# APPLIED SCIENCES AND ENGINEERING

# Bio-coal: A renewable and massively producible fuel from lignocellulosic biomass

Bin-Hai Cheng<sup>1</sup>\*, Bao-Cheng Huang<sup>2</sup>\*, Rui Zhang<sup>1</sup>, Ya-Li Chen<sup>1</sup>, Shun-Feng Jiang<sup>1</sup>, Yan Lu<sup>3</sup>, Xue-Song Zhang<sup>1</sup>, Hong Jiang<sup>1†</sup>, Han-Qing Yu<sup>1†</sup>

Development of renewable energy is essential to mitigating the fossil fuel shortage and climate change issues. Here, we propose to produce a new type of energy, bio-coal, via a fast pyrolysis coupled with atmospheric distillation process. The high heating values of the as-prepared bio-coals from the representative biomass are within 25.4 to 28.2 MJ kg<sup>-1</sup>, which are comparable to that of the commercial coals. Life cycle assessment further shows that the bio-coal production process could achieve net positive energy, financial, and environmental benefits. By using available biomass wastes as feedstock, China is expected to have a total bio-coal production of 402 million tons of standard coal equivalent, which is equal to 13% of national coal consumption. It would grant China an opportunity to additionally cut 738 million tons of CO<sub>2</sub> emission by substituting an equal amount of coal with bio-coal in 2030.

#### **INTRODUCTION**

Excessive exploitation and consumption of fossil fuel will not only gradually exhaust its storage in the earth but also cause severe climate change and environment pollution problems (1, 2). In comparison, biofuels can be massively produced and are recognized as a promising alternative for future energy (3, 4). The Energy Independence and Security Act of the United States has anticipated the yield of 16 billion gallons of cellulose-derived biofuels in 2022 (5). However, most of the current biofuels are produced from grain, which inevitably impairs the global food supply. Renewable bio-oil obtained from the fast pyrolysis of lignocellulosic biomass has been found to be an alternative for grain-derived biofuels and undergoes practical applications (6, 7). Nevertheless, since bio-oil is a multicomponent mixture including water, hydrocarbons, and oxygenated compounds (8), it has some undesirable properties, such as strong corrosivity, low heating value, and chemical instability (9). Therefore, great efforts have been made to upgrade bio-oil to obtain high-quality liquid fuels or chemicals (10). For instance, hydrocarbon biofuels (gasoline, diesel, and jet fuel) were produced through several conversion routes from pyrolytic bio-oil (11). An integrated catalytic approach to convert pyrolytic bio-oil into industrial commodity chemicals (C<sub>2</sub> to C<sub>6</sub> monohydric alcohols and diols, C6 to C8 aromatic hydrocarbons, and  $C_2$  to  $C_4$  olefins) has been developed by Huber and co-workers (12). Although great progress in upgrading bio-oil has been achieved and a suite of technologies have been demonstrated at pilot scale, the inherent drawbacks of bio-oil such as thermal polymerization and causing poison of catalysts still present as a big challenge to impede its massive applications.

Atmospheric distillation is a simple and cost-effective technique to separate components from mixtures and has been widely used in industries for over one century. However, such a mature technique has not been successfully used to separate bio-oil because only a small

\*These authors contributed equally to this work. †Corresponding author. Email: jhong@ustc.edu.cn (H.J.); hqyu@ustc.edu.cn (H.-Q.Y.) Copyright © 2020 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

quantity of distillates can be recovered owing to the thermal polymerization properties of bio-oil. Bio-oil is very thermo-unstable and would form coke when being heated, which hinders further distillation. Although molecule distillation has been used to separate bio-oil, the recovery efficiency of carbon content in light distillates is low (~17% of C in bio-oil) (13). To date, lack of effective separation methods has hindered the development of renewable fuel production from biomass pyrolysis.

In pyrolysis, lignin, cellulose, and semicellulose, the main components of biomass are quickly thermo-chemically decomposed in seconds to form small-molecule compounds, in which about 50% of the volatiles can be condensed to form bio-oil. The carbon content of bio-oil ranges from 30 to 50%, and the high heating value (HHV) is about 15 MJ kg<sup>-1</sup>. Apart from organic compounds, bio-oil contains about 30% water, which notably reduces the HHV. Thus, it is highly desirable to elevate the HHV of the residues by removing the moisture than obtain the light distillates with a low HHV. Therefore, instead of alleviating the thermal polymerization of bio-oil by racking one's brain, we propose a new strategy to treat bio-oil. We aim to obtain a solid fuel by accelerating the thermal polymerization of bio-oil. Such a thermally polymerized residue of distillation with a high HHV is named bio-coal. Producing bio-coal has several merits: (i) Bio-coal could be quickly prepared at large scale to partially replace coal; (ii) "carbon-neutral" utilization of biomass is realized to mitigate the global warming problem; (iii) liquid chemicals are harvested without the need of catalysts; (iv) bio-coal can be long-term stored and conveniently transported; and (v) bio-coal can be a carbon warehouse when it is not used. This work would open a shortcut for partially resolving the fuel and environmental crisis faced by the world.

#### **RESULTS AND DISCUSSION**

#### **Properties of bio-coal**

The bio-coal preparation process is illustrated in Fig. 1A. Briefly, the renewable biomass (e.g., rice husk, saw dust, corn stalk, etc.) was first fast pyrolyzed at 500°C under anaerobic atmosphere to produce bio-oil and biochar. Then, the bio-oil was distilled under air atmosphere from room temperature to approximately 240°C to obtain the liquid chemicals and bio-coal. The preparation of bio-coal

<sup>&</sup>lt;sup>1</sup>CAS Key Laboratory of Urban Pollutant Conversion, Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026, China. <sup>2</sup>College of Life and Environmental Sciences, Hangzhou Normal University, Hangzhou 310036, China. <sup>3</sup>State Key Laboratory of Clean Energy Utilization, College of Energy Engineering, Zhejiang University, Hangzhou 310027, China.

involved conventional chemical engineering processes and did not need complicated and costly refinery equipment or operation, which could be readily scaled up.

The rice husk-derived bio-oil was first distilled to prepare biocoal, and its properties were characterized. The element analysis shows that C and H in the bio-coal were notably higher, and O was lower than that in the bio-oil after the distillation (Table 1), indicating that the oxygen-containing groups were taken off. The as-prepared biocoal was a blocky solid with glossy black surface, which is similar to

commercialized coal in color. The scanning electron microscopy (SEM) images show that bio-coal was an amorphous and imporous bulk (Fig. 1, B and C). More images of the bio-coal are provided in fig. S1.

Thermogravimetric analysis (TGA) was then applied to evaluate the thermostability of the obtained bio-coal. The bio-coal had a negligible mass loss below 250°C (Fig. 1D), which was generally attributed to the evaporation of physically adsorbed water and the nondistilled organic compounds. A considerable weight loss was observed in the temperature region of 300 to 750°C, where almost



Fig. 1. Preparation route and characteristics of lignocellulosic biomass-derived bio-coal. (A) Schematic illustration of bio-coal preparation from lignocellulosic biomass. (B and C) Photograph and SEM image of bio-coal. (D) Thermogravimetric analysis (TGA) and differential thermal gravity (DTG) spectrum of bio-coal. (E) Mass energy densities of various coals and bio-coal. Photo credit: Bin-Hai Cheng, University of Science and Technology of China.

	C (%)	H (%)	N (%)		O* (%)	Bulk density (tons m <sup>-3</sup> )	Volumetric energy density (GJ m <sup>-3</sup> )
Bio-oil	34.75	8.04	1.28		55.93		
Bio-coal	64.82	5.88	1.11		27.42	0.674	17.14
*By difference.							
Table 2. Contents o	of heavy metals in t	he bio-coal (weight	%), ND. not detected.				
Metal species	Cd	Pb	Cu	Cr	Zn	Mn	Ni

Table 1. Element analysis (weight %) and physical properties of bio-coal.

~62% weight loss occurred. It has been reported that the weight loss of coals usually mainly occurs in a temperature range of 100° to 800°C in differential thermal gravity (DTG) curves (14), implying that the bio-coal has similar thermogravity properties with commercial coals.

Mass energy density is the most important criterion to evaluate the quality of solid fuel. The HHV of bio-coal was ~25 MJ kg<sup>-1</sup> (Fig. 1E). The mass energy densities of coals A (Alberta sub-bituminous Coal), B (Indonesian Tinto Coal), C (Australia Collie Coal), D (China Pindingshan Bituminous Coal), and E (China Yangquan Anthracite coal), which were acquired from previously reported literature, are ~21, ~28, ~26, ~26, and ~19 MJ kg<sup>-1</sup>, respectively (*15–18*). Thus, the mass energy density of the bio-coal was much higher than that of coals A and E and slightly lower than that of coals B, C, and D, indicating that the bio-coal is a potential alternative to the commercial coals.

The content of heavy metals (e.g., Cd, Pb, and Zn) is a very important factor to evaluate solid biofuels as they can be retained in particulate matter ( $PM_{2.5}$  or  $PM_{10}$ ) after combustion and then float in the air and cause health issues through breathing (19). The species and contents of heavy metals in the bio-coal are presented in Table 2. The contents of Cd, Pb, Cr, Zn, and Mn were very low, while Cu and Ni were even not detected, suggesting that the combustion of the bio-coal would not cause heavy metal–related pollution.

In the atmospheric distillation process, the C content in the residue increased continuously from 34.75 to 64.82% and was greatly enriched in the final bio-coal (Fig. 2A). On the contrary, the O content decreased continuously from 55.93 to 28.19%. The H content also decreased continuously from 8.04 to 5.88%, while the N content remained at around 1  $\pm$  0.3%. The C/O and H/O ratios increased in the atmospheric distillation process, which led to the improvement of the HHV (13.2 MJ kg<sup>-1</sup> for the bio-oil and 25.4 MJ kg<sup>-1</sup> for the bio-coal). The bio-oil and residues retained in the atmospheric distillation process were also characterized by Fourier transform infrared spectroscopy (FTIR) (Fig. 2B). The FTIR spectrum of the bio-oil shows its high oxygen functional groups with strong absorption peaks of O-H (3408 cm<sup>-1</sup>) and  $C=O(1709 \text{ cm}^{-1})$  moieties, as well as phenolic hydroxyl groups  $(1211 \text{ cm}^{-1})$  and C–O–C groups  $(1082 \text{ cm}^{-1})$ . Carbon existed in the form of aromatic rings (1609, 1512, and 1450  $\text{cm}^{-1}$ ) and aliphatic moieties (2964, 2928, and 1377 cm<sup>-1</sup>). No obvious differences were observed from the FTIR spectra of the atmospheric distillation residues and bio-coal, indicating that no new functional groups were formed in the atmospheric distillation.

# Effect of biomass type on the quality of bio-coal

Considering the universality of the proposed bio-coal production route, five common biomass wastes, including rice husk, saw dust, wheat straw, bagasse, and soybean straw, were selected as representatives to produce bio-coals (fig. S2). The bio-coal yields derived from the bio-oil were 45.2, 37.2, 33.9, 41.8, and 34.3%, respectively. Moreover, the bio-coals had similar element compositions (67 to 70%) carbon, ~6% hydrogen, 22 to 27% oxygen), as well as low nitrogen (<1.6%) and sulfur (<0.8%) content (Table 3). The five types of biocoals obtained from the different biomass wastes exhibited similar functional groups, as revealed from the FTIR results (fig. S3). In addition, the estimated mass energy densities of the rice husk-, saw dust-, wheat straw-, bagasse-, and soybean straw-derived bio-coals were 25.4, 28.0, 28.2, 26.3, and 27.6 MJ kg<sup>-1</sup>, respectively, which were comparative to those of commercial coals. These results indicate that the proposed route could be used as a universal method to produce bio-coal from worldwide biomass wastes.

# Energetic, financial, and environmental footprints of bio-coal production

Two scenarios composed of fast pyrolysis for bio-oil production (scenario A) and fast pyrolysis plus atmospheric distillation for biocoal production (scenario B) were assessed in life cycle assessment (LCA) (Fig. 3A). In scenario B, some chemical products could be derived from bio-oil after the two-stage distillation, leaving bio-coal as fuel simultaneously (fig. S4). Before the distillation, there were 51% oxygen, 40% carbon, 8% hydrogen, and 1% nitrogen in the biooil. After the distillation, the yields of the bio-coal and other chemical products were 50 and 15%, respectively.

For the different end uses of biochar, another subscenario was additionally analyzed, in which biochar was used as fuel in scenarios A1 and B1, while as soil amendment in A2 and B2. Results show that the different uses of biochar would result in a varied output while keeping the input unchanged (Fig. 3, B and C). In scenario A, the energy consumption, greenhouse gas (GHG) emission, and economy cost stemmed mainly from the pyrolysis stage. The net energy production yielded roughly 10,752 MJ/ton of dry rice husk in scenario A1, where biochar was used as a coal substitution, and 4532 MJ/ton of dry rice husk in scenario A2, where biochar was



Fig. 2. Compositional change during bio-coal production. (A) Change in the element content during the atmospheric distillation. (B) FTIR spectra of the residues during atmospheric distillation. ADR, atmospheric distillation residue.

Biomass	Bio-coal yield (%)	C (%)	H (%)	N (%)	S (%)	O* (%)	Mass energy density (MJ kg <sup>-1</sup> )
Rice husk	45.2	64.82	5.88	1.11	0.77	27.42	25.4
Saw dust	37.2	70.40	5.85	0.16	0.62	22.97	28.0
Wheat	33.9	69.82	6.05	1.28	0.51	22.34	28.2
Bagasse	41.8	67.65	5.71	0.23	0.37	26.04	26.3
Soybean	34.3	67.13	6.48	1.55	0.44	24.40	27.6

applied for soil amendment. For net GHG emission, there was a negative output around -450 kg in scenario A1, while there was a positive output around 906 kg in scenario A2. Although using biochar as fuel would result in a raised energy production, 42 g/MJ energy GHG would be discharged rather than sequestration of 200 g/MJ energy with soil application of biochar. The net economic performances remained similar between the two subscenarios, as the economic revenue of using biochar as coal substitution was cost-effective.

In comparison, two-stage distillation was applied in scenario B for the production of bio-coal and chemicals, which would further increase the overall input compared to scenario A. In the distillation process, the energy consumption, carbon dioxide emission, and capital costs for every ton of dry rice husk were 2531 MJ, 478 kg, and US\$64, respectively. For the distillation products, the bio-coal was used to substitute the equivalent coal, which could additionally provide 6505 MJ energy and US\$24 profit per ton of dry rice husk compared to scenario A. Moreover, chemical products would bring US\$546 under scenario B (details are listed in tables S1 to S3). Since the bio-oil is not used as fuel, about 456 kg of carbon dioxide emission could be reduced, bringing a cost compensation of US\$12.3 (scenario B1) and US\$39 (scenario B2).

The LCA results show that the net energy and economic revenues were positive under both scenarios A and B. However, for GHG emission, the revenue would be negative when biochar was used as fuel. Use of biochar as soil amendment could enhance the fixation of both

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carbon and nitrogen from fertilizer (20, 21), and thus, there should be an extra benefit for GHG net for scenarios A2 and B2, which is not considered in the present analysis. In addition, since the GHG emission in China is large (22), the government has to make a plan to improve environmental quality (23). Here, in terms of mitigation of climate change, it will be more advisable to apply biochar as soil amendment (scenarios A2 and B2). In system B2, only half of biooil was converted into bio-coal as fuel. In this case, the output of net energy production was reduced from 6600 to 3974 MJ in system A2, and the net GHG sequestration was reduced by 22 kg. However, the net economic revenue of scenario B2 was expected to reach US\$525, as the chemical products doubled the benefit of bio-oil.

#### Benefits for developing bio-coal-based renewable energy

The above results show that it is feasible to use the widely produced and easily accessed biomass such as forestal and agricultural wastes to prepare bio-coal by using our proposed route. It is estimated that the global biomass production is around 146 billion tons/year (24), of which about 3% is agricultural wastes. Thus, it would be a great chance for developing countries to substitute the conventional fossil fuel-based energy with bio-coal-based renewable bioenergy. Taking China as an example, about 402 million tons of bio-coal could be produced with agricultural and forestal wastes, which is equal to 384 million tons of standard coal equivalent (tce) (table S4). Heilongjiang, Henan, Shandong, and Jilin provinces are found to be

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Fig. 3. Costs and benefits of producing bio-coal from lignocellulosic biomass. (A) System boundary for biomass to bio-coal in LCA. (B and C) LCA results covering net energy, greenhouse gas (GHG) emission, and economy performances between different scenarios (positive value represents net output, while negative direction indicates net consumption). (D) Potential of bio-coal production in China. (E) Prediction of bio-coal production, GHG reduction, and financial benefit due to carbon trade in 2030 by using Monte Carlo simulation. The center lines represent median values, boxes refer to 25th to 75th percentiles, while bars represent 5th to 95th percentiles.

the four highest bio-coal production areas, which account for 37% of total agricultural and forestal wastes production (Fig. 3D). At present, coal is still the dominant energy source in China. In 2017, a nationwide energy of about 4.49 billion tce was consumed, 60% of which stemmed from coal (25). By using bio-coal as an alternative, 14% of coal equivalent could be reduced, which would reduce the pressure for coal demand.

With the Paris Agreement successfully made in 2015, China has taken great actions to tackle climate change issues (23). Because of the zero emission of agriculture wastes target in 2030 (26), an increased bio-coal production could be expected in the future. It is estimated that about  $402 \pm 32$  million tce bio-coal could be produced in 2030. If the equal quantities of coal were replaced, 738 million

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tons of  $CO_2$  emission could be reduced. Meanwhile, China is currently piloting  $CO_2$  emission trade, and it is expected to take force in 2021 to 2025 (27). In this case, the reduced  $CO_2$  emission would additionally bring US\$2.4 billion of financial benefit in 2030 (Fig. 3E).

As one of the biggest farm population owners, China has a large crop residue production annually. In the previous practice, the residues were openly burned, resulting in severe atmospheric pollution. To resolve this problem, the Chinese government has made great efforts to forbid open burning and guided a multiple utilization of agriculture residues. Our work demonstrates a new biomass residue utilization route, which would bring about financial and climatic benefits and obviate the atmospheric pollution raised by open burning. However, one should notice that the collection and transportation cost of biomass residues is the key factor influencing the overall economic performance of using biomass residue. To simplify the estimation, a hypothetical transport distance was ascertained in this work. However, future works are still warranted to optimize biomass collection, storage, and transportation systems to take a profitable trade-off between stakeholders, i.e., farmer household, market operator, and government. National financial compensation is an efficient means to stimulate the entire market, which, fortunately, has already been implemented by the Chinese government.

In summary, we propose a new concept to produce a new type of energy, bio-coal, to substitute the widely used coal. Bio-coal could be synthesized via a fast pyrolysis coupled with atmospheric distillation process from different biomass wastes, and the obtained bio-coals have HHVs of 25.4 to 28.2 MJ kg<sup>-1</sup>, which are comparable to that of the commercial coals. LCA further shows that the bio-coal production process could achieve net positive energy, financial, and environmental benefits. By using the available biomass wastes as feedstock, a great deal of  $CO_2$  emission reduction and financial benefits could be expected.

# **MATERIALS AND METHODS**

#### **Biomass origins**

The rice husk used in this work was locally collected from rice mills. The saw dust was supplied by a local lumber mill. The other biomass wastes (wheat straw, bagasse, and soybean straw) were collected from local farms. All the biomass wastes were milled and screened and sieved with a particle size between 100 and 60 mesh (150 to  $250 \,\mu$ m) for the subsequent studies. Before the fast pyrolysis, the samples were dried in an oven at  $105^{\circ}$ C for 12 hours to remove moisture. The resulting dry biomass particles were collected for the subsequent fast pyrolysis and analysis.

## **Bio-coal preparation**

The bio-oils were initially prepared by the fast pyrolysis. Briefly, 5 g of the predried biomass waste was placed in the feed pipe under  $N_2$  flow (400 ml min<sup>-1</sup>) for 30 min to remove excess air. When the temperature was increased to 500°C,  $N_2$  flow was adjusted to 200 ml min<sup>-1</sup>, and the biomass waste was quickly inserted into the quartz tubular reactor. The produced volatiles were purged by  $N_2$  flow and condensed using cold ethanol to obtain bio-oil.

The bio-coal was then produced via the atmospheric distillation of the bio-oil. Briefly, the atmospheric distillation was carried out in a round-bottom flask placed in an oil bath, in which a weighed amount of bio-oil was slowly heated to 240°C under vigorous magnetic stirring. In this batch-mode distillation, volatiles flew upward, and bio-oil was continually condensed along with the elevated temperature, leaving the residues increasingly viscous. The bath was kept at the highest temperature for 20 min and then cooled to room temperature. The viscous atmospheric distillation residue gradually turned out to be a black solid (bio-coal) at room temperature. Then, it was crushed, ground, and sieved to below 100 mesh (150  $\mu$ m), vacuumdried at 80°C for 12 hours to partially remove residual water, and kept in a desiccator for further use.

## Characterization

The elemental compositions (C, H, O, N, and S) of biomass wastes and bio-coal were determined on a Vario EL cube elemental analyzer

(VARIO EL III, Elementar Inc., Germany). As for the proximate analysis of dry rice husk and bio-coal, the ash content was measured using the gravimetric method prescribed in ASTM D 3174-04, the content of volatile matter was determined using an on-isothermal thermogravimetric (TG) method, and the content of fixed carbon was calculated by the difference. In the TG method, 3.0 to 8.0 mg of samples was heated in a TG analyzer (TGA-Q5000, TA Co., USA) under an atmosphere of 25 ml min<sup>-1</sup> of  $N_2$ . The temperature was programmed from room temperature to 110°C at a rate of 10°C min<sup>-1</sup> and held for 10 min before ramping to 900°C at a rate of 25°C min<sup>-1</sup>. Apart from the contents of volatile matter, the thermal characteristics of rice husk and bio-coal were also obtained by the TG method. The specific surface area of bio-coal was determined by N<sub>2</sub> adsorption-desorption isotherms at -196°C using a Micromeritics Gemini apparatus (ASAP2020 M+C, Micromeritics Co., USA) and calculated according to the Brunauer, Emmett, and Teller method.

Bulk and volumetric energy density of bio-coal were determined using a filling and tapping method (28). Briefly, the bio-coal was loaded into a glass column with a specific volume, and then the glass column was tapped onto a bench until no volume change was observed. The final volume and sample weight were recorded. Multiple measurements were conducted for each sample, and the results are reported in kilograms per cubic meter. For bulk density measurements, the SE was 1.5%.

The mass energy density of bio-coal was calculated according to Dulong's formula: mass energy density (kJ kg<sup>-1</sup>) = 337 C + 1419 (H – 1/8 O) + 93 S + 23.26 N. C, H, O, S, and N correspond to the element composition in bio-coal, which were measured using the elemental analyzer. The contents of heavy metals in bio-coal were measured by inductively coupled plasma mass spectrometry (Plasma Quad Co., USA) after HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> digestion.

## Life cycle assessment

LCA was performed according to the ISO 14040 and ISO 14044 standards (29, 30). All the studied objects were packaged as a vector system, and the profit was set to be the positive direction, while the consumption was with the negative direction. The rice husk was selected as a representative biomass, and its physicochemical characteristic is detailed in tables S5 and S6. The system boundaries of LCA were defined and are illustrated in Fig. 3A. Since the rice husk is an agricultural waste, the consumption of planting, growing, and harvesting related to agrochemicals and fertilizer is not counted in this system. In this work, the pyrolysis reactor had a capacity of 10 dry tons/day. The pyrolysis zone was heated to 500°C and swept by nitrogen gas after the condensable fraction was quenched by cold ethanol (-10°C) to obtain bio-oil. The residual biochar was cooled to room temperature, and the noncondensable gas was recycled into the pyrolysis system. In LCA, the energy efficiency, GHG reduction, and economic benefits were chosen as evaluation indices of the system, so the input and output of these items were explored. The data for constructing the LCA model are provided in the Supplementary Materials.

Either bio-oil or bio-coal was used as fuels to substitute coal in the above two scenarios, and the bio-chemicals produced in scenario B were sold as industrial products for financial profits. On the basis of the difference in their boiling points (table S2), a further atmospheric distillation was applied to separate and recover the products into pure chemicals. According to the different end uses of biochar, another subscenario was additionally analyzed. Biochar was used as fuel in scenarios A1 and B1, while it was used as soil amendment in A2 and B2.

#### National bio-coal production estimation

In this work, the bio-coal production potential in China was estimated by using available biomass wastes. The bio-coal production  $Q_{bc}$  (million tce) was estimated according to the following equation

$$Q_{\rm bc} = Q_{\rm ar} \times \eta \times f_{\rm tce} \tag{1}$$

where  $Q_{\rm ar}$  is the available biomass residues (million tons),  $\eta$  is the bio-coal yield according to our experimental results, and  $f_{\rm tce}$  is the factor of converting bio-coal into standard coal equivalent according to their calorific values. The calorific value of standard coal is 29.27 MJ kg<sup>-1</sup> (25).  $Q_{\rm ar}$  is calculated from the following equation

$$Q_{\rm ar} = Q_{\rm ac} \times f_{\rm ar} \times \lambda \tag{2}$$

where  $Q_{ac}$  (million tons) is the acquired agriculture crops and wooden yield,  $f_{ar}$  is the residual coefficient, and  $\lambda$  is the intergrated utilization ratio.

In this work, agricultural crops (i.e., wheat, rice, maize, soybean, potato, cotton, oilseed rape, peanut, and sugarcane) and forestal woods (i.e., log for processing purpose) were selected to calculate the bio-coal production potential. The data of annual  $Q_{\rm ac}$  of agricultural crops and forestal woods were acquired from the National Bureau of Statistics (*31*) and *China Forestry Statistical Yearbook* (*32*). The provincial  $f_{\rm ar}$  was obtained from the National Development and Reform Commission, China (*33*), and the Department of Agriculture and Rural Affairs of Guangdong Province, China (*34*). Because of the deficiency of data sources, the integrated provincial utilization ratio of agriculture waste in 2014 was adopted (*35*) to calculate  $Q_{\rm ac}$  in 2017. According to the National 13th Five-Year Sustainable Development Plan for Agriculture, China (*26*), 100% of  $\lambda$  was used to predict the 2030 status.

The autoregressive integrated moving average was used in this work to fit the historic trends of grain production and predict the estimated quantities in the future. On the basis of the carbon price survey in 2018 (27), the national average carbon trade price of US\$3.3/ton of  $CO_2$  was used to estimate the potential financial benefit via reduced GHG emission. The uncertainties were predicted with Crystal Ball software (Edition 11.1.2.4, Oracle Co., USA) by using 100,000 Monte Carlo simulations.

#### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/1/eaay0748/DC1

- Table S1. Consumptions in thermal process.
- Table S2. Prices of the bio-chemicals (found in the quotes online).
- Table S3. Prices of products of the system-B (US\$/dry rice husk metric ton).
- Table S4. Estimated available biomass residues ( $Q_{ar}$ ) and bio-coal ( $Q_{bc}$ ) amount (million tons).
- Table S5. Ultimate and proximate analyses of rice husk (weight %, on dry basis).
- Table S6. Ultimate analyses of products of fast pyrolysis.
- Fig. S1. SEM images of the bio-coal derived from rice husk.
- Fig. S2. Photographs of the five typical biomass wastes used in this work.
- Fig. S3. FTIR spectra of the five bio-coals derived from the typical biomass wastes.
- Fig. S4. Compositional variations of products after atmospheric distillation.

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