

Molten Salt Carbonization and Activation of Biomass to Functional Biocarbon

Ishioma L. Egun, Haiyong He, Di Hu, and George Z. Chen*

Functional carbon materials are useful for energy storage, catalysis, and pollutant adsorption, and are in high demand, for which biomass has become a valuable raw material. Molten salt carbonization and activation (MSCA) is a promising approach to converting biomass to functional biocarbon and reducing or neutralizing carbon impact on the environment. It uses a single thermal treatment and features high-efficiency conversion, rapid production, and low resource and processing costs. More importantly, in this process, the unmatched purely ionic environment at high temperatures can lead to in situ activation (pore generation) of the biocarbon and introduce desired ions into the carbon to enable unique functionalities. The biocarbon obtained possesses a fairly large specific surface area (SSA), balanced pore structure, and specific surface oxygen-containing groups for diverse applications. This review explains the fundamental and technological aspects of MSCA of biomass, focusing on the approaches, salt compositions (mixtures), processing conditions, and products. The properties of the obtained biocarbon are analyzed and compared in the context of practical applications. Areas for further investigation are also explored with the hope of this molten salt route becoming optimized and industrialized for a circular economy.

reservoirs. Over the years, the concentration had been on fossil fuels with their associated technologies.^[1] With the wake-up call of achieving a balanced carbon cycle, and environmental protection, the need for renewable resources that are economical for energy use and other industrial application has become a priority.^[2] Biomass is such an energy source due to its abundant sources, regeneration, and renewability. Biomass as a unique source of energy can be transformed into liquid fuel, solid (biochar), and gases.^[3] Though solid fuel has existed for a long time in terms of biochar, it became more relevant when it was transformed into activated carbon which has improved the properties needed for various functions.

Porous biocarbon also referred to as functional biocarbon (improved biochar), is an environmentally friendly material produced from biomass precursors, which reduces environmental pollution caused by biomass across the globe.^[4]

It contains mainly carbon and low proportions of oxygen, hydrogen, nitrogen, and mineral species such as potassium, calcium, sodium, silicon, and magnesium depending on the biomass source.^[5] Its properties such as high surface area, well-developed pore structure, and tunable surface oxygen-containing functional groups in both acidic and basic media make it a unique material.^[6] It has been applied in wastewater treatment,^[6c] air purification and gas separation,^[7] hydrogen storage, heterogeneous catalysis, composite,^[8] and electrode materials for battery and supercapacitors. The economic value of porous biocarbon and environmental protection instigates the search for new precursors (various biomass sources) and new technologies for the production of functional biocarbon.

Production of this functional biocarbon on a large scale is currently expensive as the existing processing route often involves multi-steps. Carbonization of biomass precursor and activation of the obtained carbon at high temperatures (≥ 900 °C)^[9] affects the overall production cost. Molten salt carbonization and activation (MSCA) seeks to simplify the process into a single thermal step coupled with in situ activation of the biocarbon at lower temperatures from 500 to 800 °C and reduce the cost of production.^[10] The process maximizes the advantages of molten salts in cracking and liquefaction of large molecules found in biomass.^[6c,11] This process is attracting growing research attention but some certain aspects of the


1. Introduction

The energy demand and consumption for various sectors across the globe have led to harnessing energy from various

I. L. Egun, D. Hu
 Department of Chemical and Environmental Engineering
 Faculty of Science and Engineering
 University of Nottingham Ningbo China
 Ningbo 315100, P. R. China

I. L. Egun, H. He
 Ningbo Institute of Materials Technology and Engineering
 Chinese Academy of Sciences
 Ningbo 315201, P. R. China

G. Z. Chen
 Department of Chemical and Environmental Engineering
 Faculty of Engineering
 University of Nottingham
 Nottingham NG7 2RD, UK
 E-mail: george.chen@nottingham.ac.uk

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adsu.202200294>.

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Figure 1. Biomass examples for biocarbon production.

process and what it entails have not been considered in the body of knowledge. Therefore, this review focuses on the approaches of MSCA specifically for plant biomass and plant-derived polymers which are amongst the most abundant biomass sources due to their regenerative advantage. Also discussed includes various salt mixtures used in the approaches and the proposed reactions, then the properties of the biocarbon, and its applications.

2. Biomass

Biomass refers to all organic matters, particularly those from plants as well as organic wastes. Global annual production of biomass is estimated to be more than 10 billion tons,^[12] including that generated from the growing agriculture to the processing industry.^[13] Biomass can be categorized into agricultural residues (Plants and animals), municipal solid wastes, and dedicated energy crops which are mostly lignocellulosic.^[14] Other biomass types are algal biomass, poultry litter, sewage sludge, and seaweed (which refers to a large number of species of macroscopic, multicellular, and marine algae)^[15] as revealed in **Figure 1**. The lignocellulosic biomass refers to the dry plant biomass, primarily made up of three constituent units: cellulose, hemicellulose, and lignin. Contents of these components in biomass vary depending on the biomass type. Woody biomass has been one of the most investigated biomasses due to its composition.^[16] Biomass is prone to biological decomposition, which facilitates enzymatic processes, such as anaerobic fermentation and fermentation, creating problems for storage and leading to further research on its transformation to functional carbon.

3. Biomass to Biocarbon Conversion

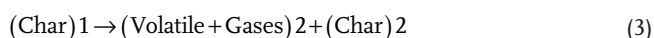
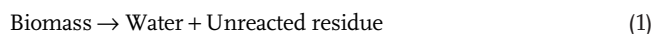
The conversion of biomass into biocarbon (green carbon) with higher carbon content is of decisive importance because these methods make it possible for target-oriented applications. The conversion process for biomass to biocarbon involves the alteration of the physical and chemical nature of biomass by thermal interaction in a controlled inert environment (oxygen-deficient).^[17] Research has shown pyrolysis, and hydrothermal carbonization with activation can be used. The recent molten salt carbonization and activation approach is showing promising indicators for a large-scale application.

3.1. Pyrolysis

Pyrolysis is considered a straightforward conversion route for biomass to biochar. The pyrolysis of biomass to biochar occurs at temperatures between 300 and 500 °C where moisture, volatiles, and most of the hetero-elements in biomass (e.g. N, P, O and S) are removed with the resultant charred material having a higher carbon content.^[5,18] In pyrolysis, the gases emitted include methane, hydrogen, carbon monoxide, and dioxide.^[19] These gases can be utilized for other functions, moving with the current trend to minimize carbon emissions. During pyrolysis, the biomass undergoes different reactions according to the operating conditions (e.g. temperature, residence time, and particle size).^[12] Research in pyrolysis of biomass has shown that temperature and residence time are key process parameters. These parameters could affect the product distribution of particular biomass. Temperature plays a crucial role in tuning

the structure and contents of heteroatoms which are natural dopants in the produced porous carbon and also affect the specific surface area (SSA) (as these atoms attach to the carbon).^[20] Though the micro and internal structures and composition of the char vary in line with the complex components of the biomass source,^[21] the temperature of the process greatly affects the yield.^[22] For pyrolysis of lignocellulosic biomass, the fundamental chemical reaction is complex and consists of several steps leading to end products consisting of biochar, bio-oil, and gases.

The reaction mechanisms of biomass pyrolysis can be defined in three main stages.^[16b]



The char obtained from the above reactions is called biochar but requires further treatment to become functional. This biochar obtained from pyrolysis suffers from a low SSA and undesirable pore structures needed for specific applications.^[11–12] These drawbacks call for the improvement of biochar to better functional biocarbon via activation of the biochar, for example, alteration of composition, structure, and texture.^[23] Research to possibly reduce the time and obtain biochar with better properties using less energy gave rise to hydrothermal carbonization.

3.2. Hydrothermal Carbonization

Hydrothermal carbonization (HTC) of biomass involves contacting the raw feedstock with hot, pressurized water. The process is carried out at low temperatures between 250 and 350 °C with a reaction time from 1 to 6 h when compared to pyrolysis. Through reactions such as hydrolysis, dehydration, and decarboxylation, gaseous and water-soluble products, and solid char are produced.^[24] HTC accommodates a broad range of feedstocks including wet feedstock sources like sugar cane bagasse,^[25] and lignin.^[26] The advantage of this process is using wet biomass compared to pyrolysis which uses dried stock saving the cost of energy required for drying. The pressurized condition for the process is a major challenge leading to complicated process equipment making it expensive compared to conventional pyrolysis. Though it has a shorter residence time, research has shown its residence time is dependent on the application of the biochar.^[27] The biochar from HTC suffers from low porosity and SSA but is better than that obtained from pyrolysis. However, this biochar still requires further activation, which negates the green advantage of the process (especially for large surface area carbon applications).

3.3. Activation of Biochar to Functional biocarbon

Due to the limitation of the biochar from pyrolysis and hydrothermal carbonization, activation strategies were developed and have been used to upgrade biochar to functional biocarbon. They include physical carbonization and activation and chemical carbonization and activation. They are employed to

enhance carbon functionality.^[6b,8b] The properties of interest include structural features, SSA, pore structure, and surface functional groups. The presence of these catalytic minerals affects the reactivity of biocarbon toward other materials. These different properties affecting the reactivity can be grouped into three categories: 1) The char textural properties related to the char porosity and pore size distribution; 2) The char structural properties related to the char carbonaceous structure and graphitization (ordering); 3) The char chemical properties related to the surface functional groups as well as the catalytic mineral species.^[28] Achieving these properties from biomass with a feasible and sustainable route will be advantageous to biocarbon research and technologies.

3.3.1. Physical Carbonization and Activation

The term physical activation is widely used in the literature, but it means both carbonization and activation. Its first step is the pyrolysis and carbonization of raw biomass in an inert atmosphere at temperatures below 750 °C. In this step, most, if not all, volatile matters are removed, leaving behind the char or biochar of much higher carbon content. In the second step, the biochar is treated or activated at relatively higher temperatures (>900 °C) in the presence of oxidizing gases such as carbon dioxide, steam, air, or their mixtures to obtain a biocarbon with high SSA, variable pore size and volume, chemical inertness and stability.^[29] The activation step leads to the formation of biocarbon with various functionalities, particularly an increased SSA of up to 1000 m² g⁻¹.^[7,30] It is worth noting that these two steps involve not only physical changes but also thermochemical reactions, although the term physical activation seems to have been historically misused. Also, the two steps can proceed consecutively in the same reaction vessel, for example, a fixed or packed bed reactor.^[30] This would however require a piece of sophisticated process equipment and utilities to monitor the process, especially on a large scale which is likely to increase the production cost.

3.3.2. Chemical Carbonization and Activation

Like the term physical activation, the term chemical activation also actually means both carbonization and activation which are however often performed in a single step at temperatures ranging from 700 to 1000 °C. In the process, before thermal treatment, the biomass precursor biochar is mixed with activating agents such as KOH, NaOH, Na₂CO₃, MgCl₂, H₃PO₄, and ZnCl₂.^[6c] Compared with physical activation, chemical activation has several remarkable merits, such as shorter activation times, higher carbon yields, larger porosities, and hence SSA.^[29a] The chemical activation process using KOH, NaOH, and other hydroxides is a common tool for preparing porous carbon materials with a rich porous structure, especially for micropores.^[31] A specific comparison between physical and chemical activation was reported on converting walnut shells to biocarbon. The findings showed a significant increase in SSA from just under 700 m² g⁻¹ via CO₂ activation to about 2300 m² g⁻¹ via KOH activation.^[2] It should be pointed out that

the functionality of biocarbon from chemical activation seems to be strongly dependent on the precursor biomass. It was shown that KOH-activated plum stone could reach an ultrahigh SSA of over 3200 m² g⁻¹.^[32] The use of harsh and corrosive chemicals is one of the disadvantages of this process as most of these chemicals have been used in a minimum ratio of 1:3 or 1:4 for biochar to salt to obtain desired properties.^[33] These chemicals if not properly handled cause corrosion of plant equipment, the utilization of acids (HCl, HNO₃) for washing carbon from this process could affect the carbon structure and carbon functionality and increase production costs for industrial applications.

From the perspective of the activation strategies, it can be summed up that the concept of physical and chemical activation has been misrepresented over the years, this is because despite the use of various materials for the process, the activation reaction for both processes involve chemical reactions that occur at similar temperatures and affect the carbon structure and texture. While the chemical activation has shown to yield better textural carbon properties though dependent on the biomass source. The reactivity of metals in chemicals used and carbon is a major factor, especially for potassium and carbon at high temperatures. These metals are absent in physical activation material (steam, CO₂) therefore such reactions could be the trigger for the large SSA and pore structure.

4. Molten Salt Carbonization and Activation

Similar to the chemical activation process, carbonization and activation of biomass proceed simultaneously in molten salt, thereby greatly saving energy consumption. The main difference between chemical activation and MSCA is that molten salts can function as 1) a catalyst to accelerate the biomass-to-biocarbon conversion, 2) a physical barrier to prevent direct contact and hence reactions between the carbon and the atmosphere, and 3) a fluid carrier for mass transfer, i.e., both the biomass reactants and the biocarbon product, that is crucial in designing a continuous process.

In MSCA, the biomass can be broken down into gas, liquid, and carbon materials mainly because of their thermal instability that can be further worsened by the ionic environment of molten salt. Most inorganic salts are ionic crystals at room temperatures but transform into the respective ionic liquids, i.e., molten salts, at temperatures above their melting points. Commonly used molten salts consist of alkali and alkaline earth metal cations and halide, nitrate, silicate, carbonate, hydroxide, and phosphate anions.^[21b,34] These salts are used largely owing to their availability and low costs.^[6b] Molten salts have the advantages of a broad range of working temperatures, favorable thermal stability, low vapor pressure, large heat capacity, low viscosity, and good solubility for many impurities. These properties make molten salts excellent reaction media for the carbonization and activation of biomass, allowing also the doping of the biocarbon obtained from this process.^[35] In addition to acting as a catalyst during carbonization, molten salts can function as a pore-forming agent for preparing porous carbon materials. Being a liquid medium of high thermal conductivity, molten salts can effectively disperse and rapidly heat the biomass (particles) and hence facilitate the catalytic conversion process.^[35a,36] The catalytic effect of MSCA is reflected by the

reactions occurring at low temperatures and hence reduced activation energy for cracking and liquefying biomass molecules.^[6c,11] Interestingly, the use of molten salts as hydrocracking catalysts (molten salt catalytic carbonization) dates back to the 1980s.^[37]

A feasible hypothesis that can account for the catalytic role of molten salts is that the physical changes and chemical reactions occurring during carbonization and activation are mostly either endo- or exothermic processes. This means that any pathways that can increase the heat supply to or remove from the individual processes will accelerate or catalyze the overall process. This is exactly what molten salts can function ideally because they are highly efficient heat conductors. This unique thermal property of molten salts results from their almost pure ionic nature, liquid state, and high temperature. In other words, within the molten salt, because of the high mobility of ions, heat transfer can proceed via all three pathways, namely radiation, conduction, and convection. The benefits of high heat conductivity are particularly important in terms of localized heat transfer near the reaction sites on the biomass and biochar (particles).

The ions in molten salts can also help the carbonaceous material retain its nanostructure. The ions also behave as structure-directing agents/modifiers to tailor the microstructure and physicochemical properties of carbon materials.^[38] This is linked to the diffusion of ions into the material and its reactivity as the process occurs. Also, the ions in the salt affect the surface chemistry of carbon and speed up the process of breaking chemical bonds in biomass precursors.^[39] This is dependent on the temperature of the salt, because the mobility of ions is affected by the temperature and will affect the energy of the collisions.^[40] This can only occur when the salt is above its melting point. Therefore, low melting point salts will be needed to achieve this function, especially in terms of energy consumption which is needed for heating the salt.

A major advantage of MSCA over other separated carbonization and activation processes is that MSCA transforms the biomass precursor into porous biocarbon without the intermediate retrieval of biochar (which is what most existing processes yield from biomass). The process of using the salt ions especially the cations to increase the rate of reaction was confirmed using carbonate salt mixtures. It showed that the reaction rate increased by four times for the intermixture of Na₂CO₃ and K₂CO₃ and by five times when Li₂CO₃ was present. The changes in the process were linked to the alkali metals which catalyze the breaking of the (1,4)-glycosidic bonds found between the biomass components^[11] thereby increasing the reactivity and conversion time to produce functional biocarbon in a single step, in situ activation, and the incorporation of desired functional groups in the carbon product (dependent on applications and the salt used for the process).^[10b,41] This approach simplifies the process utilities (equipment and energy resource) compared to existing methods that require separated pre-carbonization and activation. The advantages and disadvantages of MSCA over existing strategies are compared in **Table 1**.

4.1. Approaches of MSCA of Biomass

The general trend of progress in research on biomass conversion to biocarbon has not been well followed by the MSCA,

Table 1. Comparisons of biomass carbonization processes for functional biocarbon.

Process routes	Advantages	Disadvantages	Carbon properties
Traditional pyrolysis/	High carbon yield greater than 20% feed input ^[42] High temperature < 800–1000. Easy recovery of samples Mature process equipment and operating conditions for various biomass.	Carbon is not activated. Long residence time (3 to 24 h). Multiple process steps.	Low SSA. Carbon is mesoporous. Highly disordered Not Graphitic. Not doped with atoms.
Hydrothermal	High carbon yield. ^[43] Low temperature (150–350 °C). ^[3] Easy sample recovery. Mature process equipment and operating conditions for various biomass.	Carbon not activated and requires further activation. Long residence time (6 h). ^[44]	Low SSA. ^[29a] Little micropores and large mesopores. Not Graphitic. Doped with heteroatoms (if added during the process).
Molten salt Carbonization Activation	Single thermal process, fast heating rate, short residence time (1–2 h). ^[11] In situ activation of carbon samples. ^[45] Doping of heteroatoms (N, P, S) to carbon from salts or salt mixtures. ^[46] Salt's low melting point causes low-temperature activation of carbon samples. ^[6b] Low energy conservation. ^[45] Water-soluble salts can be used for the treatment of precursors to carbon and are washed easily. ^[10b] The ability to dissolve inorganic materials from waste biomass and prepare capacitive storage carbon materials. ^[47]	Salt recyclability challenge, the optimum process, and route still lacking. Lack of mature operating conditions for various biomasses. Equipment corrosion from the use of harsh salts. ^[48] Low carbon yield, but dependent on the salt mixture, temperature, and biomass precursor. ^[49]	Large SSA. ^[45] Abundant micropores. ^[45] Graphitic in nature. Doped with Heteroatoms arising from the salt used for the process.

despite its many advantages. Though many researchers use the generic name molten salt carbonization.^[6c,10a,50] A detailed review of what the MSCA entails, the approaches, and their possible reactions have not appeared in the literature. Here is our review of various approaches to biomass-salt interactions, salt types and mixtures, and the possible reactions in the MSCA of biomass. A comparison of two currently used approaches in MSCA is shown in **Table 2**. The authors have deemed it fit to refer the two approaches as the “mixing route” and the “immersion route” as illustrated in **Figure 2**.

Briefly, in the mixing route, the biomass is firstly mixed with the salt in a designated ratio at room temperature. The mixture is then treated by heating to and maintained at a temperature above the melting point of the salt for a given time, under a suitable atmosphere. In the immersion route, the salt is melted first, followed by immersion of the biomass in the

molten salt under a suitable condition. After a designated time of heating, the sample and molten salt may be cooled together, or with a proper design, the treated sample can be lifted out of the molten salt which is then ready for the next sample treatment (e.g. washing with water). One key difference between the mixing and immersion process is that the polymerization or depolymerization of biomass (the breakdown of certain compounds or the coming together of certain compounds) start before the melting point of the salt in the mixing approach which will likely affect the overall carbonization process as the carbon source is not fully soluble in the salt melt compared to the immersion approach. The described mechanism can only be taken as a reference that helps to understand the process. More details of these two approaches are explained later.

4.2. Mixing Route

The mixing route approach basically involves three stages i) mixing the biomass source with the salt, ii) heating the mixture under an inert atmosphere up to a temperature that ensures the carbonization of the carbon source immersed/dissolved in the liquid salt, and iii) washing out the salts with water or diluted acid. The biomass, in a powdery form, and salt become a homogenous mixture before heat treatment. Once placed in a furnace, the temperature of the furnace is increased gradually beyond the melting point of the salt to the temperature for carbonization (depending on biomass precursor) and maintained for the desired reaction time as illustrated in **Figure 2a**. The biomass may or may not need a pretreatment, e.g. the

Table 2. Comparisons of different approaches to molten salt carbonization and activation.

Parameter	Mixing route	Immersion route
Biomass feed	Pretreatment or no pretreatment	No-pretreatment
State of salt	Mixing followed by melting	Molten
Temperature	Gradually increases to the target	Fixed before biomass introduction
Biomass to salt ratio	Dependent	Fixed salt volume based on reactor volume
Residence (reaction) time	1 to 5 h	1 to 2 h

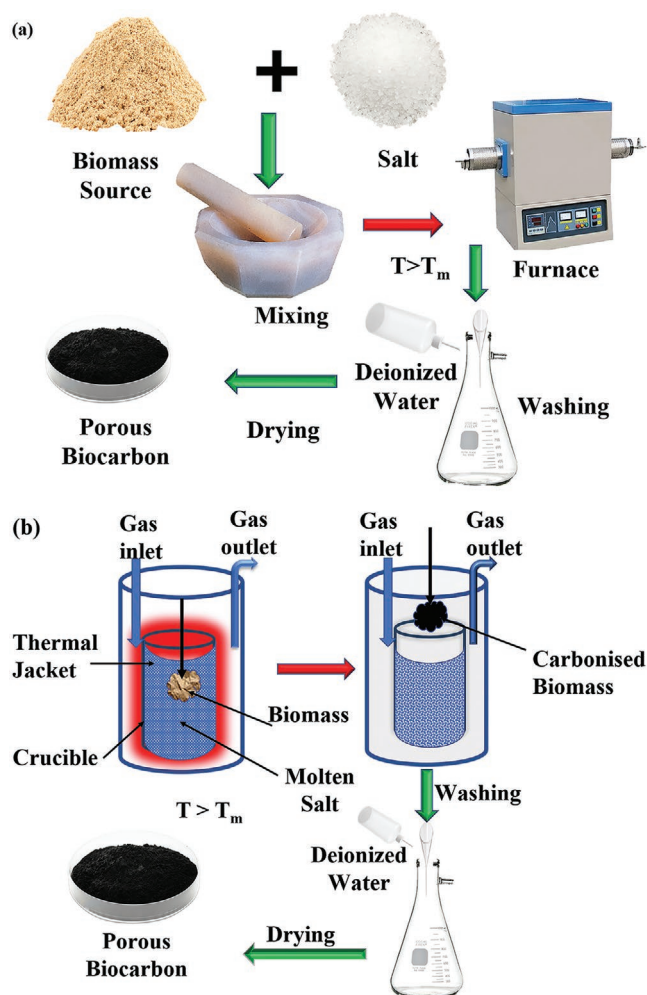


Figure 2. Schematic representation of molten salt carbonization and activation of biomass. a) mixing route, and b) immersion route. (With $T > T_m$, the temperature for carbonization (T) is greater than salt melting point (T_m)).

impregnation, and an allowed time for mixing the salt and biomass before heating in the furnace to the desired temperature and residence time for the MSCA.^[6c,10a,51] The molten salt is used to increase the reaction kinetics of the process as the temperature increases. This approach can be referred to as salt-temperature dependent because the salt is used as a catalyst to enhance the conversion and to improve the properties of the carbon product but the salt changes form which defies the definition of a catalyst. Also, there exists the likelihood for the salts to change their initial state to another state of intermediates or compounds as temperature increases,^[52] creating room for researchers to investigate if the initial state of salt is used as the catalyst or the new salt derivatives are responsible for the catalytic effect. There may be interactions between the salt and biomass in the solid-state before proceeding into a liquid phase at elevated temperatures when carbonization proceeds, as illustrated in **Figure 3** for different biomass sources.

The mixing route dates back to the 19th century when the pyrolysis of lignin was investigated in the presence of $ZnCl_2$ -KCl at 500, 550, and 600 °C with reference to earlier work in 1992.

Nineteen phenolic compounds were identified. The char yield increased with an increasing amount of salt, whilst the gas yield increased with an increase in the residence time.^[37] This revealed that biomass could be transformed into biocarbon using molten salt to increase the rate of decomposition.

In 2012, mixtures of $KHCO_3$ with several biomass powders (α -cellulose, xylose, glucose, starch, chitin, and sucrose) were studied in various mass ratios. The result was 3D hierarchically porous carbon with a nanostructure of micro, meso, and macropores with high SSA ($1893 \text{ m}^2 \text{ g}^{-1}$) which were attributed to the reaction of biomass with $KHCO_3$ at elevated temperatures. The average size of the macropores and the SSA can be controlled by the variation of the temperature.^[54] This indicates that morphology, pore structure, and pore size of biocarbon can be tuned with particular salt ratios and temperature. It is worth mentioning that instead of hydrogen carbonate salts, carbonate salts have been more often reported as a reagent for altering the chemical composition of commercial activated carbon and enhancing its capacitive storage performance.^[10b,55]

Glucose was used as the model carbon precursor to produce carbon of porous structures with SSA up to $2000 \text{ m}^2 \text{ g}^{-1}$. The molten salt was a mixture of LiCl and KCl containing dissolved oxysalts (KZ_yO_x), where Z represents nonmetal elements of H, B, C, N, P, S, and Cl in a mass ratio of 1:1:10 (glucose/oxysalt/chloride salts). The mixing of biomass and salts was achieved using a ball mill, and the mixture was heated to and maintained at 900 °C for 5 h. These oxysalts dissolved in molten LiCl-KCl exert a dominating influence on the pore formation as well as the two-dimensional growth of the carbons.^[46b] It revealed that other salt types could be mixed with the base to generate a complex salt mixture used to improve the energetics of the redox reaction during the carbonization process.

Nanostructured graphene was prepared by mixing glucose with metal chloride (LiCl/KCl), heating the mixture to and keeping it at a temperature between 200 and 800 °C for 5 h. The increase in temperature resulted in the evolution of diverse microstructures in the produced carbon. Mixing glucose with the salt at a mass ratio of 1:10 and heating at a temperature of 400 °C yielded a high carbon content with a 30% oxygen content. The product showed good dispersity in water, in agreement with the presence of a large number of oxygen-containing groups.^[49] The presence of salt increased the rate of carbohydrate breakdown in molecular structure leading to nano porous carbon, amorphous nature, and adjustable pore size.

Highly mesoporous carbons were prepared from glucose, cellulose, and lignin in the eutectic mixture of KCl and $ZnCl_2$ at 1000 °C for 2 h. It was demonstrated that the derived carbon from glucose with a glucose to salt mass ratio of 1:6 exhibited an SSA of $1297 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $2.727 \text{ cm}^3 \text{ g}^{-1}$ dominated with mesopore volume of 92.2%. The carbon from cellulose and lignin also showed high mesoporous proportions in the range of 63.2%–87.5% and SSAs higher than $1000 \text{ m}^2 \text{ g}^{-1}$.^[56] This implies that biomass precursor composition will affect the textural properties of the obtained biocarbon.

Crushed peanut shells were mixed with $ZnCl_2$ in a ratio of 1:5, and heated to a temperature of 200 °C for 30 min., then 480 °C for 90 min. The presence of salt increased the biomass degradation rate. The obtained carbon had a large SSA ($1642 \text{ m}^2 \text{ g}^{-1}$) and surface functional groups allowing it for efficient use in methylene

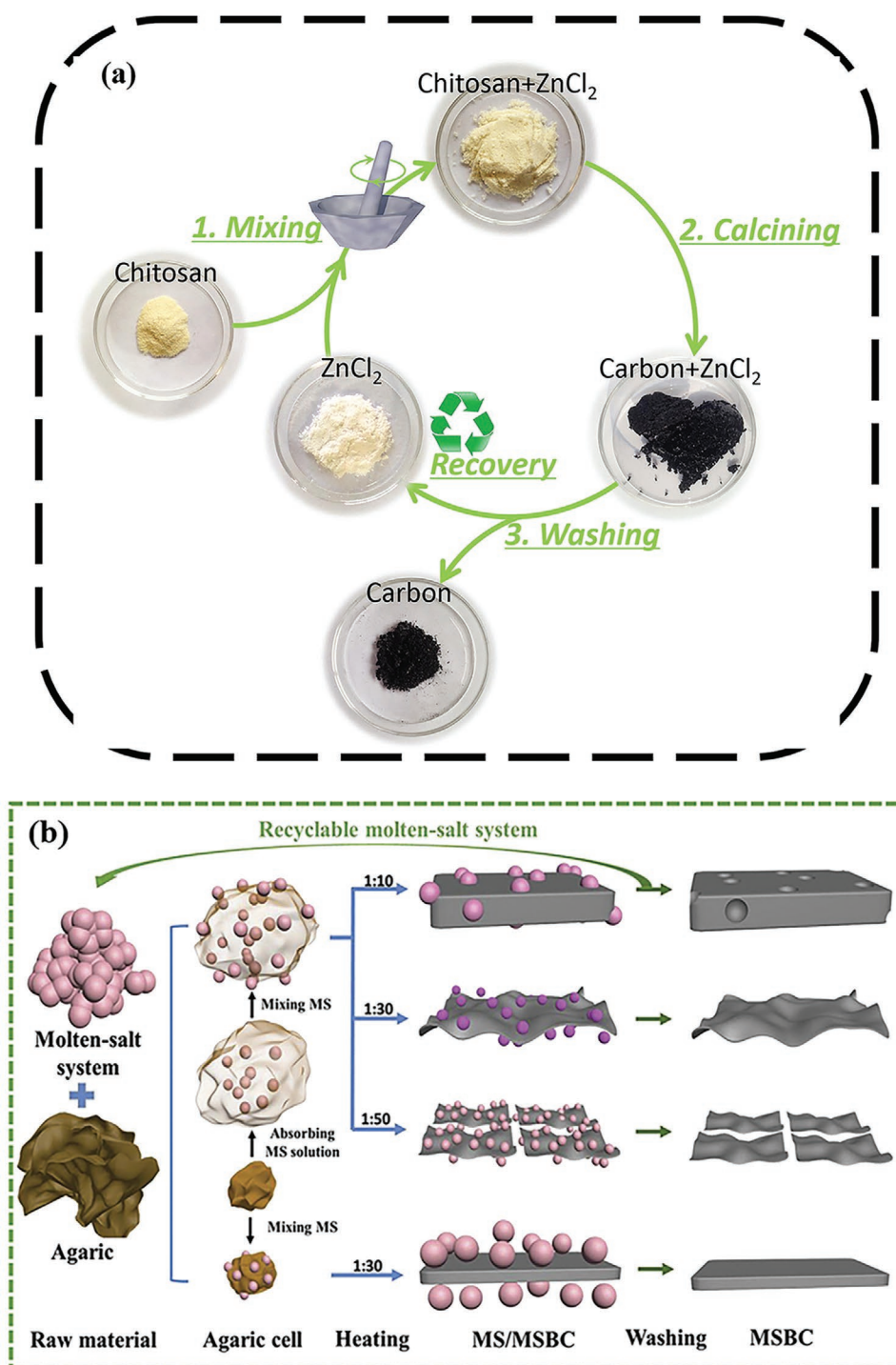


Figure 3. Schematic representations of the mixing route for biomass to biocarbon conversion. a) ZnCl₂ with chitosan (adapted from reference).^[53] b) Mixed LiCl and KCl with agaric biomass. (Adapted with permission.^[10a] Copyright 2020, Elsevier)

blue adsorption.^[6b] The ratio of salt to biomass and temperature will affect the obtained carbon. It would be interesting to investigate if the reaction of components with salt below its melting point generates certain compounds. This is because the melting point of ZnCl₂ is 290 °C, while the initial breakdown temperature for biomass materials is from 150 to 200 °C.

The mixture of chitosan and ZnCl₂ in a mass ratio of 1:10 was used for the preparation of nitrogen-doped hierarchically porous carbon material in a temperature range of 400–700 °C for 2 h. An optimal temperature of 600 °C yielded a carbon sample with a high SSA of 1582 m² g⁻¹, and high nitrogen content of 9.0 wt.% with a high carbon yield of 42 wt.% based on

the weight of chitosan.^[53] The temperature and biomass to salt ratio will affect the carbon yield and properties of biocarbon, such as the SSA and pore size distribution. The decline in SSA at 700 °C indicates there is an optimum temperature to maximize biocarbon properties using the mixing approach of MSCA. A model for temperature, salt mixture, and biomass type will help determine optimum process conditions for different biomass sources using the mixing route of MSCA.

Amorphous activated carbons were obtained by impregnating ZnCl₂ into pinewood chips, banana peels, and pine leaves and then carbonization at 500 °C for 1.5 h. The carbons samples were seen to have high SSAs and pore volumes of 1624 m² g⁻¹ and 1.16 cm³ g⁻¹ for pinewood chips, 1160.4 m² g⁻¹ and 0.81 cm³ g⁻¹ for banana peels, and 1411.8 m² g⁻¹ and 1.10 cm³ g⁻¹ for pine leaves. The biocarbon samples exhibited considerable adsorption capacities for methylene blue.^[6c] The difference in their respective SSAs and pore volumes is linked to biomass's inherent composition. This reveals one advantage of using the same salt for various biomass sources for functional biocarbon but the biomass structure and composition will affect the properties of the carbon samples despite having the same reaction condition.

In an interesting study, tofu was converted to carbon in a mixture of LiCl and KCl as the solvent to dilute LiNO₃, which acted as the activating agent based on the principle of black powder (a mixture of charcoal, an oxidizer or nitrate, and a stabilizer or sulfur to allow for a constant reaction) for the construction of porous carbon framework. The carbonization was achieved at 750 °C for 2 h, yielding a carbon with SSA of 1202 m² g⁻¹. With an increase in the content of LiNO₃ and temperature, the reaction between biomass precursor and LiNO₃ occurred faster. Also, the pores further developed with the consumption of carbon and resulted in a decrease of the carbon wall thickness until fragmentation and the diameter of macropores decreased.^[46a] The introduction of certain oxidizers using the immersion MSCA is to allow for improving the surface area and pore volume of biocarbon while maintaining its morphology. This indicates certain salts like chlorides can help biocarbon maintain its sheet-like morphology during carbonization.

In 2019, hierarchical porous carbon was obtained from glucose treated with KCl and ZnCl₂ (in the weight ratio of 1:2) in a glucose-to-salt ratio of 1:20, but with different amounts of Fe(NO₃)₃·9H₂O. The powder mixture was contained in an alumina crucible and heated at 2 °C min⁻¹ to 800 °C and soaked for 2 h. The product was amorphous and contained numerous oxygen containing functional groups on its surface. The porous carbon with 1.0 wt.% Fe(NO₃)₃·9H₂O oxidizing agent showed the highest SSA of 1078 m² g⁻¹, and the largest pore volume of 0.636 cm³ g⁻¹, among all of the samples.^[57] The concept of introducing Fe(NO₃)₃·9H₂O as an oxidizing agent was to achieve one of the advantages of this process route to dope the biocarbon with certain metals as with Fe for this case. This doping was done because the application for this carbon was for the adsorption of methylene blue and methylene orange.

In 2020, the dimension of using water to dissolve the salt to infiltrate the biomass was introduced. Agaric was converted to thin carbon sheets using LiCl-KCl mixture that was infiltrated to the biomass. The biomass to salt mass ratio was varied from 1:10, 1:30 to 1:50. The optimum carbon sample was obtained at the 1:30 mass ratio and 800 °C for 3 h.^[10a] An increased salt

content would improve carbon properties but too much salt would downgrade the carbon functionalities. Nevertheless, this work demonstrated that recycling of used salt could be achieved. This is one of the benefits of using MSCA for producing biocarbon as the industrial scale-up could integrate the recycling into the plant and reduce production costs.

Also, in 2020 Garlic seeds were processed with KOH for the production of a honeycomb-like hierarchical porous carbon between 600 and 800 °C for 2 h. The optimal condition was 700 °C with a 1:1 mass ratio of KOH and garlic seeds. The carbon displayed a high SSA of 1417 m² g⁻¹ and pore size of 2.44 nm.^[58] The temperature at 700 °C indicates there is an optimum temperature for the complete reaction of biomass to carbon in the presence of a salt. While salt to biomass ratio and heating temperature are expected to affect the properties of the biocarbon from the same biomass source, tuning certain carbon properties for a certain application can be achieved but is dependent on the process variables.

In 2021, cotton stalk which is a typical agriculture waste with 9 kinds of alkali metal salts (LiCl, NaCl, KCl, Li₂CO₃, Na₂CO₃, K₂CO₃, Li₂SO₄, Na₂SO₄ and K₂SO₄, and ZnCl₂) were investigated using seven combined mixtures including 4 binary molten salts (LiCl-KCl, KCl-ZnCl₂, Li₂CO₃-K₂CO₃, and Li₂SO₄-K₂SO₄) and 3 ternary molten salts (LiCl-NaCl-KCl, Li₂CO₃-Na₂CO₃-K₂CO₃ and Li₂SO₄-Na₂SO₄-K₂SO₄) with a biomass to salt ratio of 1:5.^[59] The carbonization process was carried out at 850 °C but with multiple transitions in heating zones. The alkali metal chlorides LiCl-KCl and LiCl-NaCl-KCl had little effect on the distribution of pyrolysis products except for the slight increase of oil products and the slight decrease in gas products, indicating the chlorides didn't participate in the pyrolysis reaction. Under the influence of Li₂CO₃-K₂CO₃ and Li₂CO₃-Na₂CO₃-K₂CO₃, the yields of char and oil decreased, while the gas yield increased significantly to 68.6 wt.% and 67.1 wt/%. This phenomenon can be attributed to: 1) Alkali carbonate can promote the secondary cracking of tar to produce more small molecules of gas so that the oil yield is reduced and the gas yield is increased; 2) Char reacts with carbonate to produce more gas, which reduces the char yield and further increases the gas yield. With the addition of Li₂SO₄-K₂SO₄ and Li₂SO₄-Na₂SO₄-K₂SO₄, the char was not recovered. This is because the sulfates Li₂SO₄-K₂SO₄ and Li₂SO₄-Na₂SO₄-K₂SO₄ can react with char. Therefore, the char was completely converted into gas (mainly CO₂). The dimension of sulphate salts to CO₂ rather than char is interesting but needs to be further investigated to understand the kinetics with other biomass sources.

While various biomass sources and different salts have been used, LiCl, KCl, and ZnCl₂ have been seen to have yielded high SSA biocarbon. Till now the criteria for choosing these salts and their mixtures are lacking as ZnCl₂ is known for its dehydrating effect and other salts have a certain high melting temperature. A critical study on ion's size, temperature, and biomass composition and how they affect reactivity and the process, would help to explain the synergistic effect of these salts.

4.2.1. Reactions in the Mixing Route

The reaction mechanism of the mixing route process can be likened to the known carbonization of biomass in

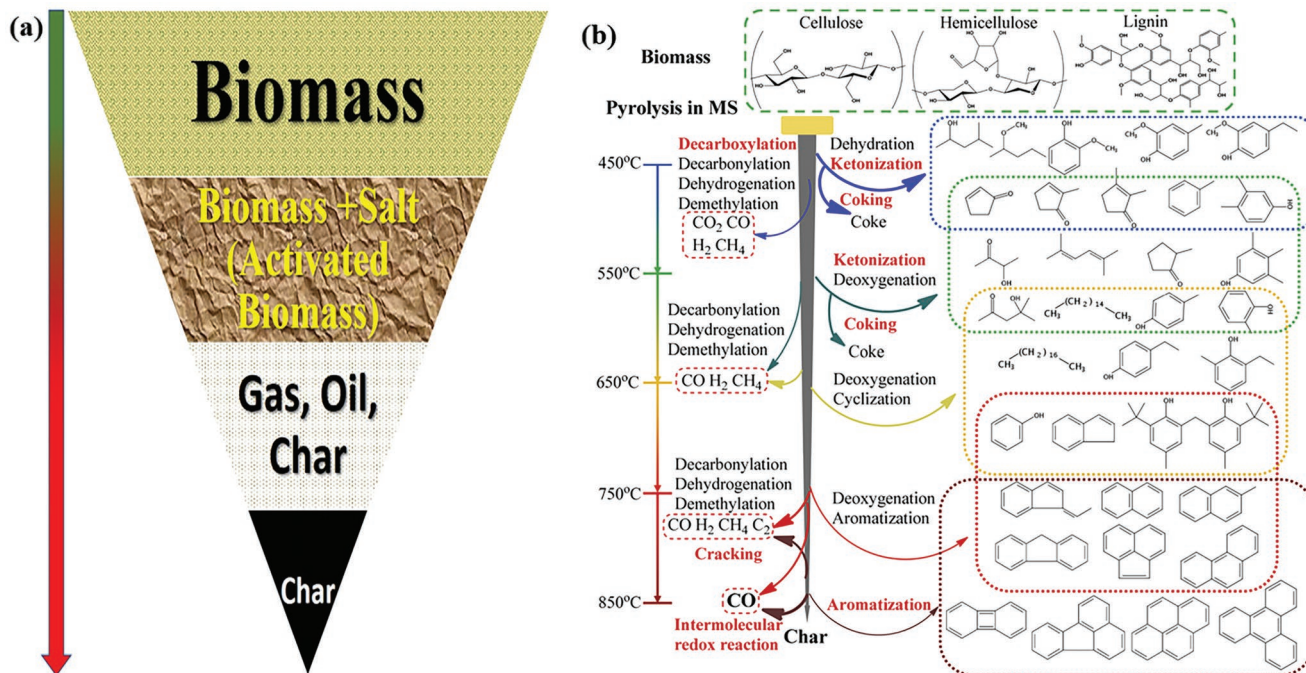


Figure 4. a) Schematic transformation of biomass and b) possible reactions of biomass carbonization in the mixing approach. (Adapted with permission.^[55] Copyright 2020, Elsevier).

Equations (1–3) except for the presence of salt which leads to faster degradation of biomass components as temperature increases. The process and reaction in this route can be summarized in **Figure 4**. The salt is mixed with the biomass and becomes activated biomass before the major transformation begins to occur. In **Figure 4a**, the gradual temperature increase results in changes intermittently. The question yet to be unraveled is if the initial salt or new forms of salt or compounds are involved in the carbonization. The answer to this question will help researchers understand the reaction mechanism of the mixing approach.

The reactions illustrated in **Figure 4b** indicate the release of gaseous products similar to the known pyrolysis of biomass, it would be interesting to investigate the kinetics and thermodynamics of the process. This will help to reveal if salt composition and temperature would affect the reactivity of biomass components and various reactions during the carbonization. It is worth noting that most research has targeted at the functionality of products, not the process routes.

4.2.2. Examples of Biomass Processed via the Mixing Route and Applications

Table 3 shows that biocarbon samples from various biomass sources were porous irrespective of salt type and temperature of carbonization which corroborates one of the advantages of MSCA. While temperature for MSCA is a factor in the mixing approach, the ratio of biomass to salt has been revealed to affect carbon properties irrespective of biomass precursor. The application area for the carbon samples has been for adsorption of contaminants and energy storage.

4.3. Immersion Route

The immersion route basically involves three stages, namely i) preparation and protection of biomass or the biomass precursor ii) heating the salt to above its melting temperature, iii) immersion of the biomass precursor into the salt melt in an inert environment. In the immersion route, the molten salt is used as the reaction media and heat source for the process. The salt is molten and set at the desired temperature for carbonization before the introduction of the biomass, see **Figure 2b**. In the molten state, the catalytic properties of the salt are maximized during the process in an inert atmosphere. During this process, liquid salt is beneficial to enhancing significantly the reactivity and reaction kinetics of carbonaceous species.^[60] Compared with conventional pyrolysis and the mixing route, the immersion route produces more gas, especially CO and H₂.^[55] This indicates that using the immersion route MSCA the conversion of biomass is a fast process.

The immersion route dates back to 1992 when mixtures of molten ZnCl₂ and KCl with molar ratios of 3:7 and 7:6 were used for the pyrolysis of two kinds of lignin. The yield of phenolic compounds was measured, whilst a variety of gaseous products yielded, irrespective of the lignin type. A higher yield of H₂ implies that the H₂O-forming reaction was partially retarded. The maximum yield of cresols from solvolysis of lignin (the salt was used as the solvent for the process) reached 4.6 wt.% higher than any figures reported, so as of the time of the experiment the maximum yield was attained at 600 °C.^[61] In another study, cellulose and rice stalks were tested in six molten mixtures (ZnCl₂, ZnCl₂-KCl, ZnCl₂-KCl-CuCl, KCl-CuCl, KNO₃-NaNO₂-NaNO₃) with various compositions in a temperature range from 400 to 600 °C. It was found that the

Table 3. Examples of biomass conversion to functional carbon via the mixing route.

Biomass	Salt Type	Temperature (°C) per Time (h)	S_{BET} [$\text{m}^2 \text{g}^{-1}$]	Application	Ref.
Glucose	LiCl/KCl	700/5.0	630	Absorption of organics	[49]
Agaric	LiCl/KCl	800/3.0	748	Negative electrode lithium battery	[10a]
Banana peels,	ZnCl ₂	500/1.5	1160	Methylene blue absorption	[6c]
Tofu	LiCl/KCl+ LiNO ₃	700/2.0	1202	Supercapacitor	[46a]
Pine leaves	ZnCl ₂	500/1.5	1411	Methylene blue adsorption	[6c]
Garlic seeds	KOH	700/2.0	1417	Supercapacitor	[58]
Chitosan	ZnCl ₂	600/2.0	1582	Supercapacitor	[53]
Peanut shells	ZnCl ₂	200/0.5 and 480/1.5	1642	Methylene blue adsorption	[6b]
Pinewood chips,	ZnCl ₂	500/1.5	1624	Methylene blue absorption	[6c]
Biomass powder	KHCO ₃	400/3.0	1893	Supercapacitor	[54]
Glucose	KCl/ZnCl ₂ + 1.0 wt.% Fe(NO ₃) ₃ ·9H ₂ O	800/2.0	1078	Methylene blue and Methylene Orange absorption	[57]
Cotton stalk	LiCl/KCl	850/0.5	161	–	[59]
	LiCl/NaCl/KCl	850/0.5	113	–	[59]
	Li ₂ CO ₃ /K ₂ CO ₃	850/0.5	889	–	[59]
	Li ₂ CO ₃ /Na ₂ CO ₃ /K ₂ CO ₃	850/0.5	821	–	[59]

product yield and compound composition varied with changing the salt mixture. It was attributed to the catalytic effects of the ions in the various salt mixtures, while ZnCl₂ made the yield of bio-oil product to its maximum reach during biomass pyrolysis. Also, it is worthy of noting that nitrate salts gave zero yields on bio-oil, indicating inefficient salts for the immersion MSCA of biomass. The bio-oil from this process is a complicated organic matter as revealed by the FTIR reflecting that the biomass-salt interaction affects the type and number of functional groups present in the final product.^[41a]

In 2015, molten salt pyrolysis of milled beech wood of 0.5–2 mm in particle size was carried out in molten salt mixtures, including FLiNaK, i.e. eutectic of LiF-NaF-KF, and the carbonate equivalent, (LiNaK)₂CO₃ over the temperature range from 450 to 600 °C. The highest yield of the pyrolysis oil was achieved in FLiNaK, with a maximum of 34.2 wt.% at 500 °C, followed by a decrease with increasing reactor temperature.^[36c] The process was likened to the fast pyrolysis process as temperature change did not affect oil yield. Carbonate salts yielded more gas than chloride salts which was attributed to the presence of CO₂⁻ ions.

Rice stalk was investigated in a ZnCl₂-KCl salt mixture with a temperature from 400 to 600 °C. Functional carbon could be obtained at low temperatures. The combination of ZnCl₂-KCl could considerably improve the solid from 30.5% to 65.7% for carbonization without and with molten salt, respectively.^[36d] The characteristics of the biocarbon can be manipulated by controlling three major variables, namely, temperature, weight ratio of carbon precursor to molten salt, and activation time. Interestingly, the use of the eutectic ZnCl₂-KCl mixture for pyrolysis could lead to maximum production of biocarbon and liquid which creates room for optimization of salt mixture ratios.

In a 2014 report, the thermal behavior and pyrolysis of beechwood were investigated. Instead of fine particles, cylindrical beechwood rods ($L = 30$ mm, $d = 3.5$ mm) were pyrolyzed using different mixtures of molten salts (FLiNaK, (LiNaK)₂CO₃, ZnCl₂-KCl, KNO₃-NaNO₃) over a temperature range from 400 to 600 °C. In the experiment, a beechwood rod was attached to the lower end of a long steel tube through which a 1 mm diameter thermal couple was inserted into the center of the beechwood rod which was immersed in the molten salt. The measured temperature of the rod center was used to evaluate the heating rate, reaction temperature, and devolatilization time. A general observation was that beechwood was heated faster in fluoride and carbonate melts, but the differences diminished with increasing the reactor temperature. The highest heating rates (from 46 to 56 °C s⁻¹) in the rod center were observed in FLiNaK at 500 °C. The effective pyrolysis temperature at which the main decomposition of cellulose and hemicellulose took place showed a weak dependence on reactor temperature, but no significant difference between the heating media was observed.^[36e] Uniform heat transfer is a challenge using large biomass particle sizes with the immersion MSCA approach as it is more of a diffusion process. Therefore, large particles would require a longer time for the salt to diffuse into the biomass.

The carbonization of bamboo shells was achieved in molten Na₂CO₃-K₂CO₃ at 850 °C for 1 hr using a nickel mesh basket to hold the biomass. The shape of the obtained carbon was determined by the biomass precursor, indicating that salt ions only diffused into the bamboo sample during the process while the biomass retained its structure during and after the process. The biocarbon was partially graphitic with SSA of 843 m² g⁻¹ and pore volume of 0.43 cm³ g⁻¹.^[62] The work revealed that trace metals in biomass precursors were removed, and that the process could

be a simple and effective route for converting waste biomasses to value-added carbon materials, especially for briquettes that require a specific shape as the final product. It should be noted that the effect of the nickel mesh basket during the process was not investigated as it was used as a tool for biocarbon recovery.

Boiled coffee beans are a very common waste biomass and were successfully carbonized in molten Na_2CO_3 - K_2CO_3 at 800 °C and molten CaCl_2 at 850 °C for 1.5 h. CaCl_2 is a strong desiccant due to its intrinsic affinity to moisture. Even when anhydrous CaCl_2 is employed, hydrolysis of CaCl_2 is still significant and the hydrolysis products, i.e., $\text{Ca}(\text{OH})_2$ and HCl tend to dissolve ($\text{Ca}(\text{OH})_2$) in, or become released (HCl) from the melts. Also, the generated $\text{Ca}(\text{OH})_2$ is readily decomposed to CaO and H_2O .^[39] Biocarbon samples from molten chloride had a higher SSA of 550 $\text{m}^2 \text{g}^{-1}$ compared to 436 $\text{m}^2 \text{g}^{-1}$ for carbonates. It also possessed more oxygen-containing surface functional groups, and a less ordered microstructure when compared to that from the carbonate salt. This is one of the advantages of MSCA maintaining certain functional groups on the biocarbon surface and microstructure modification. This attests to the fact that anion and cation of salt melt will affect the biocarbon properties despite using the same biomass precursor, giving rise to the search for the mechanism of the reaction of biomass for various salt melts. An insight that the properties of carbon samples can be tuned with salt type and heating temperature using the immersion route is interesting. The difference in temperature for comparing both salts could be a factor that can affect carbon properties, as research has shown that temperature is a key factor in biomass carbonization.^[63] A critical investigation using the same process condition should be carried out, though differences in the melting points of various salts will be a challenge to achieving that.

Different Chinese firwood feeds of powder ($L = 0.09$ mm), small ($L = 1.0$ cm) and large ($L = 2.0$ cm) woodblocks, respectively were treated in the molten eutectic mixture of Na_2CO_3 - K_2CO_3 at 850 °C for 1 h. The firewood samples were protected with nickel foam when immersed in the molten salt. The work revealed that the salt could help the as-prepared carbons to retain the shapes of the precursors, irrespective of the sizes. This indicates that the conversion process mainly involves solid to solid and solid to gas conversions. Decreasing the size of the raw materials from 2 to 0.09 cm, the SSA of the resultant carbons increased from 215 to 818 $\text{m}^2 \text{g}^{-1}$, and the specific pore volume increased from 0.10 to 0.44 $\text{cm}^3 \text{g}^{-1}$.^[38a] This reflects that immersion route MSCA is a diffusion-controlled process. As the biomass and salt ions interact at such a high temperature there is a release of volatile materials. The increased salt and biomass contact for smaller particles enhances a faster release.

In 2019, the carbonization of soybean straw in molten KOH was reported. The soybean straw was made into tablets and protected in nickel foam before heating in the KOH melt at 800 °C for 1 h. The porous carbon produced had a well-defined beehive-like structure with an SSA up to 1615 $\text{m}^2 \text{g}^{-1}$ and showed a certain level of graphitization.^[45] The carbon properties were attributed to the high fluidity of molten KOH arising from its relatively low melting temperature of 360 °C and reactivity.

The low melting temperature of salt will reduce the amount of energy required to make the salt molten. The rigorous

bubbling observed after immersing reflected in **Figure 5A** (top) needs to be investigated to examine if it's a common trend with other types of salt or particular to KOH. This is to ascertain if the bubbling would generate gases, as these gases could either be advantageous for pore generation or could alter the biocarbon properties. The intercalation of K^+ ions into the biomass components during the process led to physicochemical activation, carbon lattice expansion, and further increase of the surface area and porosity of carbon materials. The immersion route using molten KOH should be further investigated as it has shown to yield porous carbon, **Figure 5A(d)**, within a short residence time.

Undoubtedly, using KOH in the immersion route of MSCA would be an advantage for short residence time. However, various volatile substances could form because of the reaction between KOH and carbon matrix at elevated temperatures. These volatile substances, including metal K (vapor), CO , CO_2 , H_2 and H_2O led to the formation of abundant micropores but threatened the safety of the reactor because of the strong corrosiveness of metal potassium (K). Therefore, less corrosive salts should be further investigated using the immersion approach toward industrialization.

In 2020, a novel reactor design for the MSCA immersion route using a catheter. **Figure 5B left** presents the catheter which was directly inserted into the molten salt for fast pyrolysis. This reactor design was used for a cotton stalk in molten salt (top left) and with a catheter (top right) in the molten eutectic mixture of Li_2CO_3 - Na_2CO_3 - K_2CO_3 at temperatures ranging from 450 to 850 °C. It was observed that the syngas yield gradually increased with the increase in temperature indicating volatiles reforming occurred in the presence of the molten salt. Though at high temperatures more gases, especially CO and H_2 were produced leading to a large reduction in the carbon yield which is reflected in **Figure 5B (bottom)**.^[55] Salt mixtures decrease the melting and working temperatures of the process which helps to achieve one of the goals of MSCA to become a green route for biomass conversion trend. The melting temperature affects the mobility of ions, which affects ion reactivity with biomass components during the carbonization. The carbonate salts seem to be environmentally friendly but suffer from high melting points. The ternary mixture reduces the melting point from those of the individual salts but the economic cost for the salts needs to be calculated or estimated to evaluate the feasibility on the industrial scale.

While the immersion route shows promising advantages, the dimension of a reactor driven by a renewable energy source is introduced. A novel solar reactor pyrolysis concept was operated using concentrated solar energy supplied by a solar central receiver plant as illustrated in **Figure 6a**. The reactor concept comprised a set of vertical tubes to absorb concentrated solar radiation and exploited free convection of the molten salt to deliver the thermal energy to the reaction-thermal-storage medium. The biomass particles were dispersed in a molten salt phase heated by solar energy. The reactor was used to obtain gases from celluloses using the eutectic mixture of Na_2CO_3 and K_2CO_3 with a melting point of 710 °C. The cellulose tablets were introduced into the melt at 850 °C and the following gases: H_2 , CO , CO_2 , CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 were observed to have evolved. It was seen that the residual char from the

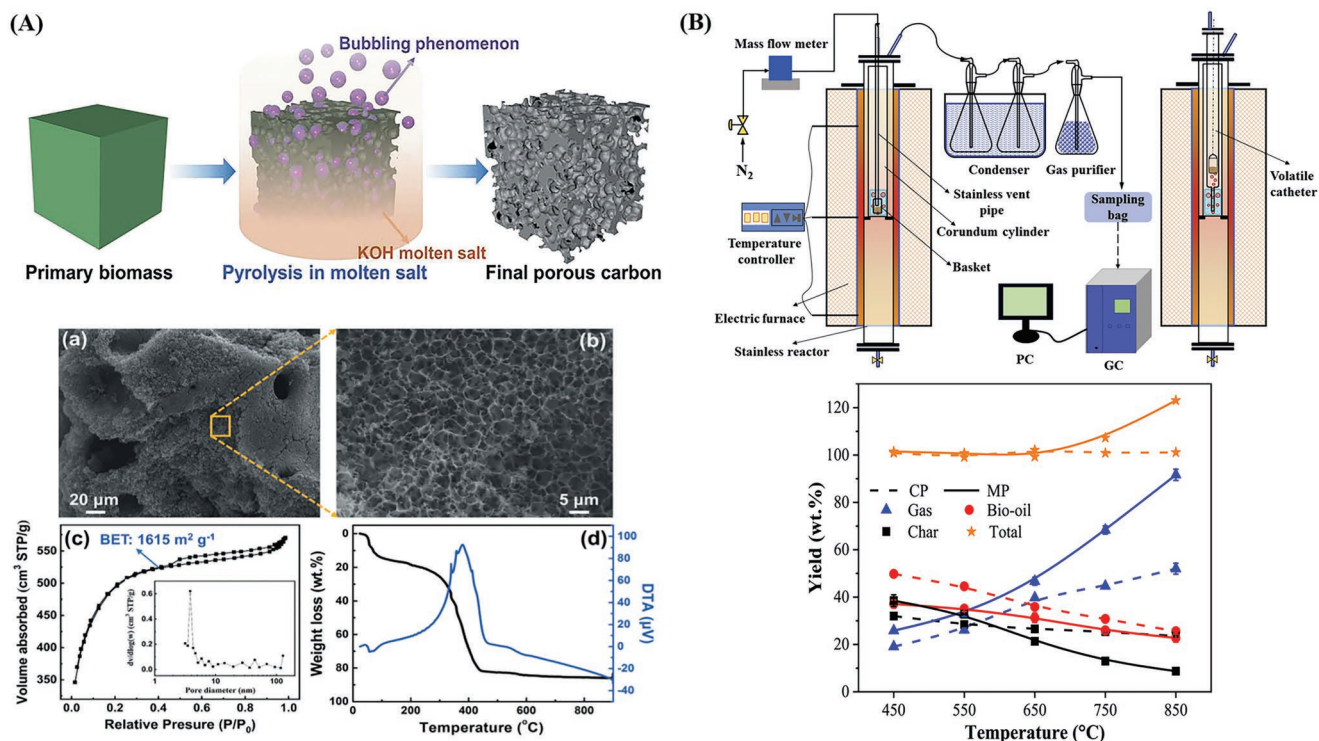


Figure 5. A) Illustration of the evolution of biomass in molten KOH (top), carbon sample SEM images (a,b), and N₂ adsorption/desorption isotherms (c) of the obtained carbon materials after pyrolysis of soybean straw in KOH molten salt at 800 °C for 1 h. The inset in (c) is the pore size distribution of biocarbon. TGA and DTA curves of soybean straw in an Ar atmosphere from room temperature to 900 °C at a heating rate of 10 °C min⁻¹ (d). (Adapted with permission.^[45] Copyright 2019, Taylor & Francis). (B) Schematic of the experimental setup of molten salt carbonization (top), distribution of cotton stalk pyrolysis products (bottom). CP: conventional pyrolysis, MP: molten salt pyrolysis, VR: pyrolysis volatiles reforming in molten salt. (Adapted with permission.^[55] Copyright 2020, Elsevier).

cellulose tablets retained their initial shape but with size reduction after the process indicating the salt melt could enhance the production of a specific shape of biochar dependent on the precursor shape. However, the size and dimension were affected as the linear dimensions were contracted by 20 to 25% relative to the initial size as shown in Figure 6b. The total porosity of the char was between 88% and 93%, although the internal surface area was only 2 m² g⁻¹, measured by the BET method. Increasing the temperature of the molten salt from 850 to 915 °C resulted in high cellulose-to-gas conversion and the total amount of residues reduces to only 1 to 2 wt.% of the initial

biomass feed.^[35a] This indicates that the precursor size will affect the pore size of the carbon as this process is diffusion controlled. The temperature for the process will determine the char yield. To maximize the char yield, the temperature has to be controlled.

This solar system was further investigated with peanut shells in four kinds of molten salt and their mixtures (Na₂CO₃-K₂CO₃, Li₂CO₃-Na₂CO₃-K₂CO₃, CaCl₂, and CaCl₂-NaCl) for 1 h at 850 °C. The SSA of the samples were 408, 380, 390, and 316 m² g⁻¹, respectively. The increase in SSA could be linked to the associated intrinsic properties, such as absorptive ability, catalytic

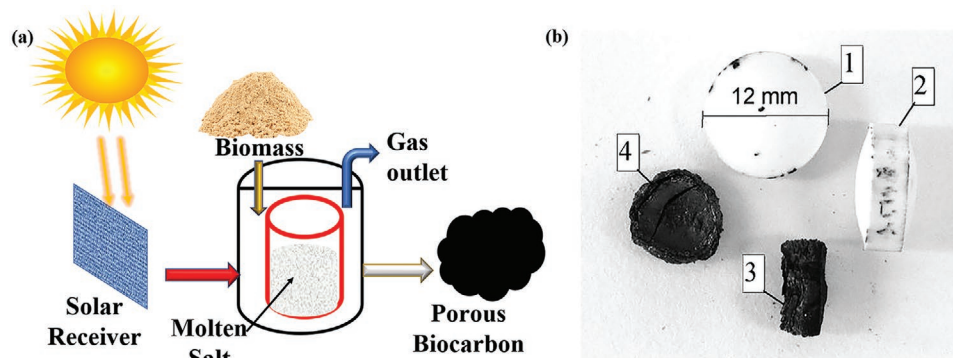


Figure 6. a) Schematic drawing of a conceptual solar reactor for MSCA. b) Cylindrical cellulose tablet before (1: top, 2: side) and after (3: side, 4: top) pyrolysis in a molten eutectic mixture of Na₂CO₃-K₂CO₃. (Adapted with permission.^[35a] Copyright 2004, ASME).

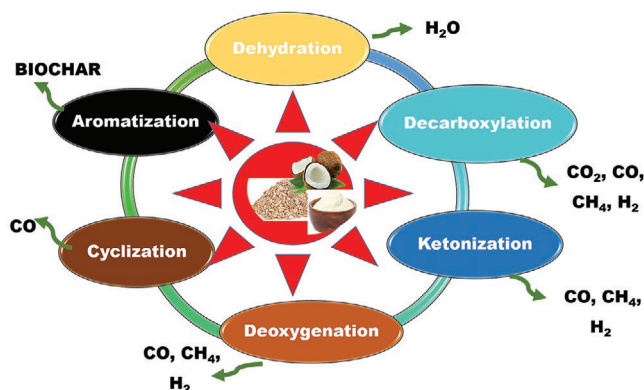


Figure 7. A cyclic representation of possible reactions in the immersion route.

activity, etc. To this point, the $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ melt appeared to be the best among the four melts for producing high-performance biocarbon using the immersion route. The appearance of NaCl as a salt melt is interesting as this is a common salt which could help reduce the cost of this process owing to the fact that it could be recovered from a cheap source. Further research would be to understand salt melt reactivity and biomass composition. As the size of cation or anion ions in a salt melt could affect the resulting biocarbon properties despite being obtained at the same temperature.

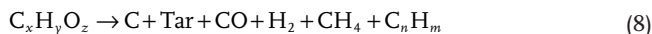
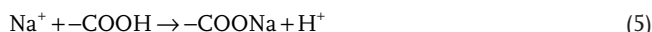
Technically, energy is required to melt the salts, but not required for a continuous operation of the carbonization. This is because molten salt is a favorable heat-transfer medium and would retain the required energy in a given period for the process. Therefore, the addition of renewable energy sources like concentrated solar heating is an option to offset energy cost for heating the salt. The other advantage of this solar-driven process is that the MSCA reactor works at a high temperature without the need for energy supply from the power grid.

4.3.1. Reactions in Immersion Route

In the immersion route, the biomass and the molten salt are in direct contact, forming dynamic solid/liquid interfaces. The salt diffuses into the biomass structure while different reactions occur at the high working temperature.^[39,45] A schematic

representation of possible reactions in the immersion route is shown in **Figure 7**. These reactions form a closed cycle but are experimentally difficult to separate because they are kinetically fast, as evidenced by the observed bubbling effect during the biomass pyrolysis in molten KOH , and at least some of which occur simultaneously.^[45,64] While the reactions in **Figure 7** could occur in a split of seconds to to minutes, further investigation is needed with the aid of, for example, gas chromatography and mass spectrometry to properly monitor and identify the gases released during the process.

A mechanism of the reaction between carbonates salts and biomass was proposed as given in Equations (4–9). The reactions in other types of salt will be quite interesting to investigate with the relevant thermodynamic properties to understand the reactions better.



where M represents an alkali metal, either lithium, sodium, or potassium.

4.3.2. Examples of Biomass using the Immersion Route and its Application

Examples of biocarbon obtained from various biomasses using the immersion route have shown high SSA and are used for various applications as summarized in **Table 4**.

From **Table 4**, molten KOH is seen to yield a carbon with the highest SSA of $1615 \text{ m}^2 \text{ g}^{-1}$ ^[29a] compared to other salts which have been reported for the immersion route using a similar temperature range. This demonstrates the effectiveness

Table 4. Examples of biomass to biocarbon conversion via the immersion route.

Biomass	Salt type	Temperature (°C) per Time (h)	S_{BET} [$\text{m}^2 \text{ g}^{-1}$]	Application	Ref.
Peanut Shell	$\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$	850/1.0	408	Supercapacitor	[47]
Boiled coffee beans	$\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$	800/1.5	436	Supercapacitor, electrocatalytic activity, oxygen reduction	[39]
Boiled coffee beans	CaCl_2	850/1.5	550	Supercapacitor electrocatalytic activity, oxygen reduction	[39]
Chinese firwood	$\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$	850/1.0	818	Supercapacitor	[38a]
Bamboo shells	$\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$	850/1.0	843	Supercapacitor	[62]
Soyabean Straw	KOH	800/1.0	1615	Supercapacitor	[45]

of KOH as widely used for biochar activation. The residence time for carbonization is short compared to the mixing route (Table 3) indicating the reaction and activation in KOH are rapid processes. The biocarbon from the immersion route is capable of capacitive charge storage and has been employed mostly in supercapacitors. More application areas for this porous biocarbon need to be investigated such as wastewater treatment, air purification, hydrogen storage, gas separation, and heterogeneous catalysis.

5. Challenges to MSCA

An anticipated challenge of this process route is to deal with the used salt. The used salt in molten salt carbonization and activation is treated differently based on the approaches. For the mixing route approach, the salt could be recycled easily as the ratio of salt used in the mixing route is smaller compared to the immersion route. Most samples are washed with water^[10a] and the salt water can be regenerated to separate the salt ions from the water. Also, salt water could be used as source for salt water applications that require such a salt solution. This is achievable with water-soluble salts. For the non-water-soluble salts, the filtrate obtained by washing with acids or base will require the use of technologies like ion exchange membrane technology to recover the salt ions and other trace inorganic residues of or containing Si, Fe, P, S and etc which originate from the biomass.

Used salts from the immersion approach is more complex as it uses more volume of salt but the replacement of salt in this approach is usually after long-time use. For the water-soluble ones and environmentally friendly salts, it is easily regenerated. However, this has not been investigated over years. According to the literature the used salt is known to be contaminated with organic compounds but these organic compounds can be oxidized to carbon at certain temperatures. The accumulation of the inorganic residues (Cu, Fe, Co and Cr depending on biomass source) from the biomass over time in the salt will result in the presence of heavy metals which would become an environmental concern but this can be solved by using electrolysis or electrodeposition of metals to overcome this challenge.

Investigation of the used salt composition could lead to certain knowledge or products as the case may be. Also, different salt mixtures may require further purification like in the use of chlorides, gaseous HCl may form during the process with undried biomass feeds. This would require the need for exit gas stream to be passed through an alkaline solution to dissolve the HCl. While the decomposition of nitrates salts produces NO_x (where x = various number) which are not environmentally friendly, this would require additional process equipment like gas scrubbers to treat the effluents. Steps to minimize the cost and management of the used salt would be an added advantage for the MSCA.

Another challenge is the trapping collection of the gases generated during the process, while most research has focused on biocarbon. There is a need to investigate the composition of the gases (CO, CO₂, H₂, and steam and other vapors) produced from the MSCA process and provide a series of suitable functional units for such gases to prevent pollution. Therefore, gas trapping technologies need to be attached to the process equipment both for the mixing and immersion approaches of MSCA.

Corrosion of reactor materials is another concern due to certain salts mixtures and various reactions especially if water is produced in large quantity. This can be suppressed with using more corrosion resistant but also likely more expensive materials such as alumina. It is also necessary to carry out a proper study of the reaction mechanism for various biomasses with different salt mixtures and operating conditions to minimize the production of those metals and compounds that trigger corrosion.

6. Summary and Prospects

Conversion of biomass to functional biocarbon using a single-step thermal process can be achieved using either the mixing route or the immersion route of MSCA. Porous biocarbon with a high SSA of above 1000 m² g⁻¹ can be obtained at temperatures below 500 °C in a residence time as short as 1 hr. The two approaches (mixing and immersion) of the MSCA process will yield porous biocarbon using different biomass sources and various salts, or their mixtures to reduce the melting temperature from those of the individual salts. The operating conditions affect the biocarbon properties from both process routes and will affect their performance in the desired application.

Till now, the process routes have different mechanisms due to the starting temperature for precursors and salt melt. They are likely to undergo the general carbonization reactions of biomass but at different rates and steps which are influenced by the salt. Despite the reactions, both the mixing and immersion routes would yield porous carbon. The detailed mechanisms of various salts and biomass interactions with their carbon properties have not been investigated for both routes. There is a need for kinetic study and energy requirement to ascertain the nature of reactions with an increase in temperature for the mixing route or the instantaneous reactions for the immersion route. Also, more research is needed to understand if the mechanism is salt-temperature dependent or biomass-salt-temperature dependent.

Temperature plays an important role in biomass carbonization in tuning the morphology, SSA, pore structures, and the functionalities resulting from the natural heteroatomic dopants such as nitrogen and oxygen. The mixing approach and immersion approach will have some variations as the starting temperature is different but the same target value. This would likely affect the final carbon from either route. Further research needs to clarify if the mixing and immersion routes will produce biocarbon with the same or comparable properties using the same biomass precursor, salt composition and the biomass-to-salt ratio, treatment time and temperature, and atmosphere. The effect of temperature with various salt types beyond binary eutectic mixture into ternary salt mixtures to optimize biochar at lower operating temperatures needs further investigation, especially for the immersion route as the mixing route seems to have better temperature control.

Residence time for carbonization is shorter for the immersion route compared to the mixing route. Both routes are shorter when compared to the conventional carbonization and activation process route. The residence time for both routes needs to be investigated to know when the reaction is complete and what time is needed to enhance the biocarbon properties for a specific application. Though the immersion route has shown that carbonization is possible in hr, further

reduction in time could be an added advantage for the process. Also, the residence time of the process should be considered for the temperature of operation and biomass precursor. Obviously, the effect of residence time to determine the optimum biocarbon properties would help research and industry maximize the biocarbon properties.

Salt types and biomass reactivity studies should be carried out to establish which salt type will yield desired functional biocarbon with certain properties using both routes of the MSCA, although the melting point and reactivity of salts vary. A correlation or simulation of a salt mixture will help to reduce the cost of the process. The use of ZnCl₂ at low temperatures using the mixing route has been impressive and should be considered in the immersion route provided the process will be safe and economically viable. It would be interesting to know if cations or anions are the reactions driver for the carbonization process via both routes. This understanding of the roles of cations and anions during the process will give insight into the overall reaction mechanism of the process using both routes.

Nickel has been proven to be a catalyst in biomass gasification. The dimension of the precursor wrapped with nickel mesh before carbonization as a mechanism for carbon recovery in the immersion route is seen in this review. It needs to be further investigated to determine if the nickel mesh induces a role in the process or if other materials could be used for carbon recovery during the carbonization. This would help researchers to know its contribution during the process and if further incorporation would enhance the process towards a better biocarbon functionality.

Biomass types suitable for MSCA processing with specific salts as research has revealed over the years include mainly plant biomasses (food and non-food), agricultural wastes (wood biomass), and other plant biomass-derived polymeric compounds (glucose and chitosan). Animal, industrial and other human solid wastes and sewages which are other biomass sources can also in principle use the MSCA process and would be an advantage as such wastes also pose environmental challenges.

Although the MSCA has been applied at the laboratory scale and showed impressive results, there is a need for the industry to look into the process. Furthermore, equipment design for the industrial application using either the mixing or immersion route for a possible combination of different biomass precursors needs to be investigated. This is because most biomass waste require sorting which involves additional costs during pretreatment. A process design that would circumvent sorting and process mixtures will be a great solution for the industry and help to reduce the level of environmental pollution arising from biomass. Also, for industrial application and energy conservation, the time for the salt to achieve a molten state will be considered for economic analysis. The incorporation of solar components to MSCA will help to achieve a circular economy for functional biocarbon from biomass, which will be of a global impact.

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Conflict of Interest

The authors declare no conflict of interest.

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Ishioma Laurene Egun holds a BEng and an MEng in Chemical Engineering (2012, 2018) from the University of Port Harcourt, Port Harcourt, Nigeria. She is currently a Ph.D. candidate with the Department of Chemical and Environmental Engineering, University of Nottingham Ningbo China, and Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo. Her Ph.D. is focused on using molten salt carbonization and activation to convert biomass to functional biocarbon for supercapacitor and supercapattery. Her general research interests are on conversion of waste materials that could cause environmental pollution to functional materials for diverse applications.



Haiyong He is professor at Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences. He obtained his Ph.D. from National Center for Nanoscience and Technology in China and worked as a research fellow at Nanyang Technological University for 3.5 years. He joined the institute in 2017 and established a new energy technology laboratory. His group focuses on the synthesis and properties of functional carbonaceous and hybrid materials with ongoing projects related to graphite, hard/soft carbon, and silicon/carbon negative electrode, aiming to understand the mechanisms and structural origin of the electrochemical properties of these materials.



Di Hu is an associate professor of chemical engineering at the University of Nottingham Ningbo Campus. Dr. Di Hu completed his BEng in Chemical Engineering and Technology at the China University of Mining and Technology (Beijing) in July 2006, and the MSc and Ph.D. in Chemical Engineering at the University of Nottingham in December 2007 and 2011, respectively. His primary research background lies in the electrochemical and molten salts innovations for the green production of metals, novel alloys, energy, and environmental materials.



George Z. Chen graduated from Jiujiang Teachers Training College with Diploma in 1981, Fujian Normal University with MSc in 1985, and University of London/Imperial College with PhD/DIC in 1992. After contracted work in Oxford, Leeds and Cambridge, he joined Nottingham University in 2003 as Reader, and became Professor in 2009. He was Li Dak Sam Chair Professor at the Ningbo Campus between 2017 and 2020. With fundings from government, industry and families of students, he has led research in electrochemical technologies, resulting in over 40 published patents, 280 peer reviewed research articles, and 180 invited lectures.