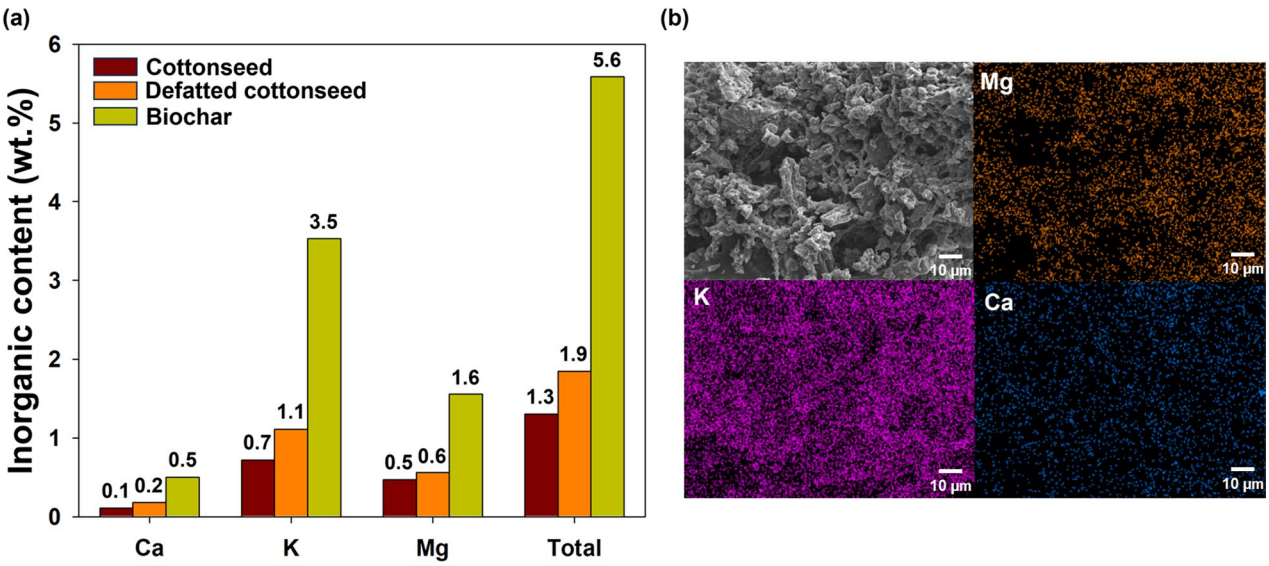


Fig. 7 **a** Inorganic-matter content of cottonseed, defatted cottonseed, and biochar, analyzed using ICP-OES, and **b** elemental distribution and image of biochar, analyzed using SEM/EDX

To observe the catalytic effect of biochar, the FAME yield was investigated in the temperature range of 150 to 380 ˚C (Fig. 8). When biochar was used instead of silica, the FAME yield began to saturate at 250 ˚C and reached a maximum of 98.2 wt.%. At 250 ˚C, the FAME yield was 83.5 wt.% for biochar, compared to the low 1.6 wt.% obtained for silica. In other words, at 250–380 ˚C, biodiesel conversion using biochar was approaching the saturation yield, while the conversion using silica was still in progress. The FAME yield of over 90 wt.% at a lower temperature indicated that biochar was catalytically active during the thermally induced process. Economically, biochar reduces the heat and energy consumption requirements of thermally induced processes. Although preparing biochar from defatted cottonseed may require additional costs and energy, this approach offers significant cost-saving potential by using waste (defatted cottonseed) as a feedstock. Note that feedstock costs generally account for ≤ 40% of the total cost of biochar production (Ahmed et al. 2016). Further economic evaluations, such as techno-economic analysis, will be necessary to determine the commercial viability of utilising defatted cottonseed biochar as a catalyst in biodiesel production.

Global annual cottonseed production of 42,130 tons and approximately 145 million MJ yearly of diesel fuel is required for cotton cultivation (United States Deaprtment of Agriculture 2023; Kazemi et al. 2018). Assuming that cottonseed oil is extracted from all cottonseed, except 1.5% reserved for seeding, and converted into biodiesel without commercial sales, approximately 7,900 tons of biodiesel can be produced annually. This biodiesel can yield approximately 304 million MJ of energy yearly, based on experimental data and literature (Yesilyurt and Aydin 2020). Therefore, cottonseed oil biodiesel production from thermally induced processes using biochar can sufficiently cover the diesel fuel consumption requirements for cotton cultivation. Moreover, the syngas produced from the pyrolysis of defatted cottonseed can be used as a raw material for the syngas-to-methanol process, thereby internally supplying the alcohol required for the biodiesel process (Ebrahimzadeh et al. 2024).

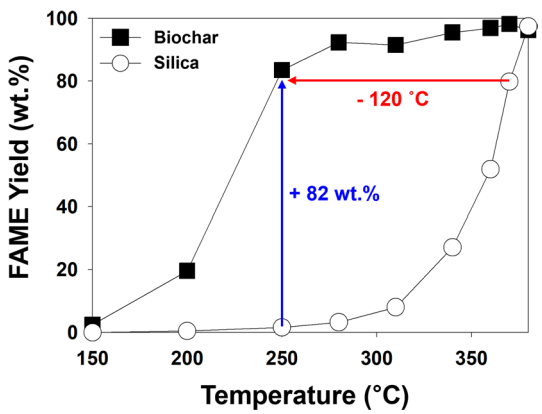


Fig. 8 FAME yield converted from cottonseed extract by thermally induced transesterification using silica or biochar. Each value is the average value of triplicate experiments, and the standard deviation was less than 2%

4 Conclusions

The sustainability of biodiesel production was explored by valorising the byproducts of oil extraction and using pyrolysis to treat defatted cottonseed. In a CO_2 environment, pyrolysis increased CO production as volatile matter reacted with CO_2. Thermally induced transesterification was introduced to address the shortcomings of catalytic conversion, using defatted cottonseed-derived biochar as a pore material. This process yielded 97.4 wt.% FAME within 1 min at 380 ˚C, outperforming KOH- and H_2SO_4-catalysed conversions. The porosity and catalytic properties of biochar lowered the reaction temperature, suggesting that this concept could be applied to a closed-loop supply chain in cotton farming, as follows:

- Cottonseed obtained from cotton farms is used as feedstock for pyrolysis and biodiesel production.
- Biochar required for thermally induced transesterification can be obtained from the pyrolysis of defatted cottonseed. Moreover, methanol can be synthesized from syngas.
- Cottonseed oil biodiesel produced from a thermally induced process can be used as fuel for cotton cultivation or for transportation in cotton farms.

Supplementary Information

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Supplementary Material 1.

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Author contributions
Gyeongnam Park: Conceptualization, Investigation, Writing-Original Draft, Writing-Review and Editing. Jonghyun Park: Conceptualization, Investigation, Visualization, Writing-Review and Editing. Jee Young Kim: Validation, Writing-Original Draft, Writing-Review and Editing. Doyeon Lee: Resources, Writing-Original Draft, Writing-Review and Editing. Eilhann E. Kwon: Supervision, Validation, Writing-Original Draft, Writing-Review and Editing. The authors read and approved the final manuscript.

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Availability of data and materials
Data will be made available on request.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
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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