

Reactivity, Kinetic, and Thermodynamic Analysis of Ionic Liquid-Assisted Thermal Degradation of Spent Coffee Ground

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ABSTRACT: In this work, the impact of Ionic Liquid (IL) pretreatment of Spent Coffee Grounds (SCG) is assessed using three analytical techniques. Four different classes of ILs were employed to compare the effect of cations and anions. Thermogravimetric analysis under the N₂ environment was done to collect analytical data at 20 °C/min. Reactivity analysis evaluated mean relative reactivity (R_m) and pyrolysis factor (PF), kinetic analysis determined activation energy (E_a) and pre-exponential factor (A), while thermodynamic analysis helped to find enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS). IL treatment aided thermal breakdown by increasing the mass loss % from 93% for untreated SCG to 97% after IL treatment. The decomposition rate for the IL-treated samples was calculated to be in the range of 6.7-7%min⁻¹. All the ILs increased R_m, with the largest increase from 2.42*10² to 2.57*10² % min⁻¹°C⁻¹; they also decreased the E_a of SCG from 42.25 to as low as 29.91 kJ/mole. This might be induced by the breakdown of the lignin structure of SCG by IL treatment leaving it sensitive to heat treatment. IL-treated SCG ΔS values indicate increased disorder and thermal instability. Among the studied ILs, relatively inexpensive and infrequently used [P66614] [Cl] and [N1444] [Cl] fared better than imidazolium-based ILs. This study could provide useful knowledge in finding effective cations for designing task-specific ILs for the thermochemical conversion process.

KEYWORDS: Spent coffee ground; Thermogravimetric analysis; Ionic liquids; Kinetic parameters; reactivity; Thermodynamic parameters.

INTRODUCTION

Biomass is a carbon-unbiased fuel and can diminish CO₂ outflows to a worthy level. Quick decrease of customary energy resources like oil and gas, constraints on the utilization of coal attributable to ecological contamination, and the need to address the effect of a global temperature boost is making

biomass exceptionally appealing as an alternative energy resource [1][2]. Biomass can be either singed directly or prepared into biofuel.

Leftover from the brewing process of coffee is called spent coffee ground (SCG). At the starting stages, SCG

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Table 1: Comparison of available biomass

Biomass	Moisture content%	Volatile matter%	Ash content%	Fixed carbon%	HHV MJ/Kg
SCG	3.66	80.30	6.76	9.41	17.53
Rice husk	8.76	64.25	6.76	11.27	16.67
Cotton stalk	20.86	60.66	6.28	12.20	13.84
Wheat straw	6.34	61.73	17.64	14.29	15.59
Bagasse	25.25	48.98	13.45	12.32	15.43

uses were not extensively explored and most of it was squandered, landfilled, or once in a while again blended in with the unadulterated coffee [3]. With the ever-increasing consciousness of SCG applications, its worth has grown tremendously [4]. The synthetic arrangement of SCG in the presence of polysaccharides, proteins, and minerals makes it of high biotechnological esteem, which may be utilized as significant information material in the maturation cycle. SCG is wealthy in potassium, magnesium, and phosphorous. Production of biogas and biodiesel, change of separated lipids into unsaturated fat and methyl ester, and the treatment of wastewater are some of the major industrial uses of SCG [5]. SCG can be utilized as solitary biomass or in a consolidated structure with different biomasses for the synthesis of syngas [6].

SCG is an attractive source of green energy. It has been used in making products like scrubs, air fresheners, phenols, and lactic acid [7]. The possibilities of SCG utilization have been elaborated on in many scientific papers. High nitrogen content facilitates the use of SCG as fertilizer or as a soil improver (compost), while high organic matter content makes it ideal for sugar production. High calorific value makes it very useful as fuel in the industrial boiler. However, high lignin content limits the use of SCG as an animal feed [8]. A brief comparison of SCG and other available biomass is given below. This table signifies the importance of using SCG as biomass clearly.

SCG has a lignocellulosic structure. To break this lignocellulose, pretreatment is important to release the monomer [9]. Hemicellulose is moderately simple to separate as opposed to cellulose. At first, acid and alkali pretreatment were utilized to separate the structure of biomass for upgraded movement. Scientists have revealed SCG pretreatment with NaOH and H₂SO₄. It was seen that with H₂SO₄ pretreatment, biogas yield increments from 0.5 to 0.6 m³/kg with an expansion in methane yield up to 55-61% [10]. Another work was done with the comparison of acidic and base pretreatment of wild mustard and it was concluded that acid pretreatment increased the yield of biochar and it is more effective [11]. In any case, acids and bases

can be destructive to the framework and the environmental factors as a result of their destructive and unstable nature. Another disservice is their absence of a recovery limit.

Ionic liquids (ILs) comprise huge cations connected with anions and have low melting point [12]. They are proclaimed as solvents of the future because of their astounding tunable capacity and high dissolvability [13]. Its properties like high substance solvency, non-combustibility, and simplicity of recuperation make them incredibly helpful for various applications [14–16]. One significant impediment of ILs is their significant expense which can be countered by their capacity for recovery [17]. ILs are getting well known as pretreatment specialists due to their non-receptive, non-destructive nature, and amazingly low vapor pressure [18]. *Maki-Arvela et al.* performed a survey on ILs for pretreatment of lignocellulosic material. They inferred that among the ILs utilized, 1-allyl-3-methylimidazolium chloride [Amim][Cl] and 1-ethyl-3-methylimidazolium acetate [Emim][Ac] demonstrated the best dissolubility [19]. The capacity of IL to altogether diminish the crystallinity and increment explicit surface territory have been distinguished as potential purposes behind improving the rate and yield of enzymatic saccharification. *Jiafu et al.* [20] employed utilized thermogravimetry to comprehend the connections between IL and biomass. Pretreatment of different biomasses by 1-butyl-3-methylimidazolium acetate [Bmim][Ac] at a temperature of 50-130°C for 6 h revealed that various biomasses react diversely to pretreatment by the same IL. Besides, it was seen that pretreatment temperature and time are improved for a particular errand and serious pretreatment may even prompt a decrease in thermal strength. The insights of biomass destruction by ILs are not unmistakably perceived. One recommendation is that the ILs break the three-dimensional organization by contending with auxiliary parts for hydrogen bonding. Delignification of biomass is achieved by the association between cellulose hydroxyl gatherings and ILs which breaks hydrogen bonds bringing about cellulose disintegration.

Table 2: Details of selected ILs

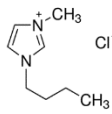
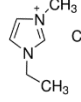
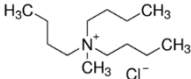
Ionic Liquid	Structure	Company	Purity (%)	Thermal decomposition temperature (°C)
1-butyl-3-methyl imidazolium chloride		Chem-Impex International	99.5	220
1-ethyl-3-methyl imidazolium chloride		TCI Chemicals	>97	228
Trihexyltetradecylphosphonium chloride	$\text{H}_3\text{C}(\text{H}_2\text{C})_5-\text{P}^+(\text{CH}_2)_{13}\text{CH}_3 \text{Cl}^-$	Sigma Aldrich	>95	330.9 to 350
Tributylmethylammonium chloride		Chem-Impex International	99.22	170



Fig. 1: Grinding & sieving of SCG

Most of the works investigating IL pretreatment of biomass have zeroed in on imidazolium-based cations while ammonium-based, phosphonium-based, and different cations need more exploration particularly since they are less expensive than imidazolium-based ILs. In this work, reactivity, kinetic, and thermodynamic properties of SCG after pretreatment with different cation based ILs are presented. Knowledge of kinetic and thermodynamic boundaries can help overhaul the thermochemical process to pilot as well as the industrial level. Results recommend that phosphonium and ammonium-based ILs that are economically less demanding when contrasted with imidazolium-based ILs can be valuable pretreatment operators before bringing biomass into thermochemical transformation processes.

EXPERIMENTAL SECTION

Sample preparation

Coffee samples were obtained from Nestle plant located at Kabirwala and filtered. The residue was dried at room

temperature for 48 h. Fritsch mortar grinder and Fritsch vibratory sieve shaker were utilized to reduce the diameter of the samples to between 0.18 and 0.21 mm (Fig. 1).

Ionic liquid pretreatment

The structure and details of the selected ILs utilized in this study are enlisted in Table 2 [21]. Pretreatment of SCG by ILs was done likewise to the one detailed by *Lei et al.* [22]. Drying of ILs was affected at 100°C for 48 h. Later, blends of SCG and ILs were prepared in equal weights and transferred to a round bottom flask for processing at 140°C for 30 min. Successive washing by distilled water enabled removal of adsorbed ILs.

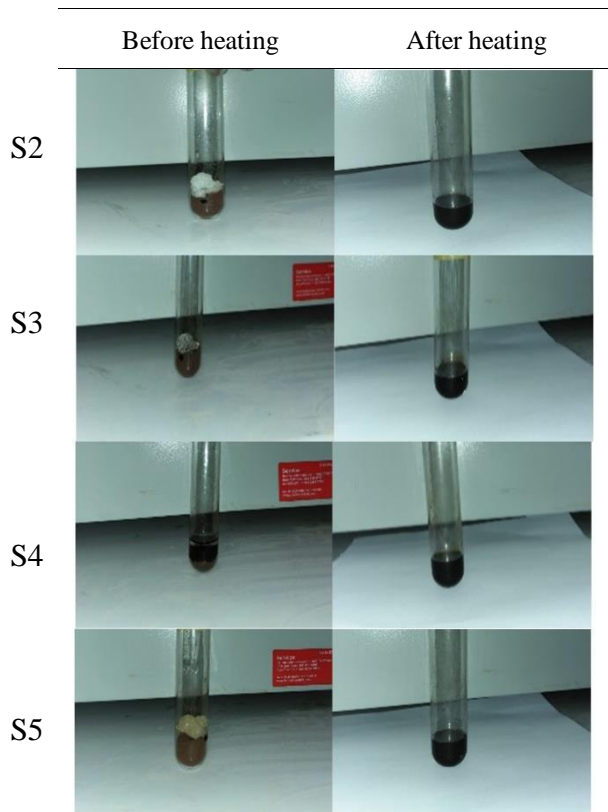
[P₆₆₆₁₄] [Cl], being highly hydrophobic, was absorbed in SCG and could not be recovered by washing. The presence of IL was detected by electrical conductivity assessment of assembled water in the wake of washing. Filtration was achieved via filter paper having pore size 11 μm, thereby separating the mixture into filter cake and filtrate containing water and IL. IL was recovered by evaporation at 100°C, while SCG was kept under vacuum at 80°C for 12 h. The appearance of the samples before and after heating is displayed in Fig. 2. Abbreviations for the samples are given in Table 3. Proximate, ultimate analysis, and HHV values are published elsewhere [23, 24].

Kinetic analysis

Researchers have tried to determine the kinetic parameters either by model-fitting or model-free analysis

Table 3: Sample names and abbreviations

Sample names	Abbreviations
Raw SCG	S1
SCG+[Bmim][Cl]	S2
SCG+[Emim][Cl]	S3
SCG+[P ₆₆₆₁₄][Cl]	S4
SCG+[N ₁₄₄₄][Cl]	S5

**Fig. 2: Appearance of samples before and after heating**

[25]–[27]. In this paper, the model-fitting strategy is applied. Mass reduction per unit time, $d\alpha/dt$, can be communicated as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Where α is the fractional decomposition of reactant, t is time (sec), and T is the absolute temperature (in Kelvin), α can be represented as:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (2)$$

Where m_i , m_b and m_f are the initial, instantaneous, and final masses of the samples, respectively. Arrhenius equation is given as follows:

$$k(T) = Ae^{-E_a/RT} \quad (3)$$

Where A , E_a , and R represent, respectively, the pre-exponential factor, activation energy, and universal gas constant.

Also, $f(\alpha)$ in terms of order of reaction (n) is expressed as:

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

Substituting Eqs. (3) and (4) into Eq. (1), we get:

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}(1 - \alpha)^n \quad (5)$$

Ramp rate, β , is given as:

$$\beta = \frac{dT}{dt} \quad (6)$$

Inserting β into Eq. (5) results in Eq. (7):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT}(1 - \alpha)^n \quad (7)$$

Presumably, the reaction order is approximately 1 for most thermochemical conversion process of coal and biomass [28]. Taking $n=1$ in Eq. 7 and integrating gives:

$$-\ln(1 - \alpha) = \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} e^{-\frac{E_a}{RT}} \right] \quad (8)$$

$$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (9)$$

$$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \right] - \frac{E_a}{RT} \quad (10)$$

From Eq. (10), a plot between $\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right]$ and $1/T$ can be drawn to calculate E_a and A of samples.

Thermodynamic parameters

Useful thermodynamic parameters such as changes in enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) were evaluated by Eqs. (11), (12), and (13), respectively:

$$\Delta H = E_a - RT \quad (11)$$

$$\Delta G = E_a + RT_p \ln \left(\frac{K_B T}{hA} \right) \quad (12)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \quad (13)$$

Table 4: Reactivity analysis of samples

Samples	Avg. decomposition rate (%min ⁻¹)	Decomposition rate at peak temperature (%min ⁻¹)	Peak temperature (°C)	Rm (x10 ³) (%min ⁻¹ °C ⁻¹)	PF (x10 ⁷)	Conversion (%)
S1	1.77	6.96	287	2.42	5.15	93.92
S2	1.61	6.76	267	2.53	3.37	96.80
S3	1.60	6.70	260	2.57	3.66	96.87
S4	1.72	7.00	277	2.53	4.82	96.58
S5	1.78	6.87	271	2.53	4.76	96.74

The peak decomposition temperature is T_p , the Boltzmann constant is K_B , and the Planck constant is h .

RESULTS AND DISCUSSION

Reactivity analysis

In order to increase the accuracy of results, after pyrolysis process of untreated and treated SCG with four ILs, various kinetic models with different kinetic mechanism were applied to find out activation energy and frequency factors. The appropriate model was chosen on the basis of linear fitting results of the main solid-state reaction kinetic models and the regression coefficient R^2 . The model with R^2 nearly equals to 0.99 could be considered as the best model as reported in this work.

Table 4 presents the average and maximum decomposition rates, mean relative reactivity (Rm), and pyrolysis factor (PF) for raw and IL treated SCG. ILs raised the Rm of SCG. [Bmim][Cl], [P₆₆₆₁₄][Cl] and [N₁₄₄₄][Cl] all recorded 2.53%min⁻¹°C⁻¹ Rm. Highest Rm was 2.57%min⁻¹°C⁻¹ for [Emim][Cl]. Previous studies showed that pretreatment temperature affects ILs' potential to increase biomass thermal stability [29]. Increasing the pretreatment temperature reduces the thermal stability of IL-pretreated biomass, which concurs with this work [20]. SCG includes lignin with no specified primary structure and a broad decomposition temperature range [27]. Untreated SCG had the greatest PF because to its substantial average weight loss. Phosphonium and ammonium-based ILs had greater PFs. IL treatment of SCG also increased the percentage conversion. The effect of all the ILs regarding percentage conversion was the same, i.e., 3% rise. This could be due to the dissolution of cellulose and hemicellulose by ILs [30].

Kinetic analysis

Activation energy is the additional energy required by reactants to be transformed into products. Eq. (10) was applied

on TGA data to determine E_a and A for order of reactions 1, 1.5, 2, and 3. E_a and A were determined in two distinct zones, 1st devolatilization zone, and 2nd devolatilization zone, which can be divided into two regions at either side of the peak temperature [31]. Table 5 presents the E_a , A , and R^2 of samples. Data shows high linearity as R^2 lies in the range of 0.98-0.99 in the 1st devolatilization zone and 0.87-0.96 in the 2nd devolatilization zone. According to expectations, the first zone had higher E_a values than the second zone. [32]. The IL treatment reduced E_a of SCG, which may have been brought about by the breakdown and disintegration of the lignin structure of SCG. IL's earlier rubberwood treatment yielded similar outcomes [33]. Comparatively, [N₁₄₄₄][Cl] treated sample required the lowest E_a . However, for [N₁₄₄₄][Cl], the difference in E_a of the two zones is the highest among the ILs. Thus, IL pretreatment reduces E_a and consequently, increases the reaction rate. Therefore, it can be inferred that ILs serve the purpose of catalysts for thermochemical conversion of SCG.

Thermodynamic parameters

Thermodynamics parameters are presented in Table 6. The amount of energy obtained or lost during a chemical process is measured by ΔH [34]. Positive values imply that the process absorbs energy. The results suggest that IL treatment reduced the ΔH of the treated samples. Amir *et al.* [33] observed the same trend with IL treated rubberwood. However, much lower values have been obtained in this study. ΔG estimates the direction of a chemical reaction. In the first zone, untreated SCG exhibited much greater ΔG than treated SCG. Overall ΔG is lower in the 2nd zone as compared to the 1st zone. Like ΔH , lower values for ΔG were obtained as compared to rubberwood showing greater susceptibility to thermal degradation. ΔS measures the disorderliness of a system. It could be inferred that lower degree of disorder is observed in products as compared to reactants. S5 recorded highest value of ΔS

Table 5: Kinetic parameters of untreated and IL treated SCG with different reaction orders

Samples	Order of reaction	1st Zone (°C)	Ea kJ/mol	A x10 ⁵ (sec ⁻¹)	R ²	2nd Zone (°C)	Ea kJ/mol	A x10 ² (sec ⁻¹)	R ²
S1	1	150-287	42.25	88.08	0.99	287-600	7.82	11.76	0.91
	1.5		44.38	170.41	0.99		10.69	33.69	0.89
	2		46.63	339.93	0.99		14.12	104.25	0.88
	3		51.43	1479.44	0.99		22.32	1198.65	0.87
S2	1	150-267	32.59	10.83	0.98	267-600	7.02	10.97	0.93
	1.5		33.63	15.84	0.99		10.01	35.39	0.91
	2		34.71	23.44	0.99		13.63	124.34	0.90
	3		36.96	53.25	0.98		22.32	1877.41	0.88
S3	1	150-260	33.92	15.99	0.99	260-600	6.71	9.82	0.93
	1.5		35.18	25.30	0.99		9.49	30.17	0.91
	2		36.49	40.52	0.98		12.86	100.44	0.90
	3		39.28	109.41	0.99		20.95	1341.03	0.89
S4	1	150-277	31.84	5.41	0.99	277-600	8.54	19.91	0.96
	1.5		32.67	7.28	0.99		13.02	92.06	0.95
	2		33.59	9.80	0.98		18.62	497.92	0.94
	3		35.33	18.35	0.98		31.97	19747.82	0.93
S5	1	150-271	29.91	5.85	0.99	271-600	10.64	32.64	0.94
	1.5		31.61	10.66	0.98		16.37	181.27	0.92
	2		33.41	20.00	0.99		23.53	1229.36	0.90
	3		37.41	77.13	0.99		40.71	82660.19	0.88

Table 6: Thermodynamic parameters of untreated SCG samples

Samples	1st Zone (°C)	Order	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol. K)	2nd Zone (°C)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol. K)
S1	150-287	1	38.17	107.28	-0.12	287- 600	1.86	116.14	-0.20
		1.5	40.30	106.34	-0.12		4.74	114.11	-0.20
		2	42.54	105.36	-0.11		8.16	112.28	-0.19
		3	47.34	103.32	-0.10		16.36	109.10	-0.17
S2	150-267	1	28.59	104.61	-0.14	267- 600	1.15	111.72	-0.20
		1.5	29.63	103.94	-0.14		4.14	109.45	-0.20
		2	30.70	103.26	-0.13		7.75	107.42	-0.18
		3	32.96	101.83	-0.13		16.45	103.93	-0.16
S3	150-260	1	29.95	103.25	-0.14	260- 600	0.87	110.52	-0.21
		1.5	31.20	102.47	-0.13		3.65	108.33	-0.20
		2	32.52	101.70	-0.13		7.02	106.37	-0.19
		3	35.31	100.09	-0.12		15.10	102.97	-0.16
S4	150-277	1	27.80	108.41	-0.15	277- 600	2.63	112.49	-0.20
		1.5	28.63	107.89	-0.14		7.10	109.96	-0.19
		2	29.54	107.45	-0.14		12.71	107.85	-0.17
		3	31.29	106.33	-0.14		26.05	104.36	-0.14
S5	150-271	1	25.89	105.27	-0.15	271- 600	4.75	111.19	-0.20
		1.5	27.59	104.26	-0.14		10.48	109.17	-0.18
		2	29.39	103.21	-0.14		17.64	107.67	-0.17
		3	33.39	101.11	-0.12		34.82	105.82	-0.13

indicating diversity in behavior affected by different ILs. Similar to a prior research, greater values of S for IL treated samples suggest increased Ea, structural deformation, vibration, and degrees of freedom of rotation [33].

CONCLUSIONS

This article studied the thermogravimetric pretreatment potential of four ILs using spent coffee ground as biomass. The pretreatment performance was assessed via reactivity, kinetic, and thermodynamic parameters. During the

pretreatment phase, SCG absorbed all of the [P₆₆₆₁₄] [Cl]. IL pretreatment significantly enhanced the mean reactivity and reduced the activation energy thereby increasing the reaction rate. Ammonium-based IL [N₁₄₄₄] [Cl] produced the lowest E_a. ILs increased the entropy showing higher degradation of SCG structure. Overall, relatively low-cost phosphonium and ammonium-based ILs outperformed imidazolium-based ILs, and they might be potential pretreatment agents in the thermal conversion of biomass. In the future, morphological studies on IL pretreatment should be carried out to better understand the mechanism.

Nomenclatures

Degree of conversion	α
Temperature related rate constant	k(T)
Activation energy	E _a
Frequency factor	A
Order of reaction	n
Heating rate	β
Boltzmann constant	K _B
Planck constant	h

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