

Reactive Co-Solvent Regulation in Supercritical Water Gasification of Corn Stover for Enhanced Hydrogen Production and Functional Carbon Formation

Dongyang Wu, Hon Man Luk, Chengxu Sun, and Xuehua Zhang

Abstract—Supercritical water gasification (SCWG) of biomass is a promising technology for efficient hydrogen production where the introduction of reactive co-solvents is effective to regulate reaction pathways and enhance gasification performance. In this study, we systematically investigate the effects of co-solvent concentration on SCWG reaction behavior and product characteristics. Corn stover was used as the feedstock with tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP) as co-solvents. The results show that the process exhibits the best synergistic gasification performance at a co-solvent concentration of 10%, where both THF and NMP enhance gas production, while NMP shows a more pronounced effect, achieving a hydrogen volume fraction of 34.45% and a total gas yield increase of 7.98 mmol·g⁻¹. Mechanistic analysis indicates that nitrogen-containing radicals produced from NMP decomposition promote the transformation of aromatic intermediates and suppress condensation reactions, thereby significantly enhancing gasification efficiency, while THF primarily facilitates radical-mediated depolymerization and hydrogen transfer processes, contributing to improved gasification performance. Structural characterization further reveals that the solid residues from NMP system possess higher specific surface area, well-developed mesoporous structures, and abundant nitrogen-doped active sites, and exhibit promising electrochemical energy storage performance. This study elucidates the enhancement of co-solvents in SCWG through regulating radical reaction pathways and solid structural evolution.

Index Terms—Supercritical water gasification, biomass, hydrogen, co-solvent, radical.

ABBREVIATION

SCWG	supercritical water gasification
THF	tetrahydrofuran
NMP	N-methyl-2-pyrrolidone
ReaxFF	reactive force field

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Reaxff-MD	Reaxff molecular dynamics
CGE	carbon gasification efficiency
HGE	hydrogen gasification efficiency
HS	hydrogen selectivity
LHV	lower heating value
GC	gas chromatography
NMR	nuclear magnetic resonance
XPS	X-ray photoelectron spectroscopy
BET	Brunauer–Emmett–Teller
SEM	scanning electron microscopy
CV	cyclic voltammetry
GCD	galvanostatic charge–discharge
BJH	Barrett–Joyner–Halenda
PAHs	polycyclic aromatic hydrocarbons

I. INTRODUCTION

Hydrogen energy, characterized by its near-zero carbon emissions and high energy density, is widely regarded as one of the key energy carriers for building a sustainable energy system and achieving deep decarbonization in the future [1], [2]. However, current mainstream hydrogen production technologies still face significant challenges. Fossil fuel-based processes are typically accompanied by substantial CO₂ emissions [3], while water electrolysis requires high electricity consumption and operating costs, with its environmental benefits largely dependent on the renewable share of the electricity supply [4]. Therefore, developing efficient hydrogen production technologies utilizing abundant and renewable biomass resources is of great significance for improving energy utilization efficiency, ensuring energy security, and achieving carbon neutrality targets [5], [6].

Among biomass conversion technologies, supercritical water gasification (SCWG) has attracted considerable attention due to its unique reaction environment [7]. This technol-

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ogy can directly process highly-moisturized biomass feedstocks, thus avoiding the energy-intensive drying in pretreatment required for conventional thermochemical conversion processes. Under supercritical water conditions ($> 374.1\text{ }^{\circ}\text{C}$ and $> 22.1\text{ MPa}$), water acts not only as a reaction medium but also as a hydrogen donor in the reaction process. Meanwhile, the supercritical water environment can effectively suppress the formation of tar and coke, thereby increasing the conversion efficiency and gas yield of the gasification process [8], [9]. Despite its great potential, the microscopic reaction mechanisms of SCWG, particularly the regulation of reaction pathways, have not yet been fully elucidated, which constrains the rational optimization of the process [10], [11].

Fundamentally, the SCWG process is governed by radical-driven reaction pathways, in which the formation and evolution of the reaction network strongly depend on the generation and transportation of reactive radicals such as $\cdot\text{OH}$, $\cdot\text{H}$, and $\cdot\text{CH}_x$. Zhang et al. [12] first reported that phenolic compounds follow typical radical-mediated reaction pathways during supercritical water oxidation. Subsequently, Wang et al. [13] further confirmed this mechanism through reactive force field (ReaxFF) simulations of p-cymene, demonstrating that supercritical water can participate in and dominate hydrogen radical-initiated chain reactions. This process effectively suppresses the coking tendency of aromatic fuels while promoting aromatic ring opening and the formation of syngas components such as CO and H_2 . Nevertheless, current understanding of radical behavior in SCWG systems has mainly focused on identifying their existence and general roles in the reaction process [14], [15]. Systematic strategies for actively and precisely regulating the formation and consumption dynamics of key reactive species, including $\cdot\text{H}$, $\cdot\text{OH}$, and heteroatom-containing radicals, still remain largely unexplored. As a result, effective approaches and tactics for steering the reaction network toward efficient hydrogen production remain largely underexplored.

To further elucidate the role of radicals in the SCWG process and direct the gasification reaction network through control of radical reaction pathways, researchers have introduced external co-solvents to actively regulate radical speciation and concentration within the reaction system. This strategy has emerged as an important approach for enhancing hydrogen generation during SCWG through altering the formation and conversion of key intermediates, ultimately guiding the reaction pathways toward routes favorable for hydrogen production [16], [17]. Faki et al. [18] investigated the effects of several organic co-solvents in the co-hydrothermal gasification of coal and biomass. Their results showed that polar aprotic solvents tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP) exhibited clear advantages in improving both gas yield and hydrogen production. Specifically, THF demonstrated strong catalytic performance at a concentration of 10%, increasing the hydrogen yield from $6.50\text{ mmol}\cdot\text{g}^{-1}$ under solvent-free conditions to $43.4\text{ mmol}\cdot\text{g}^{-1}$. Under the same concentration, NMP also enhanced the hydrogen yield to

$26.2\text{ mmol}\cdot\text{g}^{-1}$. These results indicate that THF as a co-solvent can effectively promote hydrogen generation in SCWG systems. These findings indicate that the introduction of appropriate additives can modify the radical reaction environment in SCWG systems and optimize the transformation pathways of key intermediates, thereby enhancing hydrogen yield and carbon gasification efficiency [19].

In our previous work [17], molecular dynamics simulations were first employed to systematically evaluate the decomposition behaviors of nine potential co-solvents under SCWG conditions. The Reaxff molecular dynamics (Reaxff-MD) simulation results indicated that different co-solvents could generate characteristic radical species, which can be generally classified into hydrogen radicals, hydroxyl radicals, aliphatic radicals, aromatic radicals, and heteroatom-containing radicals. Among them, THF and NMP tend to generate highly reactive oxygen-containing aliphatic radicals and nitrogen-containing heteroatom radicals, respectively, suggesting their strong potential for regulating reaction pathways. Further experimental results demonstrated that both co-solvents could promote hydrogen generation during the SCWG of corn stover; however, their reaction mechanisms exhibited clear differences. The NMP system showed superior gasification performance, with a hydrogen volume fraction and carbon gasification efficiency reaching 34.45% and 58.88%, respectively, which were higher than those obtained in both the THF system (32.85% and 51.06%) and the solvent-free corn stover gasification system (28.71% and 35.89%).

These results indicate that the introduction of co-solvents can significantly enhance SCWG reactions, with NMP showing a more pronounced improvement. Mechanistic analysis revealed that nitrogen-containing radicals derived from NMP can induce the amination transformation of phenolic intermediates, suppressing condensation reactions and improving gasification efficiency. In contrast, oxygen-containing radicals generated from THF mainly accelerate the cleavage and conversion of organic compounds by promoting β -scission reactions. However, the previous study only explored a single co-solvent concentration of 10%, and the regulatory mechanisms of different co-solvent concentrations on SCWG reaction pathways and radical reaction networks remain poorly understood. In addition, the introduction of co-solvents not only influences the gasification process but also alters the structural characteristics of the solid residues. Notably, the solid products formed in the NMP system exhibit a distinct nitrogen-doped carbon structure, where its potential application in electrochemical energy storage still requires further investigation.

Rather than simply examining co-solvent effects, this study investigates the previously unexplored concentration-dependent regulatory mechanisms of THF and NMP in SCWG from a radical reaction perspective. Concentration gradient systems of 5%, 10%, and 20% were designed to systematically investigate the threshold effect, optimal regulation window, and potential excess effects of co-solvent addition in SCWG sys-

tems. The influence of different radical reaction pathways on carbon gasification efficiency, hydrogen gasification efficiency, and hydrogen selectivity during the SCWG of corn stover was further analyzed. The evolution behaviors and regulatory mechanisms of solid residues and liquid organic by-products under co-solvent conditions were also elucidated. In addition, the structural characteristics and potential functionalization of the gasification solid residues were evaluated. Through these investigations, this work aims to reveal, from the perspective of radical regulation, the mechanisms where THF and NMP and their concentrations influence the reaction pathways and product distribution in SCWG systems. The findings are expected to provide theoretical guidance for optimizing hydrogen production from biomass via SCWG and offer new insights into the efficient and high-value utilization of biomass resources.

II. MATERIALS AND METHODS

A. Biomass Feedstock and Co-solvents

Corn stover collected from Jilin City, Jilin Province, China was selected as the biomass feedstock in this study. The raw material was washed, dried, ground, and then sieved to 100 mesh prior to use. The basic physicochemical properties of the corn stover are summarized in Table S1. The co-solvents used in this work were THF (Sinopharm Chemical Reagent, purity > 99.5 wt.%) and NMP (Aladdin Chemical Reagent, purity > 99.5 wt.%). Based on Reaxff-MD simulation results (the detailed simulation procedures are provided in the Supplementary Materials), the possible radical species generated from the two co-solvents under SCWG conditions and their relative distributions are summarized in Table S2.

B. SCWG Experimental Procedure

The SCWG experiments of corn stover and co-solvents were carried out in a batch-type supercritical reactor (customized, Tuochuang, China). Three experimental systems were designed, including corn stover gasification alone, co-solvent gasification alone, and co-gasification of corn stover with co-solvents. The experimental procedures were conducted as follows. For the corn stover alone case, 7 g of corn stover and 70 mL of ultrapure water were loaded into the reactor. For the co-solvents alone case, 3.5, 7, and 14 g of co-solvent (corresponding to 5%, 10%, and 20% concentrations, respectively) were added together with 70 mL of ultrapure water. For the co-gasification case, 7 g of corn stover, the desired amount of co-solvent, and 70 mL of ultrapure water were introduced into the reactor. After loading the reactants, the mixture was stirred at 300 rpm, and high-purity argon (99.99%) was purged through the reactor for approximately 10 min to remove residual air from the system. For convenience, the experimental samples were denoted according to the reaction system and co-solvent concentration. The SCWG of corn stover alone was labeled as CS. The SCWG of co-solvents alone at concentra-

tions of 5%, 10%, and 20% were denoted as THF(5%), THF(10%), and THF(20%), and NMP(5%), NMP(10%), and NMP(20%), respectively. The co-SCWG systems of corn stover with co-solvents were labeled as CS+THF(5%), CS+THF(10%), and CS+THF(20%), and CS+NMP(5%), CS+NMP(10%), and CS+NMP(20%), respectively.

The reaction system was heated from room temperature to 500 °C at an incremental rate of 10 °C·min⁻¹ and maintained for 30 min. The temperature of 500 °C was selected based on our previous studies, where lignin undergoes significant conversion in this temperature range and key intermediates such as phenolic compounds become activated [20]. In addition, further increase in temperature would cause a rapid increase in system pressure due to the supercritical properties of the co-solvents, which may affect the operational stability of the reactor. After the reaction, the heating system was switched off and the reactor was allowed to cool naturally to room temperature. The gaseous products were first collected by opening the gas outlet valve of the reactor and were subsequently analyzed. The reaction mixture remaining in the reactor was then removed and subjected to vacuum filtration to separate the solid and liquid products [17]. The overall mass balance results of all SCWG experiments are summarized in Table S3.

C. Evaluation Parameters and Product Characterization Methods

In this study, the performance of SCWG was evaluated using several key parameters, including gas yield (Eq. (S1)), gas fraction (Eq. (S2)), carbon gasification efficiency (CGE, Eq. (S3)), hydrogen gasification efficiency (HGE, Eq. (S4)), hydrogen selectivity (HS, Eq. (S5)), and lower heating value (LHV, Eq. (S6)) [21]. The influence of co-solvents on the co-SCWG performance was assessed by calculating the deviation between the experimental values and theoretical values, as defined in Eqs. (S7) and (S8). A positive deviation indicates a promoting effect, while a negative deviation suggests an inhibitory effect on the gasification process.

The gaseous products from SCWG were analyzed using gas chromatography (GC) to determine the composition of the produced syngas. The organic phase of the liquid products was characterized by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy to identify molecular structural features. The solid products were analyzed using X-ray photoelectron spectroscopy (XPS) to determine the elemental valence states and surface chemical characteristics. In addition, Brunauer–Emmett–Teller (BET) analysis and scanning electron microscopy (SEM) were employed to examine the surface area, pore structure, and microscopic morphology of the solid residues. Furthermore, to investigate the potential electrochemical properties of the solid products formed during SCWG, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) tests were conducted. The detailed parameters and operational conditions of all analytical and characterization methods are provided in the Supplementary Materials.

III. RESULTS AND DISCUSSION

A. Product Yields of SCWG under Different Co-solvent Concentrations

Based on the statistical results summarized in Table S3, Figs. 1(a) and 1(b) present the product distribution of the SCWG process under different co-solvent conditions. At the same co-solvent concentration, the co-gasification system of CS with THF generally produced a higher gas yield than that obtained in the NMP system. According to the calculation methods defined in Eqs. (S7) and (S8), Fig. 1(c) further compares the differences between the experimental gas yields and the theoretical gas yields under different concentrations of THF and NMP. The results show that when the co-solvent concentration was 10%, both systems exhibited the most pronounced synergistic enhancement in gas production. Specifically, the increase in gas yield reached 1.43 g in the THF system and the NMP system showed a higher increment of 1.81 g, which is approximately 26.57% greater than that of the THF system. These results highlight an important distinction: Although the THF system achieved a higher overall gas yield due to the inherently higher gas production from pure THF, the NMP system demonstrated a significantly stronger syner-

gistic effect. This is primarily because pure NMP gasification generated a relatively low amount of gas, thus setting a lower theoretical baseline for the co-gasification system. Upon co-gasification with corn stover, the nitrogen-containing species derived from NMP actively interacted with biomass-derived intermediates, promoting cracking and reforming reactions that led to a much larger net increase in gas yield (1.81 g vs. 1.43 g). Consequently, the stronger synergistic enhancement observed in the NMP system does not contradict the higher absolute gas yield of the THF system but rather reflects the differing baseline contributions and reactivity characteristics of the two co-solvents.

Regarding the organic phase of liquid products and solid residues, Figs. 1(d) and 1(e) illustrate their variation trends under different co-solvent conditions. The results indicate that when the co-solvent concentration was 10%, both THF and NMP exhibited the most pronounced inhibitory effects on the formation of organic-phase and solid products during the SCWG of corn stover. Specifically, in CS+NMP (10%), the organic-phase products decreased by 1.18 g and the solid residues decreased by 0.27 g compared with the theoretical values, and CS+THF (10%) showed a reduction of 0.93 g in organic-phase products and 0.21 g in solid residues.

Furthermore, Fig. 1 shows that when the co-solvent concen-

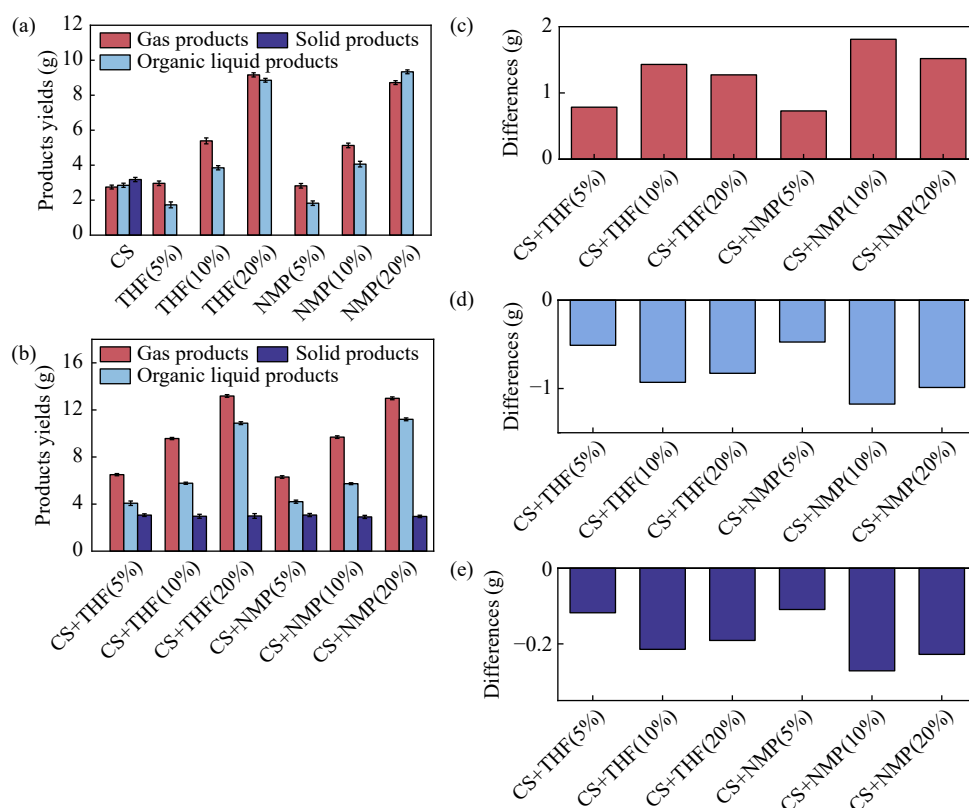


Fig. 1. (a) Productions of gaseous, organic liquid, and solid products from individual SCWG of CS and co-solvents. (b) Productions of gaseous, organic liquid, and solid products from co-SCWG of CS with co-solvents at different concentrations. Comparison between experimental and theoretical productions of (c) gaseous, (d) organic liquid, and (e) solid products obtained from co-SCWG of CS with co-solvents at varying concentrations. All experiments were conducted in triplicate, and the results are presented as mean values with error bars representing standard deviations.

tration was 10%, both the THF and NMP systems exhibited the most pronounced synergistic effect. At this concentration, a favorable balance was achieved between the radical supply generated from co-solvent decomposition and the chain scission and ring-opening reactions of corn stover. In this case, sufficient reactive radicals were produced to promote the cleavage of carbon skeletons, while excessive radical accumulation and related side reactions were suppressed. Consequently, the system exhibited the most favorable performance in terms of enhanced gas yield, reduced organic-phase intermediates, and suppressed solid residue formation.

When the co-solvent concentration was further increased to 20%, the radical concentration in the system became excessively high. Under such conditions, radical-radical interactions, including mutual scavenging and chain termination reactions, are more likely to occur, which reduces the number of effective radicals participating in gasification reactions and consequently leads to a decline in desired gas production. This result is consistent with what reported in literature. Man et al. [22] reported that highly reactive oxygen radicals derived from olefins readily undergo radical-radical cross-coupling reactions, particularly in systems lacking persistent radical stabilization mechanisms. Similarly, Wei et al. [23] demonstrated that radical coupling termination is a dominant pathway for the consumption of active radicals during styrene radical reactions, forming head-to-tail structures that further confirm the significant reduction of effective radical concentrations under high radical concentrations.

B. Gaseous Products and Gasification Performance

B.1 Gas Fraction

During the SCWG process, the composition of gaseous products directly determines the quality of syngas and its potential for energy utilization. To investigate the influence of co-solvent concentration on the distribution of gaseous prod-

ucts during the SCWG of corn stover, the gas composition was analyzed using GC, while the LHV of the produced syngas was calculated to evaluate its energy content. The corresponding results are presented in Fig. 2. The results indicate that in the co-solvent-only SCWG systems, the hydrogen volume fraction reached its maximum at a co-solvent concentration of 5%. In contrast, in the co-SCWG systems of CS with co-solvents, the highest hydrogen fraction appeared at a concentration of 10%. This difference can be interpreted from the perspective of radical reaction kinetics.

According to the results shown in Table S2, the decomposition of THF and NMP under SCWG conditions can generate abundant heteroatom-containing radicals, which possess strong hydrogen abstraction capability and can induce β -scission reactions, thereby promoting the cleavage of organic structures. Specifically, in the co-solvent-only SCWG systems, a co-solvent concentration of 5% is sufficient to generate an adequate radical flux, which facilitates the activation of water molecules and the formation of reactive radicals such as $\cdot\text{H}$ and $\cdot\text{OH}$. These radicals promote H_2 formation through pathways such as the water–gas shift reaction and 1,5-hydrogen atom transfer (1,5-HAT), while avoiding methanation reactions or radical recombination caused by excessive alkyl radicals. As a result, the hydrogen fraction in this system reaches its optimum at relatively lower co-solvent concentrations.

For the co-SCWG systems of CS with co-solvents, phenoxy radicals and aromatic condensation intermediates generated during lignin decomposition can significantly quench $\cdot\text{H}$ and compete for reactive sites, which limits hydrogen transfer and aromatic ring-opening reactions at low co-solvent concentrations [24]. Consequently, a higher co-solvent concentration (approximately 10%) is required to supply sufficient heteroatom radical flux in the reaction system. Compared with alkyl radicals, heteroatom radicals generally exhibit higher

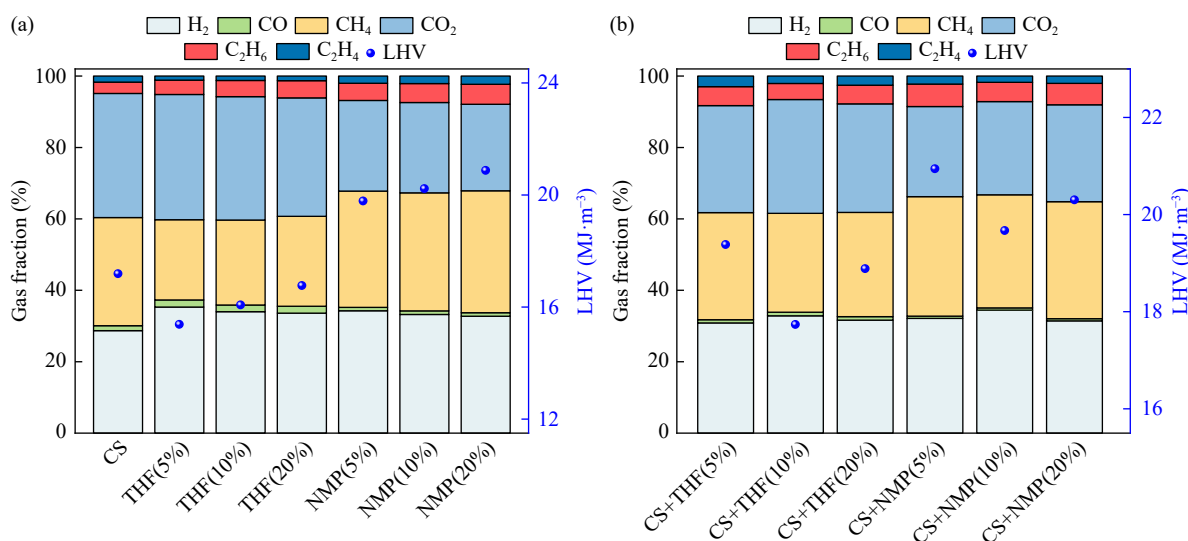


Fig. 2. (a) Gas fraction distributions from individual SCWG of CS with co-solvents at different concentrations. (b) Gas fraction distributions from co-SCWG of CS and co-solvents at different concentrations.

reactivity, enabling them to more effectively suppress aromatic condensation and promote subsequent reforming reactions, which ultimately increases the hydrogen fraction in the gaseous products. As shown in Fig. 2, the hydrogen volume fractions in CS+THF(10%) and CS+NMP(10%) reached 32.85% and 34.45%, respectively.

However, when the co-solvent concentration was further increased to 20%, the excessive radical density significantly intensified radical recombination reactions. These reactions typically possess relatively low activation energies, and their reaction rates may exceed those of radical reactions with biomass substrates. As a result, a large number of active hydrogen atoms are consumed through radical recombination before participating in effective gasification pathways, thereby weakening the dehydrogenation and ring-opening processes of biomass macromolecules. Meanwhile, an excessively high

concentration of alkyl radicals may also promote side reaction pathways such as methanation, which not only consumes $\cdot\text{H}$ but also leads to the formation of relatively stable $\text{C}_1\text{-C}_3$ hydrocarbons. The combined effects of these processes ultimately reduce the relative proportion of hydrogen in the gaseous products.

B.2 Gas Yield

The gas yields of individual gaseous components were calculated according to Eq. (S1), and the results are presented in Figs. 3(a) and 3(b). Furthermore, to evaluate the promoting or inhibiting effects of different co-solvents on specific gaseous products during the co-SCWG of CS, the differences between the experimental gas yields and theoretical gas yields were calculated based on Eqs. (S7) and (S8). The corresponding results are shown in Figs. 3(c)–3(f). The results indicate that when the co-solvent concentration was 10%, both

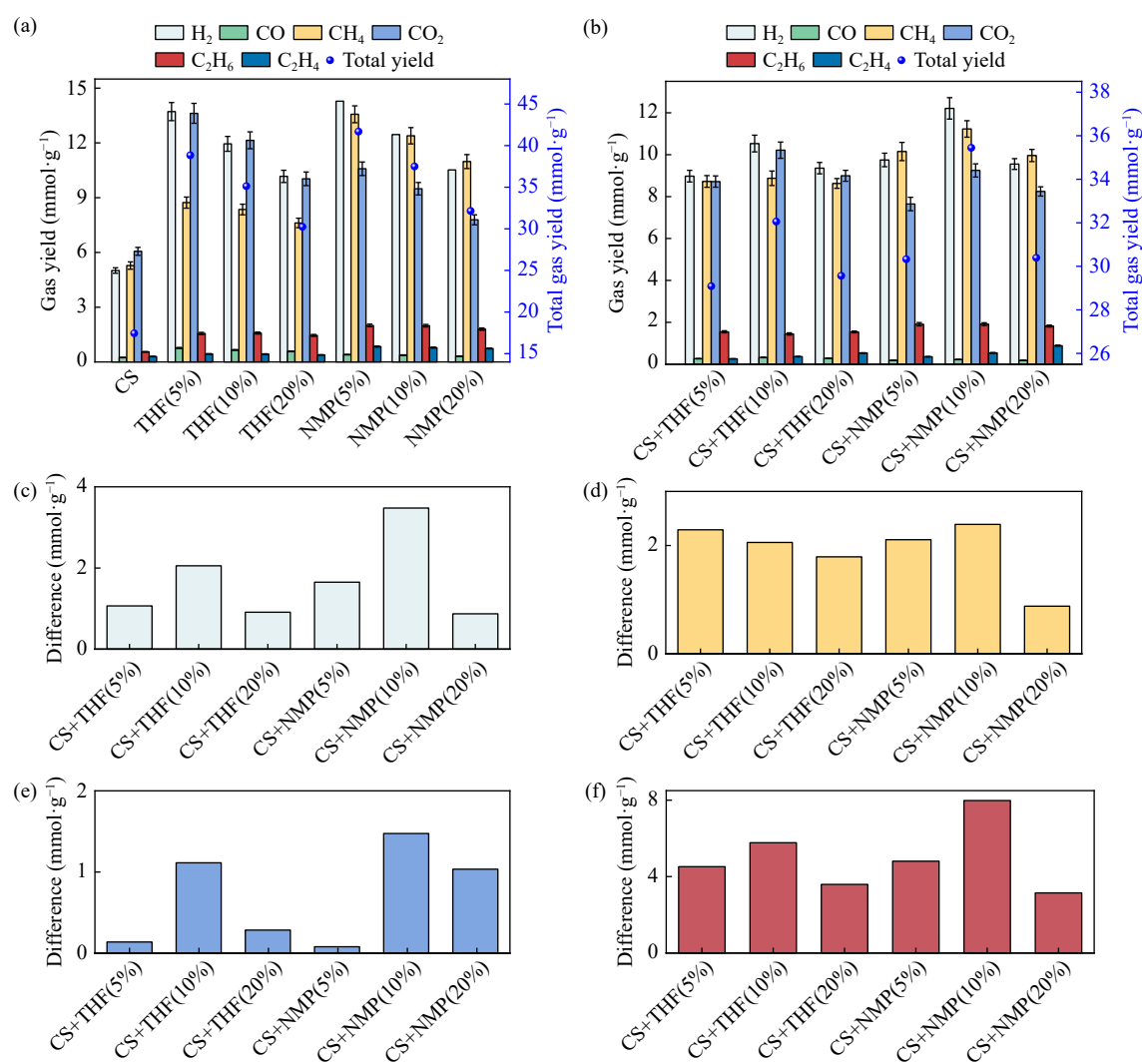


Fig. 3. (a) Gas yields from individual SCWG of CS with co-solvents at different concentrations. (b) Gas yields from co-SCWG of CS and co-solvents at different concentrations. Differences between experimental and theoretical gas productions during co-SCWG of CS with co-solvents at varying concentrations: (c) H₂, (d) CH₄, (e) CO₂, and (f) total gas. All experiments were conducted in triplicate, and the results are presented as mean values with error bars representing standard deviations.

CS+THF(10%) and CS+NMP(10%) exhibited the most pronounced gas production enhancement, with CS+NMP(10%) showing a significantly stronger synergistic effect. Specifically, the increase in total gas yield reached $7.98 \text{ mmol}\cdot\text{g}^{-1}$ in CS+NMP(10%), which is higher than that in CS+THF(10%) ($5.77 \text{ mmol}\cdot\text{g}^{-1}$). Among the gaseous products, the increment in H_2 yield reached $3.48 \text{ mmol}\cdot\text{g}^{-1}$ in CS+NMP(10%), compared with $2.05 \text{ mmol}\cdot\text{g}^{-1}$ in CS+THF(10%), further demonstrating the superior capability of NMP in promoting hydrogen generation.

The difference in the increase of total gas yield between the two co-solvents mainly originates from the significant variation in hydrogen production, indicating that the role of co-solvents is not limited to a simple physical dilution effect, but rather involves the regulation of reaction pathways during the SCWG process, thereby influencing the distribution of products.

From a mechanistic perspective, nitrogen-containing radicals generated from NMP decomposition can facilitate intramolecular rearrangement reactions, such as 1,5-HAT, during ring-opening and bond-cleavage processes [25]. These radicals are also more effective at abstracting hydrogen atoms from the aqueous phase or reaction intermediates, thereby generating a larger amount of $\cdot\text{H}$. Furthermore, nitrogen-containing intermediates tend to undergo dehydrogenation and deamination reactions during subsequent reforming processes, which directly promotes H_2 formation. In contrast, the oxygen-containing radical pathways derived from THF are more likely to lead to the formation of by-products such as CO_2 and CH_4 , rather than contributing efficiently to H_2 generation.

Furthermore, compared with the oxygen-centered radicals generated from THF decomposition, the nitrogen-containing radicals derived from NMP exhibit stronger electron-donating ability and higher reactivity. These radicals can more effectively attack lignin-derived aromatic ring structures, thereby promoting the cleavage of C–O and C–C bonds [26]. Meanwhile, nitrogen-containing radicals can participate in nitrogen-doping reactions, leading to the formation of aniline-like intermediates, which suppress further aromatic condensation and promote the generation of nitrogen-containing intermediates [27]. The C–N bonds in these intermediates possess relatively lower bond dissociation energies, making them more susceptible to cleavage under supercritical conditions [28]. As a result, additional radical fragments can be continuously released, maintaining the radical flux in the reaction system and driving the gasification process toward the formation of small gaseous molecules.

It is also noteworthy that the NMP-derived system significantly increased the total gas yield while simultaneously promoting the formation of carbon-containing gaseous products. This observation indicates that NMP effectively suppresses the conversion of carbon into condensed aromatic structures and coke. The incorporation of nitrogen atoms disrupts the conjugated stability of aromatic rings, thereby inhibiting the polycondensation growth of polycyclic aromatic hydrocarbons

(PAHs). Consequently, more carbon atoms are converted into small gaseous molecules such as CO_2 and CH_4 , rather than remaining in solid residues or large molecular structures within the organic phase.

As shown in Fig. 3(f), when the co-solvent concentration increased to 20%, the enhancement in total gas yield decreased to $3.15\text{--}3.59 \text{ mmol}\cdot\text{g}^{-1}$. In contrast, at the optimal concentration of 10%, the generation of heteroatom radicals from co-solvent decomposition and their consumption in the main gasification reaction chain reached a dynamic equilibrium. Under these conditions, radicals were efficiently utilized in key steps such as hydrogen abstraction, β -scission, and aromatic ring opening, thereby promoting the conversion of biomass carbon into gaseous products. As shown in Fig. 3(f), when the co-solvent concentration increased to 20%, the enhancement in total gas yield decreased to $3.15\text{--}3.59 \text{ mmol}\cdot\text{g}^{-1}$. At higher co-solvent concentrations, the generation rate of radicals exceeds the consumption capacity of the reaction system. As a result, excess radicals are more likely to be rapidly consumed through radical coupling or nonproductive interactions with stable intermediates, leading to a decline in gasification efficiency.

Similar radical overloading phenomena have been reported in radical-dominated reaction systems [29], [30]. Therefore, in this study, a co-solvent concentration of 10% represents a kinetically favorable window for radical-driven SCWG reactions, whereas further increases in concentration lead to an equilibrium disruption between radical supply and reaction demand, ultimately reducing gasification efficiency.

B.3 Evaluation of CE, HE, and HS During Co-SCWG

During the SCWG process, CE, HE, and HS are important indicators for evaluating the extent of carbon conversion and hydrogen production performance [31]. CE represents the proportion of carbon in the raw material converted into gaseous products, HE reflects the proportion of hydrogen in the raw material converted into gaseous hydrogen, and HS indicates the selectivity of hydrogen formation relative to other carbon-containing gases. Fig. 4(a) presents the CE, HE, and HS values for CS and the individual co-solvent SCWG systems. Meanwhile, by comparing the differences between the experimental values and theoretical values in the co-SCWG systems of corn stover with different co-solvents (Figs. 4(b)–4(d)), the influence of co-solvents on SCWG performance can be further elucidated. Overall, with increasing co-solvent concentration, the CE, HE, and HS values of CS+NMP exhibited a rise–decline trend, reaching optimal values at a concentration of 10%, with peak performance clearly higher than that of CS+THF. As shown in Fig. 4(b), when the co-solvent concentration increased from 5% to 10%, the CE of CS+NMP increased from approximately 55.81% to 58.88%, whereas the CE of CS+THF increased from about 50.00% to 51.06%.

This difference mainly arises from the nitrogen-containing species generated from NMP decomposition, which can selectively modify the aromatic intermediates formed during the reaction, thereby reducing the tendency for aromatic ring con-

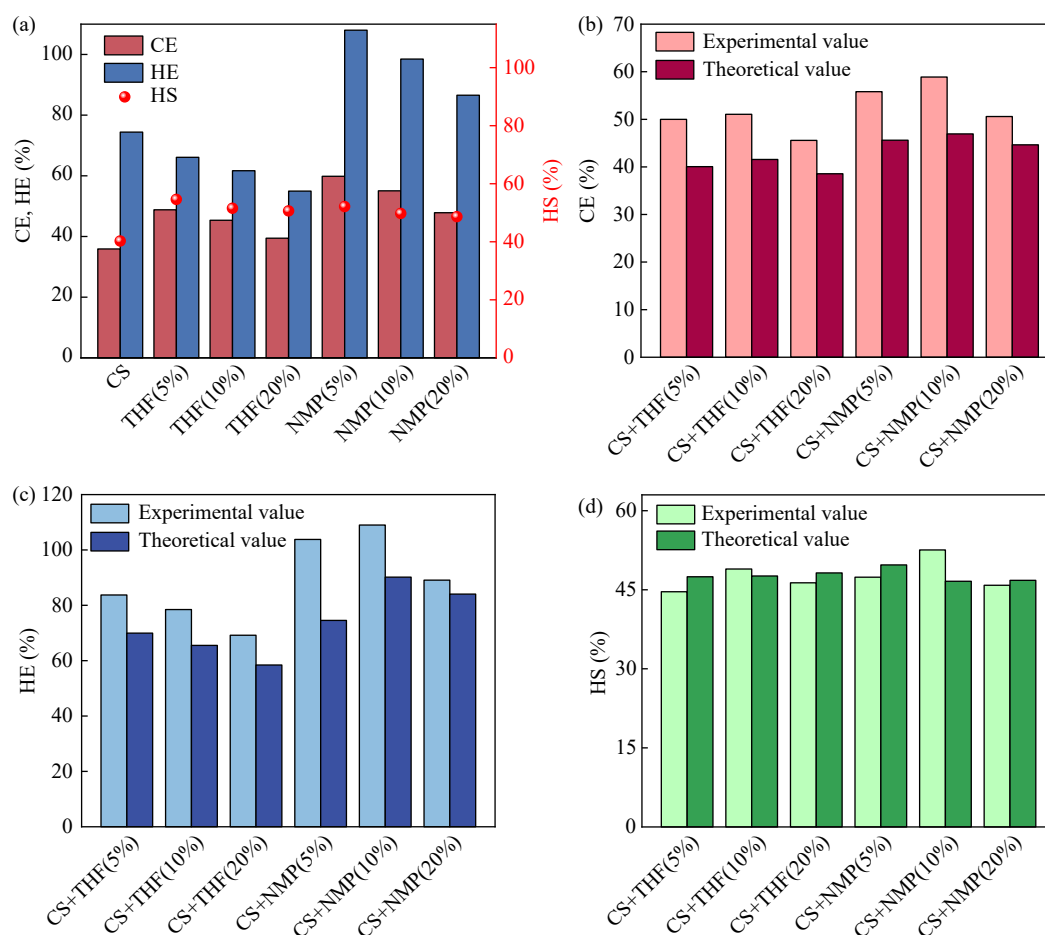


Fig. 4. (a) CE, HE, and HS from the individual SCWG of CS and reactive co-solvents. Differences between experimental and theoretical values of (b) CE, (c) HE, and (d) HS in the co-SCWG of CS with various co-solvents.

densation and suppressing coke formation [32]. Meanwhile, the resulting aniline-like nitrogen-containing intermediates, characterized by relatively low C–N bond energies, are more susceptible to cleavage under supercritical water conditions. This process provides a more favorable pathway for the continuous fragmentation of carbon frameworks and their subsequent conversion into gaseous products. In contrast, the CS+THF system primarily promotes the oxidative cleavage of organic structures through oxygen-centered radicals. Although these radicals can facilitate C–C bond scission, their effectiveness in suppressing aromatic condensation and promoting the conversion of carbon into gaseous products is lower than that of the NMP-derived pathways.

When the co-solvent concentration was further increased to 20%, the CE values of both systems decreased, as shown in Fig. 4(b). Specifically, the CE in CS+THF decreased from 51.06% to 45.48%, while that in CS+NMP decreased from 58.88% to 50.60%. This phenomenon may be attributed to the solvation or physical adsorption effects induced by excessive co-solvent and its derived intermediates. Such effects can partially stabilize large molecular precursors, reducing their effective contact with supercritical water and reactive radicals, which ultimately leads to a decline in gasification efficiency.

As shown in Fig. 4(c), the HE of CS+NMP(10%) reached approximately 108.99%, representing an increase of nearly 19% compared to a concentration of 5%. The HE of CS+THF (10%) also increased from 65.53% to 78.48%. Since supercritical water acts not only as the reaction medium but also as an important hydrogen source, the nitrogen-containing radicals generated from NMP decomposition can enhance the water–gas shift reaction and related radical pathways, thereby converting hydrogen atoms from water into H_2 and resulting in HE values exceeding the theoretical 100%. Similar phenomena have been reported in previous SCWG studies. For example, Marcelino et al. [33] found that during the supercritical water gasification of coconut shells, a higher nickel loading can cause the HE value reaching 133%, exceeding the critical value of 100%. Likewise, Ning et al. [34] reported that the Ni–Cu/AC catalyst promoted water–gas shift and steam reforming reactions during the SCWG of indole, resulting in an HE value up to 135.1%. In contrast, the oxygen-centered radicals derived from THF tend to promote organic cracking while simultaneously favoring the formation of by-products. Consequently, their ability to utilize hydrogen from water is relatively weaker, leading to a smaller increase in HE compared with the NMP-derived pathway. When the co-solvent concen-

tration was further increased to 20%, the HE values of both cases decreased, although the NMP case still maintained a relatively high level of approximately 89%.

HS is defined as the ratio of the volume fraction of hydrogen gas to that of other gases, and is used to characterize the relative selectivity of hydrogen in the gaseous products; higher HS values are preferred for direct hydrogen production applications. As shown in Fig. 4(d), the HS of CS+NMP(10%) reached 52.55%, while that of CS+THF(10%) was approximately 48.93%, both of which were clearly higher than those obtained at other concentrations. Overall, at a co-solvent concentration of 10%, both THF and NMP exhibited favorable synergistic effects in terms of CE, HE, and HS. However, the nitrogen-containing radicals generated in NMP system showed a more pronounced promoting effect than the oxygen-centered radicals derived from THF.

C. ^{13}C and ^1H NMR Analysis of the Organic Phase in Liquid Products

The ^{13}C NMR and ^1H NMR spectra of the organic phase in liquid products obtained from the co-SCWG of CS with different co-solvent concentrations are presented in Figs. S1 and S2, respectively. The spectral analysis indicates that the introduction of co-solvents significantly alters the chemical composition of the liquid organic phase. In the ^{13}C NMR spectra, the signal intensity in the aromatic region (110–160 ppm) decreased markedly, whereas the signal intensities in the alkyl region (0–50 ppm) and oxygenated alkyl region (50–90 ppm) increased. Correspondingly, in the ^1H NMR spectra, the intensities of aliphatic hydrogen (1.0–4.5 ppm) increased, while those of aromatic hydrogen (6–9 ppm) decreased, indicating a reduction in aromatic structures accompanied by the formation of more aliphatic structures. Quantitative integration of the different chemical shift regions was performed, and the corresponding results from ^{13}C NMR and ^1H NMR analyses are summarized in Tables S4 and S5, respectively. The division of the above chemical shift regions is based on the assignment rules in [35].

As shown in Table S4, in CS+NMP(10%), several types of aromatic carbon structures decreased markedly. For instance, protonated aromatic carbon (f_{ar}^{H}) decreased from 60.51% in the CS to 17.16%, while aromatic bridgehead carbon (f_{ar}^{B}) decreased from 7.30% to 1.89%. Meanwhile, the integral of

aniline-type carbon (f_{ar}^{N}) in the NMP case was significantly higher than that in the THF case. These results indicate that the nitrogen-containing radicals generated from NMP under supercritical water conditions exhibit high reactivity toward aromatic π systems, which can induce nucleophilic attack, ring opening, or amination substitution reactions on aromatic rings [36]. As a result, a portion of the originally phenolic-dominated aromatic structures is converted into aniline-like nitrogen-containing intermediates, while further polycondensation of PAHs is effectively suppressed. By stabilizing aromatic radicals and inhibiting their coupling and polymerization reactions, nitrogen-containing radicals reduce the formation of PAHs and tar-like macromolecules. Consequently, more carbon atoms are converted into small fragments that are more readily gasified, which is consistent with the significant increase in gas yield ($7.98 \text{ mmol} \cdot \text{g}^{-1}$) observed in Fig. 3(f).

This structural evolution is further confirmed by the quantitative results of the ^1H NMR analysis. As shown in Table S5, in CS+NMP(10%), the proton signals associated with aliphatic structures in the organic phase increased markedly. For example, the proportion of H_{α} increased from 32.90% in the CS to 73.52%, while the signal of aromatic protons (H_{ar}) decreased significantly from 46.28% to 12.84%. These results indicate that the nitrogen-doping process induced by NMP promotes the cleavage and dearomatization of aromatic structures. By introducing C–N bonds with relatively lower bond dissociation energies, stable aromatic structures are converted into nitrogen-containing intermediates that are more susceptible to secondary cracking, thereby facilitating the conversion of organic compounds into gaseous products and ultimately enhancing the overall gas yield.

Based on the distribution of different types of carbon and hydrogen species in Tables S4 and S5, key structural parameters, including the aromatic carbon fraction (f_{ar}) and aliphatic carbon fraction (f_{al}), were further calculated, and the results are summarized in Table 1. The detailed calculation methods for these structural parameters are provided in the Supporting Information (Eqs. (S9)–(S13)) [35]. The results indicate that in CS+NMP(10%), f_{ar} decreased markedly from 79.40% in CS to 23.12%, while f_{al} increased simultaneously to 74.72%. The significant attenuation of aromatic structural signals was most pronounced at the 10% co-solvent concentration and was highly correlated with the increase in gas yield, particularly

TABLE 1
STRUCTURE PARAMETERS FROM ^{13}C NMR AND ^1H NMR FOR SCWG SOLID PRODUCTS.

Structural parameters	Symbols	Relative abundance (%)						
		CS	CS+THF (5%)	CS+THF (10%)	CS+THF (20%)	CS+NMP (5%)	CS+NMP (10%)	CS+NMP (20%)
Ratio of aromatic carbon	f_{ar}	79.40	61.54	54.44	78.88	45.08	23.12	31.06
Ratio of aliphatic carbon	f_{al}	20.39	38.14	45.17	20.76	54.39	74.72	67.94
Average carbon number of substituent	N	1.24	1.57	1.30	1.24	1.11	1.18	1.05
Branched degree of aliphatic chain	BI	0.03	0.06	0.06	0.02	0.24	0.26	0.26
Non-protonated aromatic carbon	$f_{\text{ar}}^{\text{NP}}$	18.89	6.99	7.84	7.46	9.05	5.96	6.96

the peak formation of H_2 and CH_4 shown in Fig. 3(b). This suggests that aromatic intermediates that would otherwise remain in the organic phase underwent further cleavage in the presence of co-solvents, ultimately converting into small gaseous molecules.

Furthermore, in the NMP-derived pathway, the decrease in the average number of carbon atoms in substituents (N) and the increase in the branching index of aliphatic chains (BI) indicate enhanced formation of small alkanes and the accumulation of alkyl carbon structures. In contrast, the regulatory effect of THF on the organic-phase structure was significantly weaker than that of NMP. In CS+THF(10%), f_{ar} decreased from 79.40% to 54.44%, while f_{al} increased to 45.17%. When the THF concentration was further increased to 20%, the f_{ar} value even rebound to 78.88%, suggesting that excessive THF may weaken the effective cracking of aromatic structures and consequently reduce the gasification efficiency.

These results demonstrate that the NMR structural analysis of the liquid organic phase provides molecular-level insight into the regulatory role of co-solvents in SCWG reaction pathways. In the NMP-assisted system, nitrogen-containing radicals selectively interact with aromatic structures, inducing a nitrogen-doping reconstruction that disrupts aromatic stability and suppresses condensation reactions. As a result, aromatic intermediates are more readily transformed into nitrogen-containing species that undergo further cracking, thereby facilitating the conversion of carbon into gaseous products. In contrast, the THF-derived oxygen-centered radicals mainly promote oxidative cleavage of organic structures and show a comparatively weaker performance in directing deep conversion and product selectivity.

D. Structural and Performance Characterization of Solid Residues

D.1 Surface Chemical Composition and Functional Group Evolution

The XPS peak-fitting results of C, O, and N elements for the solid products obtained from the co-SCWG of CS with different co-solvent concentrations are shown in Fig. 5, and the assignments of the binding energy peaks and their relative proportions are summarized in Table 2 [37]. For the solid residue produced from the SCWG of CS, the surface carbon mainly exists in the forms of C–C/C–H (72.67%), C–O (24.57%), and a small amount of O–C=O (2.77%). After the introduction of NMP, the surface chemical structure of the solid products changed significantly, with the most pronounced variation observed in CS+NMP(10%). Specifically, the proportion of C–C/C–H bonds decreased to 61.61%, while the fractions of C–O and O–C=O increased to 35.20% and 3.19%, respectively. Lower C–C/C–H content in CS+NMP(10%) was observed when compared to CS+NMP (5%), whereas the C–O and O–C=O contents increased to their highest values, suggesting that this condition provides a favorable balance between radical generation and mass transfer efficiency.

Under these conditions, radicals effectively attack the aromatic structures on the char surface, resulting in substantial consumption of the carbon framework. However, in CS+NMP(20%), excessive radicals are more likely to undergo quenching or induce intermediate recombination, triggering secondary polymerization reactions and causing the carbon skeleton structure (C–C/C–H) to dominate again. The cleavage of the carbon framework is accompanied by the evolution of surface functional groups.

When NMP was used as the co-solvent, the O 1s spectra show that the content of active hydroxyl groups reached a maximum value of 25.69% in CS+NMP(10%). The N 1s spectra further indicate that nitrogen-containing functional groups underwent a thermal evolution from pyrrolic N to pyridinic N, in which the initially formed pyrrolic nitrogen intermediates were transformed into the more thermodynamically stable pyridinic nitrogen through aromatization and cyclization processes. This agrees with the findings of Katoh et al. [38], who reported that pyridinic nitrogen has higher thermal stability compared to pyrrolic nitrogen in their study on synthesizing nitrogen-doped graphene using different nitrogen-containing molecular precursors.

These results collectively reveal that the introduction of NMP not only promotes the cleavage of C–C/C–H bonds and the cracking of aromatic rings, but also constructs an *in situ* functional reconstruction layer on the solid surface enriched with hydroxyl and nitrogen-containing functional groups. The newly generated surface sites on this reconstructed layer may act as hydrogen transfer mediators or catalytic active centers, thereby facilitating the interfacial reactions between supercritical water, the solid surface, and organic intermediates. This mechanism is consistent with the significant enhancement in gas yield observed in Fig. 3(f), where CS+NMP(10%) exhibits the highest gas production increase (7.98 mmol·g⁻¹). In essence, NMP induces a functionalized reconstruction of the solid surface, creating an active interface favorable for further carbon gasification and thereby improving the overall gasification efficiency.

In contrast, in CS+THF(10%), the surface chemical structure of the solid residue also reached an extreme state. The proportion of C–C/C–H bonds decreased to its minimum (54.54%), while the fractions of C–O and O–C=O increased to 41.20% and 4.26%, respectively. This further confirms that 10% co-solvent concentration represents a common optimal condition for carbon framework cleavage in this system. Notably, as the THF concentration increased from 5% to 20%, the relative proportion of O–C bonds in the O 1s spectra continuously increased, reaching 89.24% in THF(20%). This monotonic trend suggests that the oxygen-containing radicals derived from THF decomposition tend to accumulate in the solid residue as ether-type structures, rather than undergoing deep functional group reconstruction as observed in the NMP pathway. These oxygen-enriched surface structures, particularly C–O bonds, exhibit relatively high reactivity under supercritical water conditions and may act as direct precursors

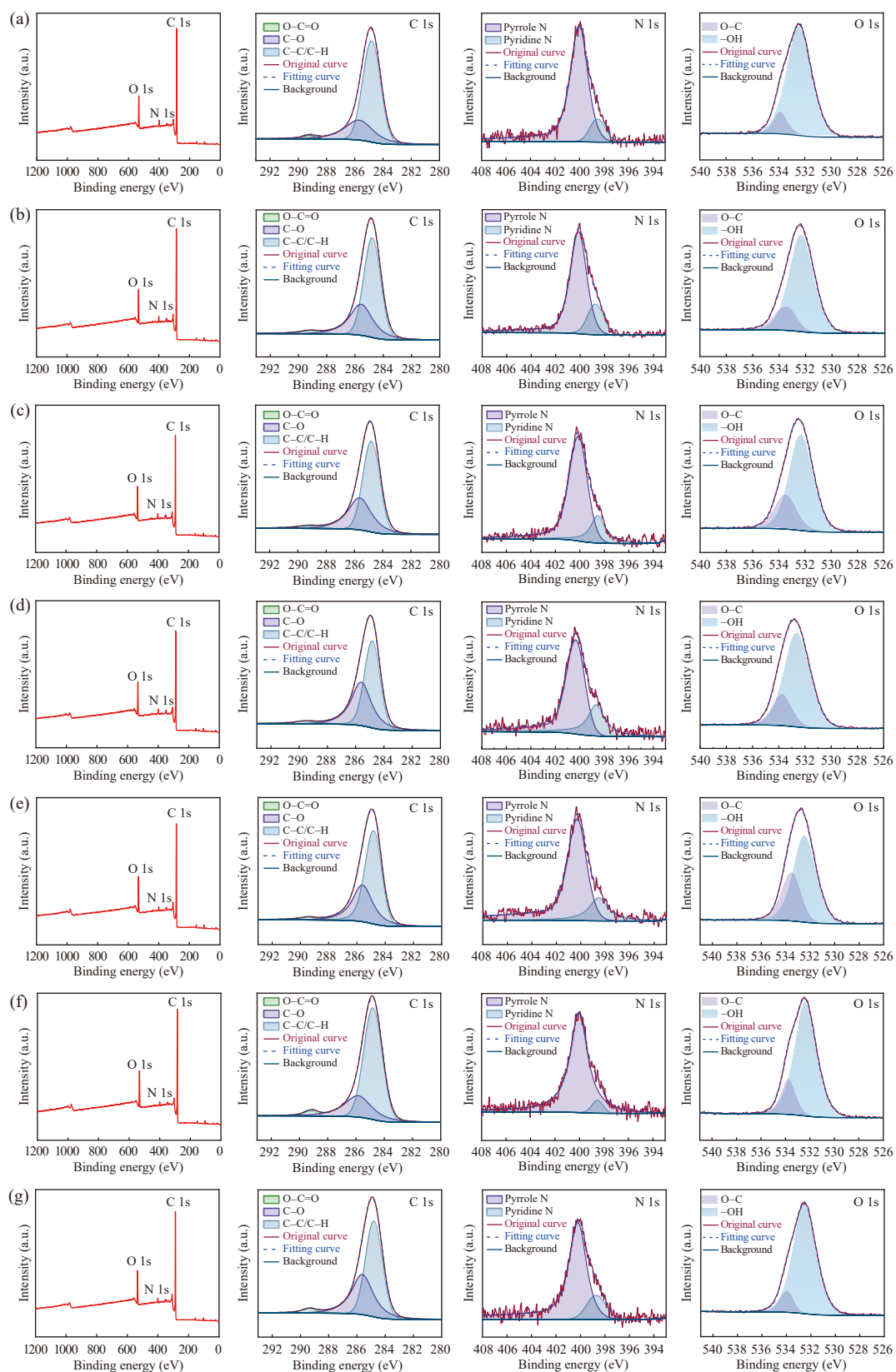


Fig. 5. XPS measurement results of solid products generated from CS individual SCWG and co-SCWG. (a) CS, (b) CS+THF(5%), (c) CS+THF(10%), (d) CS+THF(20%), (e) CS+NMP(5%), (f) CS+NMP(10%), and (g) CS+NMP(20%).

TABLE 2
ASSIGNMENT AND PROPORTIONS OF PEAKS AT EACH BINDING ENERGY.

Test type	Binding energy (eV)	Assignment	CS	CS+THF(5%)	CS+THF(10%)	CS+THF(20%)	CS+NMP(5%)	CS+NMP(10%)	CS+NMP(20%)
C 1s	284.8	C–C/C–H	72.67	62.30	54.54	59.05	71.32	61.61	64.39
	286.2	C–O	24.57	34.40	41.20	37.42	26.12	35.20	32.25
	287.5	O–C=O	2.77	3.30	4.26	3.54	2.56	3.19	3.36
O 1s	532.5	O–C	82.21	67.62	79.48	89.24	89.36	74.31	82.15
	533.5	–OH	17.79	32.38	20.52	10.76	10.64	25.69	17.85
N 1s	398.8	Pyridine N	7.31	19.68	11.62	16.55	12.50	19.85	20.28
	400.2	Pyriole N	92.69	80.32	88.38	83.45	87.50	80.15	79.72

for the water–gas shift reaction, facilitating the conversion of carbon-containing intermediates into CO_2 . This interpretation is consistent with the results shown in Fig. 3(b), where the CO_2 yield in the THF-assisted system ($9.10 \text{ mmol} \cdot \text{g}^{-1}$) being significantly higher than that of CS.

D.2 Pore Structure and Specific Surface Area Analysis

The BJH pore size distribution curves and BET adsorption-desorption isotherms of the solid products obtained from the co-SCWG systems are presented in Fig. 6. The BJH pore distribution results are consistent with the characteristics of the BET isotherms, indicating that the introduction of co-solvents significantly alters the pore structure of the solid residues, and this effect varies with co-solvent concentration. Under the

10% co-solvent condition, the solid products from both systems exhibited the largest mesopore volume (2–50 nm), specific surface area, and total pore volume, among which the structural optimization in the CS+NMP(10%) case was the most pronounced. In contrast, no effective mesoporous network was formed in CS+THF(5%) and CS+THF(20%), and their pore volumes were even lower than those of the solid residue obtained from CS.

The BET specific surface area, BJH pore volume, and average pore diameter of the solid products are summarized in Fig. 7. Under the 10% co-solvent condition, both systems exhibited the highest values of BET surface area, BJH pore volume, and average pore size, with the most pronounced

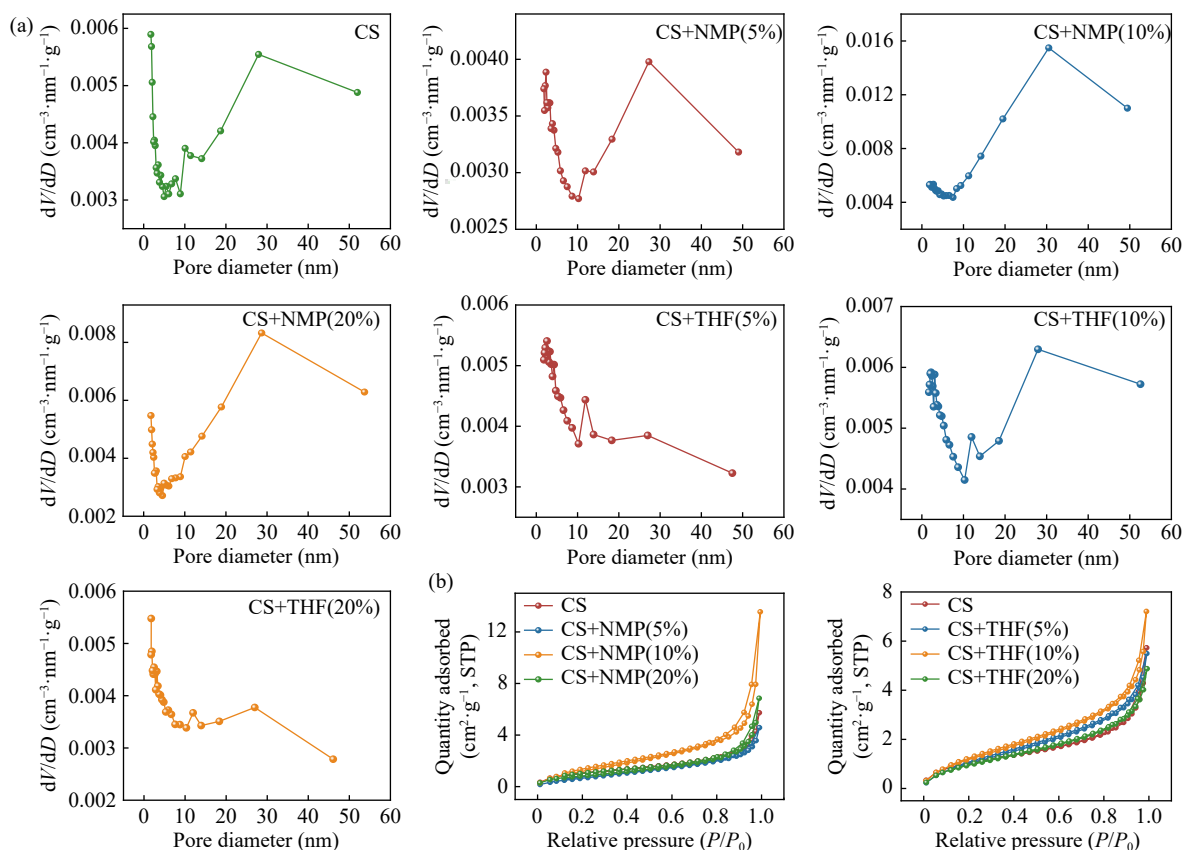


Fig. 6. (a) BJH pore distribution and (b) BET isotherm of solid products in the co-SCWG system.

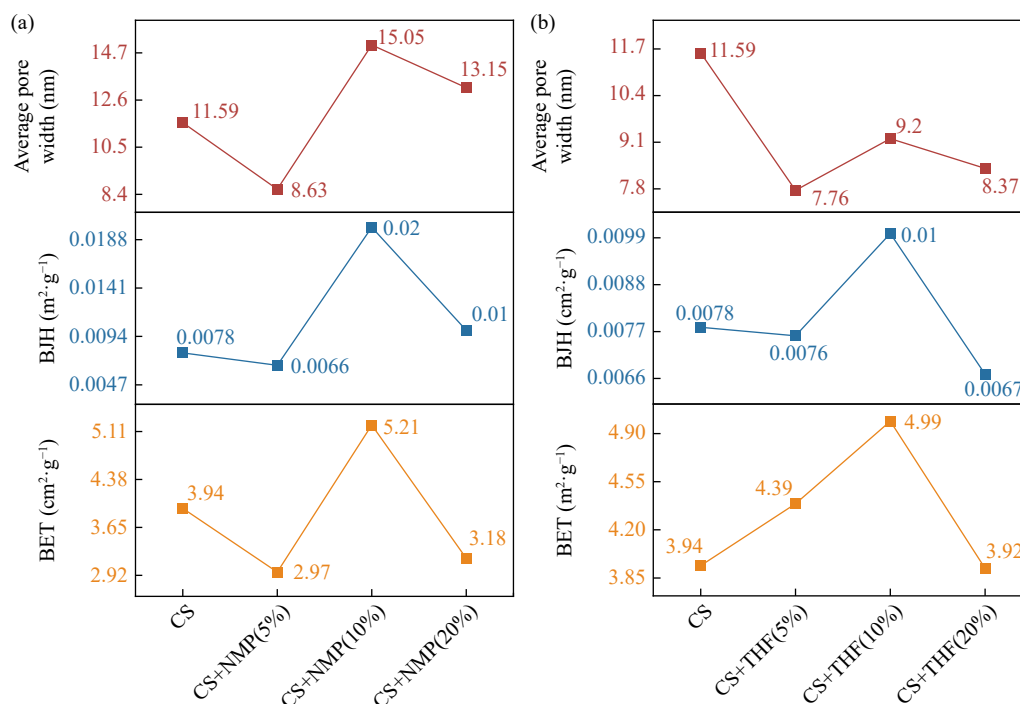


Fig. 7. BET specific surface area, BJH pore volume, and average pore size of solid products.

structural optimization observed in CS+NMP(10%). Specifically, the specific surface area increased from $3.94 \text{ m}^2\cdot\text{g}^{-1}$ in CS to $5.21 \text{ m}^2\cdot\text{g}^{-1}$, while the pore volume increased significantly from 0.0078 to $0.0201 \text{ cm}^3\cdot\text{g}^{-1}$, approximately 2.6 times higher than that of CS. Meanwhile, the average pore diameter increased to 15.05 nm . These results are consistent with the XPS observations, which revealed the most pronounced disruption of the carbon framework, the lowest C–C/C–H content, and the highest abundance of surface functional groups under this condition. Together, these findings confirm that 10% co-solvent addition represents an optimal balance between radical attack and mass transfer efficiency. In contrast, the pore structure parameters decreased to varying degrees at 5% and 20% co-solvent levels. In particular, the pore volumes in CS+THF(5%) and CS+THF(20%) were even lower than those in CS, indicating that both insufficient or excessive co-solvent addition are unfavorable for the formation of an effective mesoporous network.

The evolution of the pore structure is closely related to the SCWG gasification process. At the optimal co-solvent concentration (10%), radicals generated from co-solvent decomposition effectively cleave the bonding networks of biomass macromolecules, promoting the release of volatile components and leading to the formation of interconnected mesoporous structures in the solid residues. This pore-forming process is consistent with the surface chemical changes revealed by XPS analysis, such as the enrichment of reactive hydroxyl and nitrogen-containing functional groups, indicating that extensive cracking and activation reactions occurred in the system.

The developed mesoporous structure plays two important

roles. On the one hand, it acts as a mass transfer channel [39] by significantly increasing the contact area between supercritical water, the solid surface, and retained intermediates, eventually facilitating interfacial reactions such as the water–gas shift and reforming reactions. On the other hand, the internal surfaces of these pores can serve as active sites for subsequent gasification reactions [40]. As a result, under the CS+NMP (10%) condition, the system exhibited not only the highest specific surface area and mesopore volume but also the highest hydrogen yield and total gas production.

D.3 Morphology and Structural Evolution

The microscopic morphology of the solid residues was characterized by SEM, and the results are presented in Fig. 8. Under NMP addition, the samples exhibited the most pronounced structural disintegration, including extensive fragmentation of thin sheets, layer exfoliation, and clearly developed interlayer cracks, leading to the formation of extensive open pore channels. This highly developed porous structure is consistent with the BET analysis, which shows that this sample possesses the highest specific surface area and mesopore volume. These structural features can be regarded as the physical traces of extensive biomass cracking and the release of volatile components. In contrast, under the same co-solvent concentration level, the THF-containing sample exhibited a lower degree of structural fragmentation and poorer pore connectivity, along with relatively intact layered structures. This observation indicates that NMP is more effective in promoting biomass structural disintegration and constructing porous reactive interfaces.

Combining the SEM observations with the previous structural analyses reveals that the abundant pores and fragmented

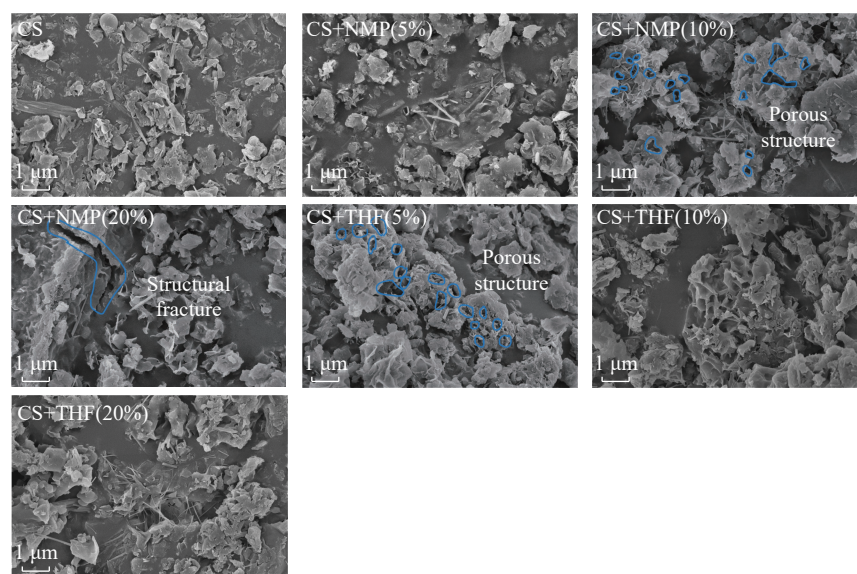


Fig. 8. SEM images of solid products of CS with co-solvent SCWG at different concentrations.

structures formed under NMP addition provide a favorable microenvironment for efficient gas–solid mass transfer and interfacial reactions. Together with the optimized pore structure (BET) and the activated surface chemical states (XPS), these morphological characteristics establish a synergistic physicochemical basis for the enhanced gasification performance. This structural synergy explains the mechanism behind the highest gas yield shown in Fig. 3(b) and the highest hydrogen selectivity in Fig. 4(d). Moreover, the developed hierarchical pore network and high surface area also provide an important structural foundation for the potential electrochemical applications of the solid residues [41,42].

D.4 Electrochemical Performance of Solid Residues

The electrochemical test results shown in Fig. 9 reveal significant differences in the energy storage performance of the solid products. The CV curves indicate that the solid sample obtained from CS+NMP(10%) exhibits the largest enclosed area, suggesting a higher charge storage capacity and specific capacitance. This trend is further confirmed by the GCD measurements. At a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$, the charge–discharge time of the solid product from CS+NMP(10%) reaches 38 s, which is significantly longer than that of CS+THF(10%) (15 s) and the CS sample (3 s).

This superior energy storage performance is well correlated with the structural characteristics discussed above. BET analysis shows that this sample possesses the largest specific surface area and the most developed mesoporous structure, which provide efficient channels for electrolyte ion adsorption and transport. Meanwhile, XPS results reveal that the surface is enriched with electrochemically active nitrogen species, such as pyridinic-N and pyrrolic-N. These nitrogen-containing sites can participate in reversible Faradaic reactions during the charge–discharge process, thereby contributing additional pseudo-capacitance to the overall capacitance.

Such a structure–performance relationship has been widely

reported in materials science. For instance, Zhang et al. [43] demonstrated that nitrogen doping in carbon materials, particularly pyridinic-N and pyrrolic-N, can significantly enhance electrical conductivity, improve surface wettability, and introduce additional pseudocapacitive behavior, which are key factors for improving the performance of supercapacitors. Similarly, Ning et al. [44] constructed bamboo-like nitrogen-doped carbon nanotube composites and showed that the synergistic effect between hierarchical pore structures and nitrogen doping can markedly enhance the energy storage performance of carbon-based materials.

Therefore, the differences in electrochemical performance provide further evidence, from an energy storage perspective, for the microstructural regulation of solid products during the gasification process. The solid residue obtained under the optimal condition CS+NMP(10%) simultaneously exhibits a high specific surface area, hierarchical pore structures, and abundant nitrogen-doped active sites, which are recognized as key structural features of high-performance supercapacitor electrode materials [45], [46]. These results indicate that by regulating the type and concentration of co-solvents during the SCWG process, it is possible to not only optimize hydrogen production performance but also achieve controlled structural design and functionalization of the solid by-products. Consequently, the gasification residues can be transformed into value-added carbon-based functional materials, providing a new pathway for the high-value utilization of all biomass components.

IV. CONCLUSIONS

This study investigated the effects of THF and NMP on the SCWG of corn stover. The results show that a co-solvent concentration of 10% provides the most significant promoting effect, with NMP outperforming THF in gasification performance. Under CS+NMP(10%), the total gas yield increased by

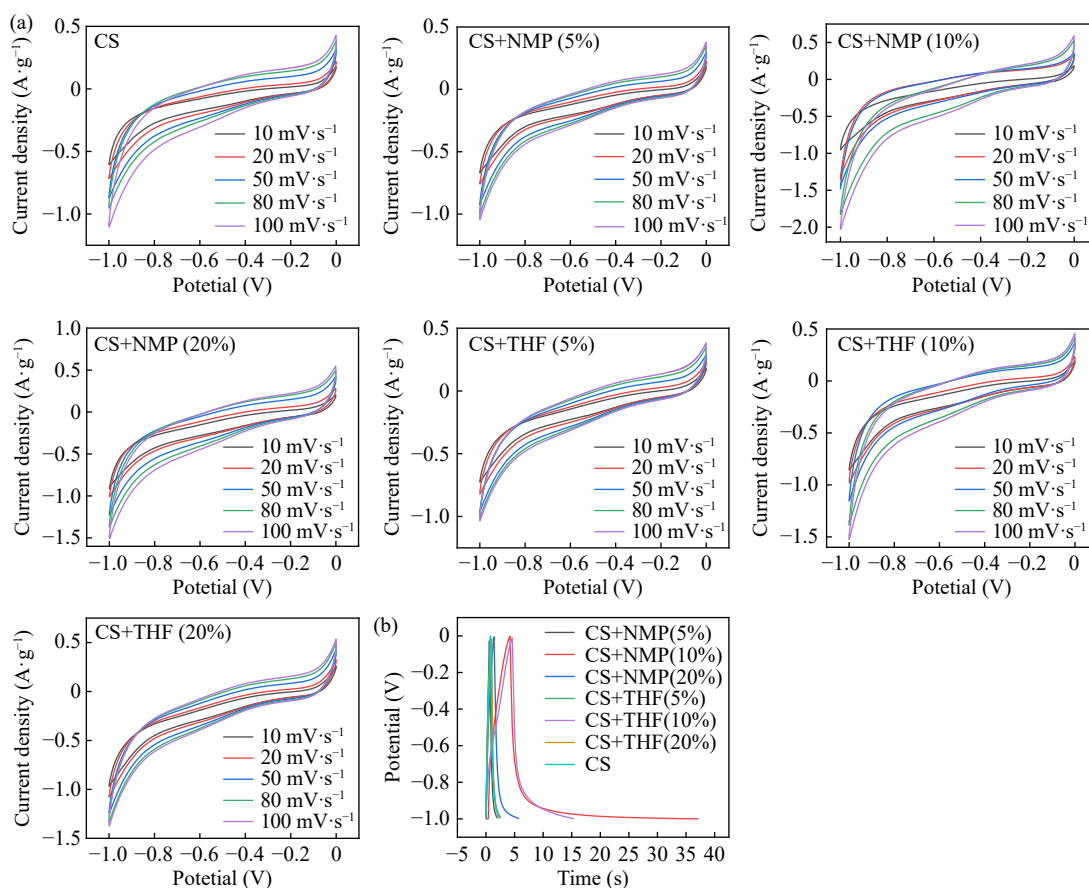


Fig. 9. (a) CV voltammograms of solid products under different concentrations of co-solvents at different scan rates. (b) GCD curves of solid products under different concentrations of co-solvents at a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$.

$7.98 \text{ mmol} \cdot \text{g}^{-1}$, the hydrogen fraction reached 34.45%, and the CGE increased to 58.88%. The enhanced performance is attributed to nitrogen-containing species derived from NMP, which promote aromatic ring transformation and suppress polycyclic aromatic condensation, thereby facilitating hydrogen and light alkanes formation. Meanwhile, the solid residue obtained with 10% NMP exhibited a typical nitrogen-doped porous carbon structure, featuring an activated surface rich in hydroxyl and nitrogen-containing functional groups and a well-developed mesoporous network. Its specific surface area reached $5.21 \text{ m}^2 \cdot \text{g}^{-1}$, with a pore volume of $0.0201 \text{ cm}^3 \cdot \text{g}^{-1}$ and an average pore diameter of 15.05 nm. Compared to the solid residue from corn stover gasification alone ($3.94 \text{ m}^2 \cdot \text{g}^{-1}$), this represents an increase of approximately 32%. Electrochemical tests further demonstrated that the solid product from the 10% NMP system possessed the largest CV integrated area and the charge–discharge time of 38 s at $0.1 \text{ A} \cdot \text{g}^{-1}$, markedly longer than 15 s for the 10% THF system and 3 s for CS alone, indicating superior charge storage capacity and specific capacitance. These results demonstrate that regulating co-solvent conditions in SCWG can simultaneously enhance hydrogen production and enable the value-added utilization of gasification residues.

Nevertheless, several limitations remain. Reaction path-

ways were inferred mainly from product distribution and structural characterization; in situ techniques are still needed to directly verify the key processes. Long-term electrochemical stability, material scalability, and comprehensive techno-economic analysis of the solid products also warrant further investigation. The recovery and recycling of co-solvents also represent critical challenges that must be addressed for future industrial applications. We recommend using membrane separation technology to recover and reuse the high-boiling co-solvents used in this study, and to guide subsequent industrialization research through a full life-cycle economic assessment.

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DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing

financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AI USAGE STATEMENT

During the preparation of this manuscript, the authors used DeepSeek-V3.2 (DeepSeek, Hangzhou, China), an AI language model, in order to refine the language and improve the readability and grammatical accuracy of the manuscript. The authors have reviewed and edited the content and take full responsibility for the final version of the manuscript.

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