

Effect of combined slow pyrolysis and steam gasification of sugarcane bagasse on hydrogen generation

Prakash Parthasarathy and Sheeba Narayanan[†]

Fossil and Alternate Fuel Processing Laboratory, Department of Chemical Engineering,
National Institute of Technology, Tiruchirappalli-620015, Tamil Nadu, India
(Received 8 July 2014 • accepted 16 February 2015)

Abstract—The present work aims at improving the generation of H₂ from sugarcane bagasse in steam gasification process by incorporating slow pyrolysis technique. As a bench scale study, slow pyrolysis of sugarcane bagasse is performed at various pyrolysis temperature (350, 400, 450, 500 and 550 °C) and feed particle size (90 < D_p < 212, 212 < D_p < 355, 355 < D_p < 500, 500 < D_p < 850 μm) to determine effective conditions of char generation. In the combined process (slow pyrolysis of biomass followed by steam gasification of char), first slow pyrolysis is carried out at the effective conditions (pyrolysis temperature and particle size) of char generation (determined from bench scale study) and steam gasification is at varying gasification temperature (600, 650, 700, 750 and 800 °C) and steam to biomass (S/B) ratio (1, 2, 3, 4, 5 and 6) to determine the effective conditions of H₂ generation. The effect of temperature and S/B on gas product composition and overall product gas volume was also investigated. At effective conditions (gasification temperature and S/B) of H₂ generation, individual slow pyrolysis and steam gasification were also experimented to evaluate the performance of combined process. The effective condition of H₂ generation in combined process was found to be 800 °C (gasification temperature) and 5 (S/B), respectively. The combined process produced 35.90% and 23.60% more gas volume (overall) than slow pyrolysis and steam gasification process, respectively. With respect to H₂ composition, the combined process generated 72.37% more than slow pyrolysis and 17.91% more than steam gasification process.

Keywords: Sugarcane Bagasse, Slow Pyrolysis, Steam Gasification, Combined Process, H₂ Generation

INTRODUCTION

Hydrogen is the most efficient fuel and is referred to as the 'fuel of the future' as it possesses high energy and emits only water when combusted [1,2]. Though the major share of hydrogen is derived from natural gas, an effective alternative renewable source is looked upon, as fossil fuels are fast depleting and turning out to be inaccessible [3,4]. Hydrogen from biomass looks a viable option as biomass are bountiful, renewable, clean and sustainable [5-7]. Hydrogen can be recovered from biomass through biochemical and thermochemical methods [8]. Biochemical methods are time consuming and pricy [9]. On the other hand, thermochemical methods are simple, fast and relatively cheaper. The possible methods of hydrogen generation through thermochemical method includes: fast pyrolysis followed by steam reforming of oil, steam critical water-gasification and steam gasification [10]. Among these three methods, only steam gasification offers better conversion efficiency of biomass into hydrogen. However, the efficiency of steam gasification can be further increased either by steam gasification of biomass followed by reforming of bio-oil (generated from steam gasification) using molecular distillation or by integrating slow pyrolysis and steam gasification techniques [11].

Reforming of bio-oil using molecular distillation is discussed

below. Bio-oil due to its high oxygen and water content, acidity and low heating value cannot be used directly as fuel. Hence, it is essential to upgrade bio-oil to improve its quality. Currently three conventional technologies such as solvent extraction, column chromatography, and distillation are employed for bio-oil separation [12]. Among them, distillation is the most common and conventional method followed in chemical industry for the separation phenomenon. Some important types of distillation employed in the separation of bio-oil are atmospheric pressure distillation, vacuum distillation and steam distillation.

The mechanism of distillation of bio-oil is as follows. Though the boiling of bio-oil gets initiated below 100 °C under atmospheric pressure, the distillation process lasts till 250-280 °C. This large temperature range is due to the complexity in the composition of bio-oil. Generally, after distillation, residue composition of 35-50% remains [13]. Owing to the thermal sensitivity of bio-oil, the effective separation of bio-oil using conventional methods is very difficult. Hence, current distillation methods employ molecular distillation as it offers low operation temperature, little heating time and high separation efficiency [14]. Upon molecular distillation, the bio-oil can be fractionated into light, middle and heavy fractions. The light fractions can undergo esterification, catalytic cracking and steam reforming to yield ester fuel, hydrocarbon and hydrogen. On the other hand, middle fraction can be subjected to steam reforming and hydrodeoxygenation to recover hydrogen and hydrocarbons. The heavy fraction can be emulsified to give emulsion fuel [15].

Combining slow pyrolysis and steam gasification of biomass is

[†]To whom correspondence should be addressed.

E-mail: sheeba@nitt.edu

Copyright by The Korean Institute of Chemical Engineers.

an interesting and emerging concept [16]. Generally, slow pyrolysis is aimed at producing more char, whereas steam gasification is destined to generate undue hydrogen [17-19]. The combined process can mitigate the demerits of both slow pyrolysis and steam gasification processes. In addition, the hybrid process offers synergistic benefits of both the processes facilitating efficient gasification reactions, better conversion efficiency into gas, reducing tar generation and offering more H₂ yield.

Numerous studies are available on individual slow pyrolysis and steam gasification [20-23]. In fact, investigations of steam gasification of pyrolyzed char are also numerous [24,25]. Conversely, study on the combined pyrolysis and steam gasification is rare as it is new and emerging. The current work aims at studying the effect of temperature and S/B on overall gas volume and product gas composition of combined process. The performance of the combined process with respect to overall gas product volume and H₂ generation is also compared with individual slow pyrolysis and steam gasification.

The specific objective of the work is stated below.

- i. To conduct bench scale slow pyrolysis study to determine the effective operating conditions (pyrolysis temperature and feed particle size) of char generation.
- ii. To conduct combined slow pyrolysis (experiments conducted at effective conditions of char generation determined from bench scale study) and steam gasification of sugarcane bagasse to determine effective conditions (gasification temperature and S/B) of H₂ generation.
- iii. To study the effect of temperature on overall gas volume and product gas composition in the combined process.
- iv. To investigate the influence of S/B on overall gas volume and product gas composition in the combined process.
- v. To conduct slow pyrolysis and steam gasification at effective conditions (gasification temperature and S/B) of H₂ generation of combined process to evaluate the performance of combined process.

MATERIALS AND METHODS

1. Biomass Samples

Sugarcane bagasse is a fibrous material obtained after the extraction of sugar juice from sugarcane [26]. India produces about 347.9 MT of sugar cane annually [27]. On an average during sugar manufacturing, 1 kg of sugarcane sheds nearly 300 g of wet bagasse. Hence, around 100 MT of wet bagasse is available in the country. Though wet bagasse is composed of 40-50% moisture, a considerable amount of usable solid possessing significant energy content is left behind. Sugarcane bagasse is used as a primary fuel to generate heat, in the cogeneration of heat and electricity, to extract ethanol a liquid fuel, to make boards similar to plywood, *etc.* [28,29]. Nonetheless, still a huge amount of sugarcane bagasse is unused. The Ministry of statistics and programme implementation projects that about 5,000 MW of power generation from sugarcane bagasse based cogeneration power plant is possible [30]. Apart from its usual application, hydrogen generation from sugarcane bagasse via thermochemical method can be also looked into.

2. Analysis of Samples

The sugarcane bagasse is collected from Kurungulam Sugar mills, Thanjavur, Tamilnadu, India. The collected biomass is sun dried until the moisture is reduced to less than 15%. The dried biomass is stored in plastic bags to prevent it from absorbing ambient moisture. Samples representation for the physical (sieve analysis, proximate), chemical (elemental analysis, wet chemical analysis) and thermal analysis (calorific value) is acquired from those dried preserved samples. The findings of the physical, chemical and thermal analysis are presented in Table 1 [31,32].

3. Bench Scale Slow Pyrolysis Experiments

Prior to combined slow pyrolysis and steam gasification experimentation, a bench scale study of slow pyrolysis is done to deter-

Table 1. Physical, chemical and thermal analysis results of sugarcane bagasse

Physical analysis			
Analysis	Variable	Value	Standard
Sieve analysis	Mean particle diameter (µm)	314	Bureau of Indian standards - IS 1607
	Moisture content (%)	3.10	ASTM D 3173
Proximate analysis	Volatile matter (%)	81.50	ASTM D 3175
	Fixed carbon* (%)	10.60	
	Ash (%)	4.80	ASTM D 3174
Chemical analysis			
Ultimate analysis	Carbon (%)	44.05	
	Hydrogen (%)	6.21	
	Nitrogen (%)	0.25	ASTM D 3176-89
	Sulphur (%)	0.00	
	Oxygen* (%)	49.49	
Wet chemical analysis	Cellulose (%)	40.80	
	Hemi-cellulose (%)	21.80	[31, 32]
	Lignin (%)	19.20	
	Extractives (%)	13.45	
Thermal analysis			
Heat content	Calorific value (kJ/kg)	15, 890	ASTM D 5865-12

mine effective operating conditions of char production. The parameters such as temperature and feedstock particle size are varied. The temperature is varied between 300–550 °C at an increment of 50 °C. Feedstock particle size of $90 < D_p < 212$, $212 < D_p < 355$, $355 < D_p < 500$, $500 < D_p < 850$ μm is taken for study. The optimization of temperature and particle sizes is essential as it influences the char quantity and quality greatly. Char quantity is measured in terms of char yield, while char quality is measured in terms of carbon content present in it. In general, char with 75% carbon content is regarded as a good quality char [33].

Experimentation is done at a slow heating rate of 4 °C for all runs. The detail of the bench scale setup is given in Table 2. A tubular furnace is used as the heating source for the pyrolysis process. 5 g

of sample is taken in a tubular reactor. The reactor is designed in such a way that it exactly accommodates the furnace tube. The reactor is placed in the furnace tube, and the top exposed part of the reactor is well insulated using glass wool and asbestos rope. The reactor outlet is connected to water circulating glass condenser. The exit of the condenser is taken to a cold water condenser system maintained at 15 °C. Before setting of furnace temperature, N_2 gas is purged for about 10 min to drive away the air and to provide an inert atmosphere in the system. Then, pyrolysis peak temperature is set in the furnace. The pyrolysis process takes place and liberates vapors and gases. The gases and vapors coming out of the reactor pass through the series of condensers. As the dew point of bio-oil is close to 150 °C, almost all vapors get condensed

Table 2. Details of bench scale and main experimental setup

Bench scale slow pyrolysis setup	
Tubular furnace	Power rating: Single phase AC, 3 kW Dimensions: 410 (Length)*410 (Width)*310 (Height) mm Furnace Tube: 150 (Length)*80 (Diameter) mm Heating range: 1,000 °C
Reactor	SS tube Dimensions: 160 (L)*60 (H) mm
Condensers	Liebig glass condenser, Dimensions: 542 mm (L)*22 mm (D) 1 litre capacity of cold water
Combined slow pyrolysis and steam gasification setup	
Tubular furnace	Power rating: Single phase AC, 3 kW, Heating range: 1,200° Dimensions: 500 (Length)*500 (Width)*500 (Height) mm Furnace Tube: 350 (Length)*65 (Diameter) mm
Reactor	GI tube, Dimensions: 450 (Length)*25 (Height) mm
Condensers	Liebig glass condenser, Dimensions: 600 mm (Length)*20 mm (Diameter) 1 litre capacity of cold water
Gas collection system	Tedlar bags Capacity: 3 litre
Steamer	Power rating: Single phase, Steam output: up to 250 °C, Power: 3 kW, Steam pressure: 2 kg/cm ²

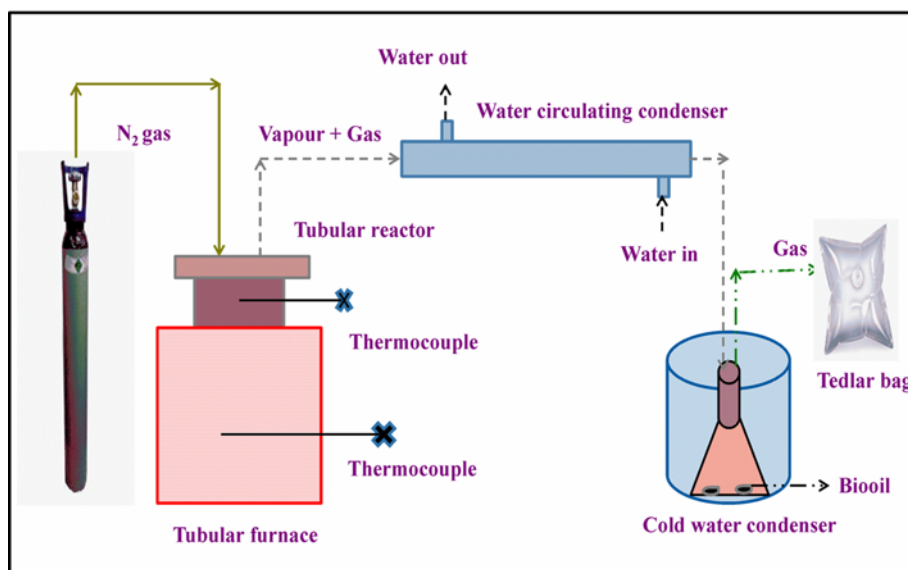


Fig. 1. Schematics of experimental setup.

and collected as bio-oil in the condensers. The gases leaving the condensers are let into the atmosphere. After 30 min of solid residence time, the reactor is taken out and allowed to cool to room temperature. Then, the char accumulated in the reactor is collected and quantified.

4. Combined Slow Pyrolysis and Steam Gasification Experiments

The schematic of the combined process setup is similar to the bench scale setup and is illustrated in Fig. 1. The only difference is the augmentation of steamer for supplying steam to carry out steam gasification and gas collection system for collecting product gas. The details of the accessories involved in the setup are presented in Table 2.

Slow pyrolysis of combined process is carried out at the same heating rate as that of bench scale study at the effective conditions (pyrolysis temperature and particle size) of char generation. After 30 min of solid retention time, gasification temperature is adjusted. The gasification process is carried out using steam at a temperature of 110 °C and pressure of 7 kg/cm². Once the gasification temperature is reached, steam is passed into the reactor closing the outlet of the reactor. Steam to char reaction time of 30 min is maintained throughout. After 30 min, the outlet of the reactor leading to condensers is opened. The gases after traversing through a series of condenser are collected in Tedlar bags. Two Tedlar bags of capacity 3 liters are employed to collect the gases of pyrolysis and gasification, respectively. To begin with, the study is done with varying gasification temperatures between 600-800 °C at an increment of 50 °C with constant S/B of 1. Then, the experimentation is carried at effective gasification temperature (temperature at which H₂ generation is highest) altering S/B between 1 to 6 (at an increment of 1) and effective S/B of H₂ generation is determined. Experiments are conducted repeatedly until consistent results are obtained. The standard deviation of product yield % (gas, liquid and char) was determined using Microsoft excel. The standard deviation of product yield % due to experimental errors was within ±2.3-13.4%.

5. Gas Analysis

The gas analysis (identification and quantification) is done using gas chromatograph. The details of the gas chromatograph are given in Table 3. Helium is preferred as carrier gases as it can determine H₂ composition accurately [34-36]. The MS5A and PQ are connected individually to the packed column. MS 5A can detect gases such as H₂, O₂, N₂, CH₄ and CO but not CO₂, while PQ detect gases

such as H₂, CO₂ and CH₄ but not CO [34]. Hence, the product gas (obtained from pyrolysis and gasification process) was passed into MS 5 A and then into PQ in batch separately. Before injecting the sample into the column, first MS5A mode is set. When MS5A is opted, the other column acts as a reference and vice versa. The sample is injected into MS5A and gases such as H₂, CH₄, and CO are detected. Then, PQ column is set. Here, the MS5A column acts as reference. The product gas is injected into PQ and gases such as H₂, CO₂ and CH₄ are detected. In this way, the presence of H₂, CO, CH₄, and CO₂ in the product gas mixture is identified. The quantification of the gas components is determined using single point external standard method [37]. The standard deviation on composition of gas components due to (GC) analysis error is within ±4.3-9.8%.

6. Individual Slow Pyrolysis and Steam Gasification Experiments

The performance of the combined process is compared to that of individual slow pyrolysis (only pyrolysis) and steam gasification (no prior pyrolysis) process. Slow pyrolysis is conducted at effective gasification temperature of H₂ generation (determined through combined process) and steam gasification is performed at effective gasification temperature and effective S/B of H₂ generation (determined from combined process).

RESULTS AND DISCUSSION

1. Results of Bench Scale Slow Pyrolysis

Though increase in pyrolysis temperature improves char quality with improved carbon content, it reduces the char yield [38]. Further, excess heat supplied results in wastage of energy. Conversely, low pyrolysis temperature produces more char, however with low carbon content. Hence, an effective temperature has to be looked upon to generate optimum generation of char. Despite the fact that small particles offer better heat and mass transfer within particles, with regard to char generation only coarser particles are advantageous [39]. Coarser particles favor char of better quality and quantity, which avoids energy being wasted in size reduction of feedstock.

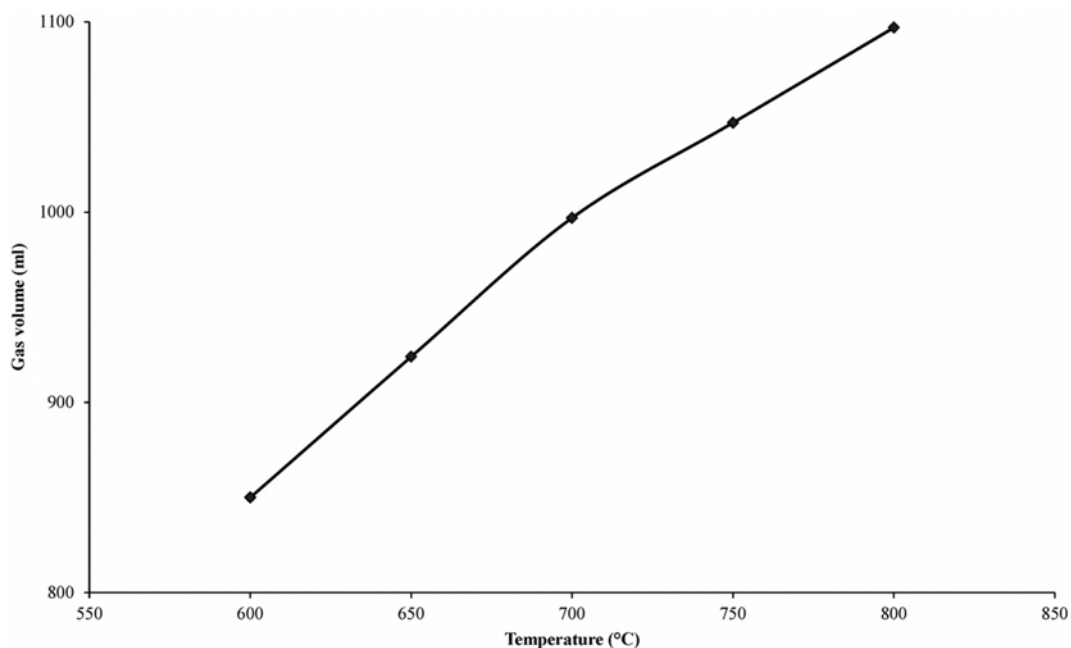
The results of the bench scale slow pyrolysis experiments are presented in Table 4. The effective temperature of char generation can be defined as the lowest temperature (between 300-550 °C) that generates reasonable char yield and produces char having carbon content of at least 75%. The effective particle size can be defined as

Table 3. Particulars of gas chromatograph

Make	ThermoFisher Scientific India Private Limited, Nasik, Maharashtra, India
Model	Trace GC 600
Carrier gas	Helium (99.995%) , 30 ml/min
Detector	Thermal conductivity detector (TCD)
Columns	Packed 1. Molecular sieve 5A (MS5A)- detects H ₂ , O ₂ , N ₂ , CO ₂ , CH ₄ , CO 2. Porapak Q (PQ)- detects H ₂ , Air, CO ₂ , CH ₄ , CO ₂
MS5A	Mesh size 80/100; Tubing-SS; Tube length-8 ft, Tube inner diameter-2.1 mm; Tube outer diameter-1/8 in, Maximum Temperature: 350 °C, Oven : 40 °C, Injector: 60 °C, Detector: 130 °C; Injection: Split less 250 µL direct
PQ	Mesh size 80/100; Tubing-SS; Tube length-8 ft, Tube inner diameter-2.1 mm; Tube outer diameter -1/8 in, Maximum Temperature: 250 °C, Oven : 40 °C, Injector: 60 °C, Detector: 130 °C; Injection: Splitless 250 µL direct
Quantification method	Single point external standard method

Table 4. Results of bench scale experiments

Parameters	Condition	Char quantity (% yield)	Char quality (% carbon) Ash free basis	Optimised value
Temperature @ Average particle size 315 μm	300 °C	37.60	68.61	Temperature @ 450 °C
	350 °C	35.27	69.69	
	400 °C	34.20	71.80	
	450 °C	32.73	75.27	
	500 °C	29.37	79.73	
	550 °C	28.73	82.53	
Particle size @ optimised temperature 450 °C	90 < D_p < 212 μ	31.07	70.44	Optimised particle size @ 500 < D_p < 850 μm
	212 < D_p < 355 μ	32.67	74.53	
	355 < D_p < 500 μ	33.53	75.07	
	500 < D_p < 850 μ	34.33	77.30	

**Fig. 2. Effect of temperature on overall gas volume in combined process.**

the largest particle size (between 90-850 μm) that generates considerable char yield and char with at least 75% carbon content.

The effective temperature for char generation is found to be 450 °C. The effective particle size for char generation is observed at 500 < D_p < 850 μm . At effective temperature and particle size, the yield of char is found to be 32.73% and carbon content of char is found to be 77.30%. The proximate analysis of the char at effective conditions (pyrolysis temperature: 450 °C, particle size: 500 < D_p < 850 μm) is as follows: Moisture content-1.98%; Volatile matter-34.65%; Fixed carbon-54.46%; Ash-8.91%. The elemental analysis results are as below: Carbon-77.30%, Hydrogen-0.45%; Nitrogen-0.54%; Oxygen-21.66 % and Sulfur-0.05%. The effective conditions (pyrolysis temperature 450 °C and particle size 500 < D_p < 850 μm) of char generation are employed in the combined process experimentation.

2. Results of Combined Slow Pyrolysis and Steam Gasification Experiments

The results of combined slow pyrolysis and steam gasification

are discussed here. The effect of temperature and S/B on overall gas volume and product gas composition in the combined process is also discussed in this section.

3. Effect of Temperature on Overall Gas Volume and Product Gas Composition

Fig. 2 shows the effect of temperature on overall gas volume. Generally, increase in temperature induces H_2 and CO generating reactions. Reactions such as water-gas, water-gas shift, steam methane reforming and tar cracking reactions are provoked with the increase in temperatures. Effective involvement of these reactions contributes for increase in the overall gaseous volume. Of the conducted temperature, highest gas volume is observed at 800 °C. Acharya et al. [40] observed a similar increase in gas volume with respect to temperature. It was asserted that high temperature facilitates enhanced conversion of char and tar which gets reflected in the gas generation.

The effect of temperature on product gas composition is illus-

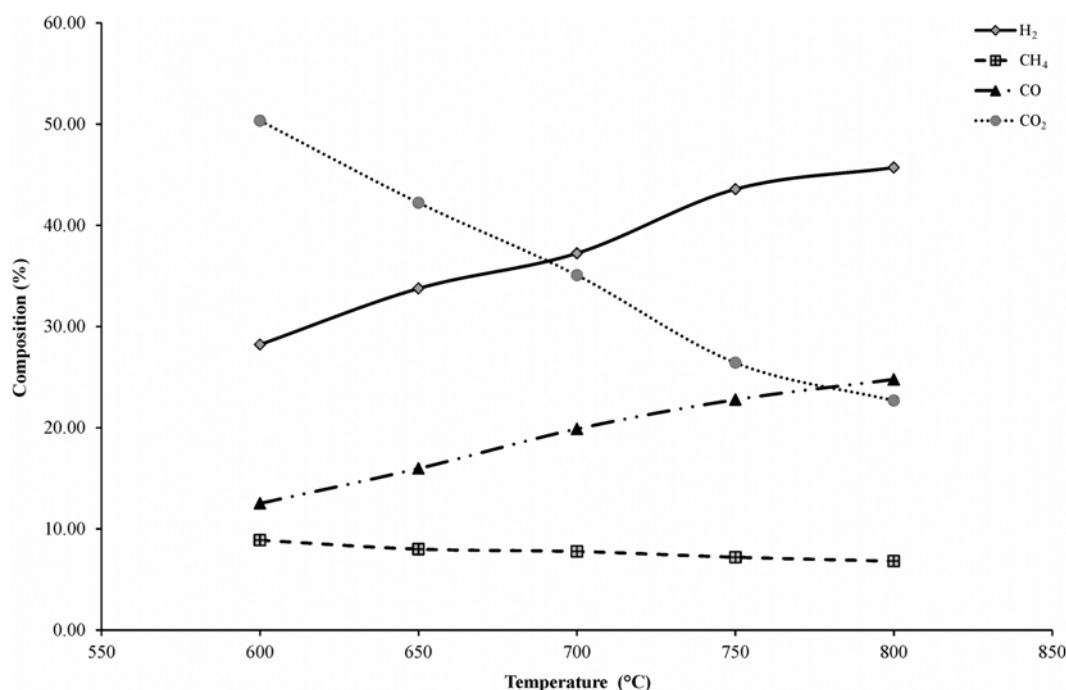


Fig. 3. Effect of temperature on product gas composition in combined process.

trated in Fig. 3. Gases such as H₂, CH₄, CO and CO₂ are identified during the process. With the increase in temperature, the composition of H₂ and CO follows an increasing trend, whereas composition of CH₄ and CO₂ takes a downward trend.

Increase in H₂ composition is due to H₂ liberating reactions such as water-gas, water-gas shift, steam methane reforming and tar cracking as these reactions are effective at high temperatures. From Fig. 3 a steep increase in H₂ composition between 700-800 °C can be observed. This indicates that reactions such as water-gas shift; steam reforming and tar cracking could have been dominant at these temperature range. Franco et al. [41] observed that reforming, tar cracking and water-gas shift reactions are dominant from 730-830 °C. However, beyond 830 °C reactions such as Boudouard and water-gas become dominant. When the temperature is increased, the CO₂ generated due to water-gas, steam methane reforming and tar cracking actively undergoes Boudouard reaction, resulting in generation of CO. Hence, CO₂ composition decreases as the temperature gets further close to 800 °C. The increase in CO composition is because of active involvement of water-gas and Boudouard reaction. The decrease in CH₄ composition is attributed to steam methane reaction as it is further cracked into H₂ and CO₂.

The generation of H₂ and CO is found to highest at 800 °C. The observed findings are in agreement with observations of Inayat et al. [42]. It was reported that increase in H₂ and CO with temperature is due to the combined effect of exothermic and reversible nature of water-gas shift reaction. Further, it was asserted that the endothermic nature of char gasification, Boudouard and methane reforming reactions is responsible for H₂ and CO increase. It was also observed that the exothermic conduct of water-gas and carbonation reactions is responsible for the decrease in CO₂ composition. Catalytic steam gasification study by Moghtaderi [43] also ob-

served similar product gas behavior as observed in this study. It was reported that the increase in H₂ composition was due to the reaction between CH₄ and steam. Wei et al. [23] performed steam gasification of biomass and observed an H₂ composition increase with respect to temperature. It was reported that increase in H₂ generation at higher temperature is due to secondary reactions occurring between heavier hydrocarbons and tars. Lv et al. [44] observed an increase in H₂ composition and a decrease in CH₄ composition with increase in temperature. It was reported that behavior of gas components is due to Le Chatelier's principle. The Le Chatelier principle states that reactants of an exothermic reaction are favored at higher temperatures, while the products of an endothermic reaction are favored at lower temperatures. Hence, during the steam methane reforming (endothermic) reactions, products CO and H₂ are favored generating undue H₂ at the expense of CH₄.

4. Effect of S/B on Overall Gas Volume and Product Gas Composition

The variation of gas volume with respect to S/B is illustrated in Fig. 4. The figure indicates that gas volume decreases when the S/B is increased. The observed decrease in gas volume to S/B is found to be consistent with the findings of Acharya et al. [40]. It was reasoned that the excess moisture existence due to steam addition would have reduced the reaction temperature. It was asserted that surplus steam proffers more negative effect than positive effect.

Fig. 5 illustrates the change in composition of H₂, CH₄, CO and CO₂ with respect to S/B. As the S/B is increased, H₂ and CO₂ show an increasing trend, while the CO and CH₄ follow a decreasing trend. Increase in H₂ and CO₂ composition is observed till S/B of 5. After S/B of 5, the curve trends of all the components reverse, i.e., the composition of H₂ and CO₂ starts to decrease, whereas the composition of CH₄ and CO begins to increase. This indicates effect

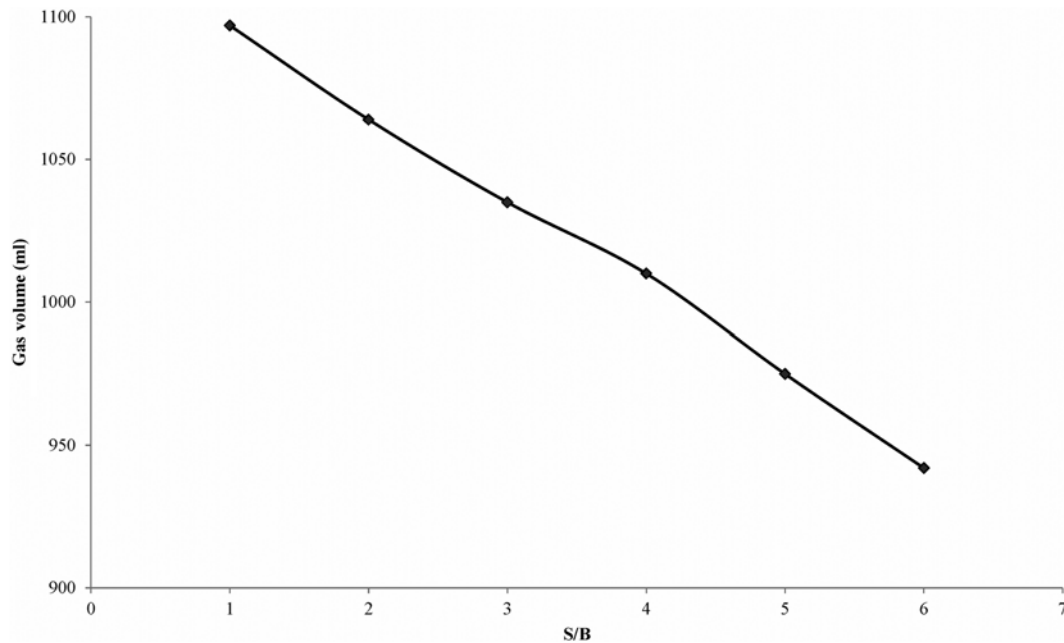


Fig. 4. Effect of S/B on overall gas volume in combined process.

of steam on product composition gets saturated after S/B of 5. The highest H_2 composition of 39.08% is observed at an S/B of 5.

The initial increase in H_2 and CO_2 is due to the stimulation of all steam involved reactions such as water-gas, water-gas shift, steam methane and tar cracking [45]. Steam reacts with carbon to generate CO , H_2 , CH_4 and CO_2 . It also reacts with CO , CH_4 to generate H_2 and CO_2 . Thus, the addition of steam increases the generation of H_2 and CO_2 . Although adding up of steam generates CH_4 and CO , it eventually yields H_2 and CO_2 generation as CH_4 and CO

undergoes further decomposition. Therefore, with the addition of steam an increase in composition of H_2 and CO_2 is observed; conversely, a decrease in composition of CO and CH_4 is noticed.

Inayat et al. [42] confirmed that increase in S/B increases H_2 and CO_2 composition while decreasing CO and CH_4 composition. They reported that reactions such as methane reforming and water-gas shift are greatly influenced by steam addition. It was asserted that at high S/B, maximum H_2 composition could be obtained. Alaudin et al. [46] observed that S/B of 1.35-4.04 was the effective S/B

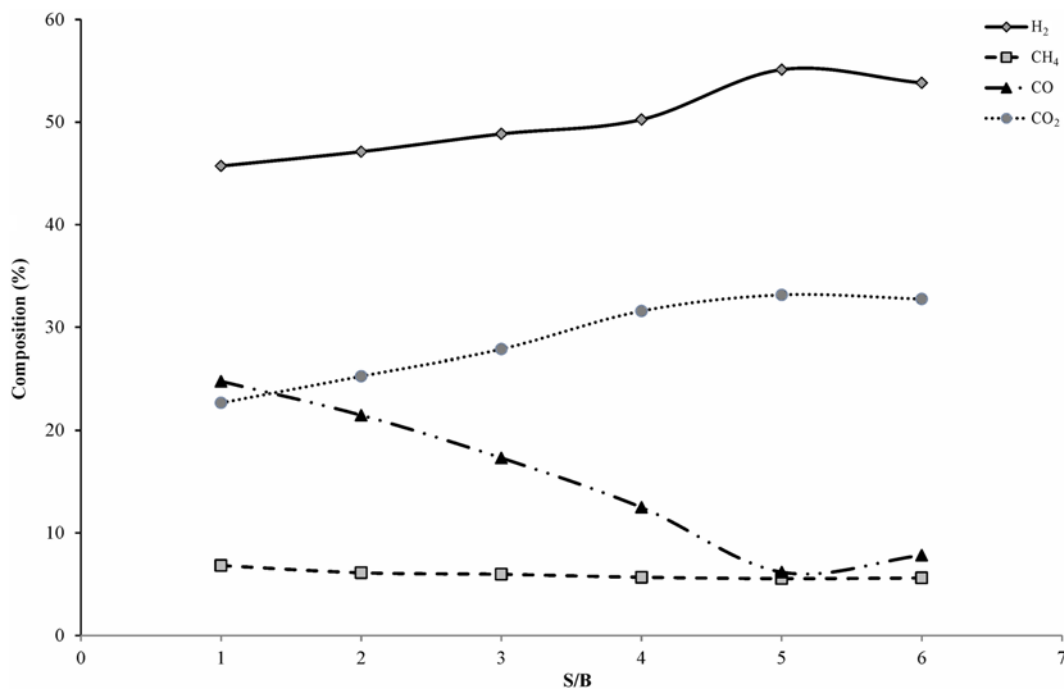


Fig. 5. Effect of S/B on product gas composition in combined process.

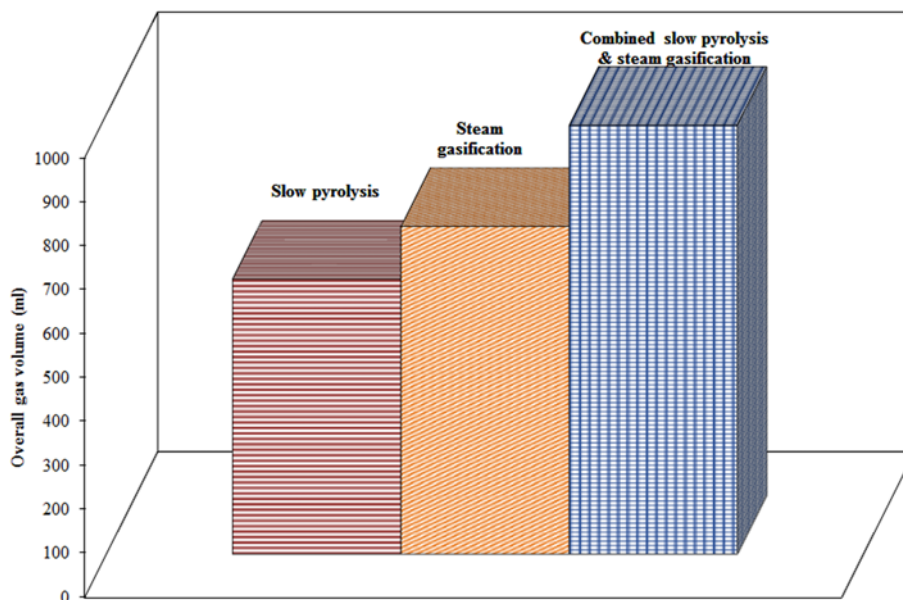


Fig. 6. Comparison of overall gas volume of processes.

range to generate rich H_2 and CO_2 . This S/B range is recommended to generate CO , CH_4 and C_2H_2 at a reduced level. They reported that in the above mentioned S/B range, steam reforming reactions are more effective and pave the way for the improved composition of H_2 and CO_2 .

Fig. 5 shows that after S/B of 5, gas components' response with respect to steam addition changes. This reversing behavior of gas components after optimum addition of steam is explained here. Though steam favors water-gas, water-gas shift and steam methane reforming reactions, undue moisture in the steam lowers the prevailing temperature in the reactor, thereby reducing the overall gas volume of the process. When steam more than optimum level is supplied, the excess steam do not take part in gasification reactions, as char particles have already engaged in gasification reactions (no free carbon particles) [47]. Instead, the excess steam takes up the heat from the reactor surrounding to get heated up, thereby reducing the reactor temperature. It is because of the reduction in reactor temperature; gasification reactions such as water-gas, water-gas shift, steam methane reforming, tar cracking and Boudouard which are dominant at high temperatures are affected. Hence, a decrease in gas volume is observed when excess steam is supplied.

Li et al. [48] conducted steam gasification varying S/B from 0 to 2.67. With an increase in S/B from 0 to 1.33, an increase in H_2 composition was obtained. Nonetheless, when the S/B was further increased from 1.33 to 2.67, a decrease in H_2 composition was observed. They inferred that additional steam supplied after S/B of 1.33 reduced the reactor temperature leading to decreased H_2 generation. Due to more steam reforming reactions in the initial stage, a reduction in CO , CH_4 and C_2 hydrocarbon was noted. Nevertheless, the excess addition of steam after an optimum level reduced the occurrence of steam reforming reactions, thereby yielding more CO and CH_4 . It was recommended to utilize S/B to an optimal level taking into account various operating conditions. Wei et al. [23] also observed that increase in S/B from 0.0 to 0.6 improved

H_2 and CO_2 composition while reducing CO and CH_4 composition. However, further increase from 0.2 to 0.6 produced a little significance in altering the product gas composition.

The observed findings indicate that low S/B produces less H_2 generation. Though increase in S/B increases H_2 generation, excess introduction of steam leads to reduced H_2 generation. Hence to obtain maximum H_2 yield, an effective S/B is important.

5. Performance Evaluation of Combined Process

The results of the combined process at varying gasification temperatures and S/B indicate that H_2 composition is highest at $800^\circ C$ and S/B of 5. To assess the performance of the combined process, an individual slow pyrolysis process at $800^\circ C$ (pyrolysis temperature) and steam gasification at $800^\circ C$ (gasification temperature) with S/B of 5 is conducted.

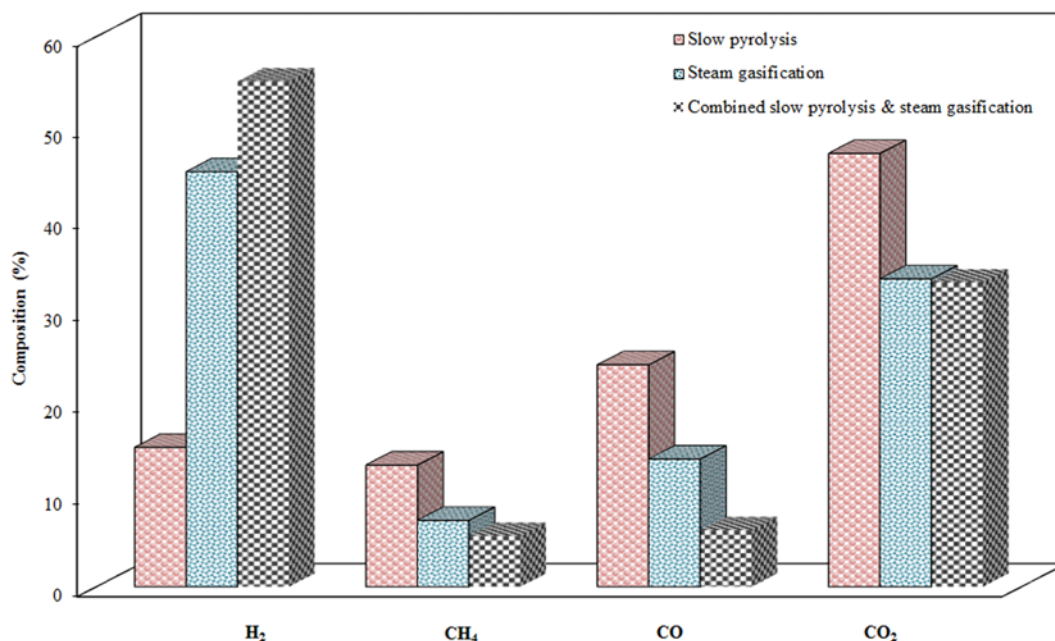
The overall gas volume of slow pyrolysis, steam gasification and combined process is compared as illustrated in Fig. 6. It is evident that the combined process has generated the maximum gas volume, followed by steam gasification and slow pyrolysis. This indicates that decomposition of biomass into gaseous products is very effective in the combined process than individual steam gasification and slow pyrolysis. The combined process produced 35.90% and 23.60% more gas volume (overall) than slow pyrolysis and steam gasification process, respectively.

The volume of gas generated per unit of biomass is presented in Table 5. The combined process generated 59.53% and 31.05% more H_2 per unit of biomass than slow pyrolysis and steam gasification respectively.

The product gas composition of slow pyrolysis, steam gasification and combined process is presented in Fig. 7. The bar chart indicates that combined process produces more H_2 than steam gasification and slow pyrolysis process. However, the combined process has generated the lowest CH_4 , CO and CO_2 composition than the other two processes. This indicates that the combined process favors H_2 generation. With respect to H_2 composition the combined

Table 5. The volume of gas generated per unit of biomass

Method	Volume of gas generated (ml)	Volume of gas generated (Nm ³)	Dry gas yield/kg of biomass (Nm ³ /kg)	Total heating value of generated gas (kJ)	g of H ₂ /kg of biomass
Slow pyrolysis	625	0.00063	0.125	5.9148	4.1685
Steam gasification	745	0.00075	0.149	6.8856	7.1011
Combined slow pyrolysis and steam gasification	975	0.00098	0.195	8.5010	10.2996

**Fig. 7. Comparison of product gas composition of processes.**

process generated 72.37% more than slow pyrolysis and 17.91% more than steam gasification. Nippattumakul et al. [49] conducted a similar study by comparing the gas composition of pyrolysis and steam gasification. Similar to the current work, they also noticed higher H₂ and lower CH₄, CO composition for steam gasification.

Table 6 compares the findings of the current study to earlier studies [50-53].

The performance of conversion processes is influenced by many factors, such as feedstock type, type of reactor, reactor configuration, type of bed materials, heating rate, steam to biomass ratio, steam temperature, catalyst, and sorbent. Hence, the H₂ composition obtained from the current study may not be consistent with the findings of earlier literatures. It can be observed from the Table that steam gasification yields more H₂ than slow pyrolysis. It can

Table 6. Comparison of the finding of current study to earlier studies

Method	Feedstock	Gasification temperature (°C)	S/B	Reported H ₂ (composition %)	Reference
Slow pyrolysis	Pomegranate seeds	800	No steam addition	1.57	[50]
Steam gasification	Legume straw	800	0.6	≈40.00	[23]
Steam gasification	Biomass char (fast pyrolysis liquefaction of pine saw dust)	850	0.357	45.70	[51]
Steam gasification	Almond shells	820	1	≈48.00	[52]
Steam gasification	Waste tyre	1000	2	≈60.00	[53]
Slow pyrolysis	Sugarcane bagasse	800	No steam addition	15.23	Current study
Steam gasification	Sugarcane bagasse	800	5	45.25	Current study
Combined slow pyrolysis and steam gasification	Sugarcane bagasse	800	5	55.12	Current study

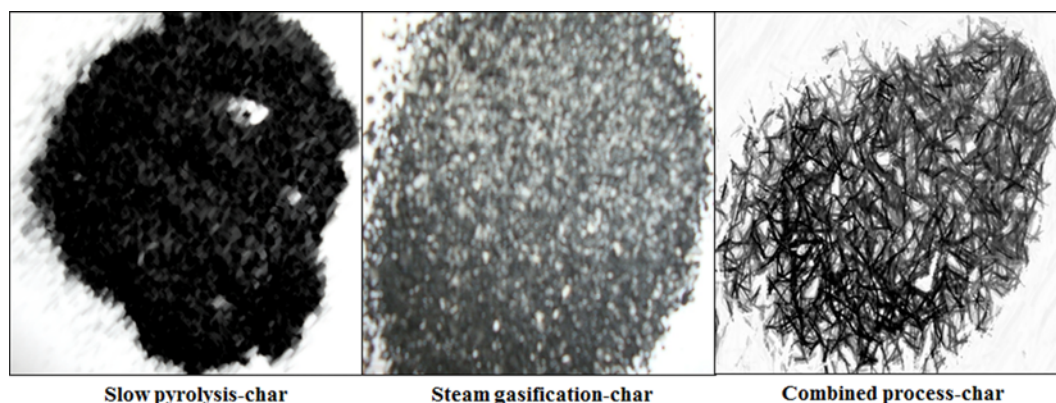


Fig. 8. Snapshot of solid residues of processes.

also be inferred that the combined process recovers more H_2 than steam gasification.

Photographs of solid residues obtained from slow pyrolysis, steam gasification and combined process are presented in Fig. 8. The solid residue of slow pyrolysis is black, indicating the presence of more carbon particles. Steam gasification solid residue is predominantly black with a tinge of grey particles. The solid residue of integrated process is almost grey with a tinge of black. The solid residue of slow pyrolysis, steam gasification and combined process is found to be 26.75%, 19.50% and 13.50%, respectively, indicating that biomass decomposition is effective in the combined process.

CONCLUSION

The combined slow pyrolysis and steam gasification of sugarcane bagasse was conducted. The effect of temperature and S/B on overall gas volume and product gas composition was investigated. The performance of the combined process was also compared with individual slow pyrolysis and steam gasification process. The observed findings are stated below.

- ▶ Increase in temperature improved overall gas volume of the combined process. The overall gas volume of combined process is maximum at 800 °C, the highest gasification temperature.

- ▶ Increase in temperature increased H_2 and CO composition and at the same time decreased CH_4 and CO_2 composition. H_2 composition was found to be maximum at 800 °C, the highest gasification temperature.

- ▶ Increment in S/B reduced the overall gas volume.

- ▶ Initially, the increase in S/B improved H_2 and CO_2 composition; however, it lowered CH_4 and CO composition.

- ▶ Addition of steam beyond an optimum level reversed the gas components behavior, *i.e.*, composition of H_2 and CO_2 decreased while composition of CH_4 and CO increased.

- ▶ The effective temperature and S/B for generating H_2 was 800 and 5, respectively.

- ▶ The combined process produced 35.90% and 23.60% more gas volume (overall) than slow pyrolysis and steam gasification process, respectively.

- ▶ Also, the combined process generated 72.37% and 17.91% more H_2 composition than individual slow pyrolysis and steam gas-

ification, respectively.

ACKNOWLEDGEMENT

The authors wish to thank DST, India for the financial support for this study under the grant no. SR/FTP/ETA-69/2009.

NOMENCLATURE

AC : alternating current
 ASTM : american society for testing and materials
 D_p : mean particle diameter [μm]
 GC : gas chromatograph
 GI : galvanized iron
 MS : molecular sieve
 MT : million tons
 PQ : porapaq
 S/B : steam to biomass ratio
 SS : stainless steel
 TCD : thermal conductivity detector

REFERENCES

1. M. F. Hordessi, *Alternative fuels: The future of hydrogen*, Second. Lilburn, GA, USA, The Fairmont Press, Inc. (2008).
2. S. M. Raj, S. Talluri and L. P. Christopher, *BioEnergy Res.*, **5**(2), 515 (2012).
3. S. Su, W. Li, Z. Bai, H. Xiang and J. Bai, *Int. J. Hydrogen Energy*, **35**(10), 4459 (2010).
4. S. Sun, Y. Zhao, F. Su and F. Ling, *Korean J. Chem. Eng.*, **26**(2), 528 (2009).
5. M. K. Cohce, I. Dincer and M. A. Rosen, *Int. J. Hydrogen Energy*, **35**(10), 4970 (2010).
6. P. Kuchonthara, B. Puttasawat, P. Piumsomboon, L. Mekasut and T. Vitidsant, *Korean J. Chem. Eng.*, **29**(11), 1525 (2012).
7. M.-J. Jeon, S. J. Choi, K.-S. Yoo, C. Ryu, S. H. Park, J. M. Lee, J.-K. Jeon, Y.-K. Park and S. Kim, *Korean J. Chem. Eng.*, **28**(2), 497 (2011).
8. Z. M. A. Bundhoo, A. Mudhoo and R. Mohee, *J. Environ. Sci. Sustain.*, **1**(1), 1 (2013).
9. M. Balat, *Energy Sources, Part A Recover. Util. Environ. Eff.*, **33**(7),

- 674 (2011).
10. Y. Lu, L. Guo, X. Zhang and C. Ji, *Int. J. Hydrogen Energy*, **37**(4), 3177 (2012).
 11. P. Parthasarathy and K. N. Sheeba, *Int. J. Energy Res.*, **39**(2), 147 (2015).
 12. S. Wang, High-efficiency Separation of Bio-oil, in *Biomass now-Sustainable growth and use*, M. D. Matovic, Ed. Intech Open-Access Publisher, 401 (2013).
 13. S. Czernik and A. V Bridgwater, *Energy Fuels*, **18**(12), 590 (2004).
 14. S. Wang, Y. Gu, Q. Liu, Y. Yao, Z. Guo, Z. Luo and K. Cen, *Fuel Process. Technol.*, **90**(5), 738 (2009).
 15. S. Wang, X. Li, F. Zhang, Q. Cai, Y. Wang and Z. Luo, *Int. J. Hydrogen Energy*, **38**(36), 16038 (2013).
 16. T.-H. Kwak, S. Lee, J.-W. Park, S. Maken, Y. D. Yoo and S.-H. Lee, *Korean J. Chem. Eng.*, **23**(6), 954 (2006).
 17. A. P. Eren, E. Onal, B. B. Uzun and N. Ozbay, *Ind. Crops Prod.*, **26**, 307 (2007).
 18. C. Fushimi, T. Wada and A. Tsutsumi, *Biomass Bioenergy*, **35**(1), 179 (2010).
 19. M. K. Ko, W. Lee, S. Kim, K. Lee and H. Chun, *Korean J. Chem. Eng.*, **18**(6), 961 (2001).
 20. K. Chaiwong, T. Kiatsirirot, N. Vorayos and C. Thararax, *Maejo Int. J. Sci. Technol.*, **6**(2), 186 (2012).
 21. L. Fagernas, E. Kuoppala, K. Tiilikkala and A. Oasmaa, *Energy Fuels*, **26**, 1275 (2012).
 22. K. Umeki, Y. Son, T. Namioka and K. Yoshikawa, *J. Environ. Eng.*, **4**(1), 211 (2009).
 23. L. Wei, S. Xu, L. Zhang, C. Liu, H. Zhu and S. Liu, *Int. J. Hydrogen Energy*, **32**, 24 (2006).
 24. S. T. Chaudhari, A. K. Dalai and N. N. Bakhshi, *Energy Fuels*, **17**, 1062 (2003).
 25. S. T. Chaudhari, S. K. Bej, N. N. Bakhshi and A. K. Dalai, *Energy Fuels*, **15**, 736 (2001).
 26. S. Lv, Q. Yu, X. Zhuang, Z. Yuan, W. Wang, Q. Wang, W. Qi and X. Tan, *BioEnergy Res.*, **6**, 1128 (2013).
 27. A. Aradhey, India Sugar Annual 2012, 2012. [Online]. Available: [http://gain.fas.usda.gov/Recent GAIN Publications/Sugar Annual New Delhi India_4-19-2012.pdf](http://gain.fas.usda.gov/Recent%20GAIN%20Publications/Sugar%20Annual%20New%20Delhi%20India_4-19-2012.pdf).
 28. S. E. Lingle and J. L. Thomson, *BioEnergy Res.*, **5**, 168 (2012).
 29. A. P. De Souza, A. Grandis, D. C. C. Leite and M. S. Buckeridge, *BioEnergy Res.*, **7**, 24 (2014).
 30. Energy statistics 2013, *Central Statistics Office. National Statistical Organisation. Ministry of Statistics and Programme Implementation*, 2013. [Online]. Available: http://mospi.nic.in/mospi_new/upload/Energy_Statistics_2013.pdf. [Accessed: 04-Aug-2013].
 31. L. Lin, R. Yan, Y. Liu and W. Jiang, *Bioresour. Technol.*, **101**(21), 8217 (2010).
 32. A. K. Bledzki, A. A. Mamun and J. Volk, *Compos. Part A*, **41**(4), 480 (2010).
 33. M. Carrier, T. Hugo, J. Gorgens and H. Knoetze, *J. Anal. Appl. Pyrolysis*, **90**(1), 18 (2011).
 34. ASTM D 1946-90. Standard practice for analysis of reformed gas by gas chromatography.
 35. GC data sheet. Shimadzu Gas Chromatograph. Analysis of Inert Inorganic Gases (2010).
 36. Packed Column GC Application Guide-Supelco Bulletin 890A.
 37. Validation of Chromatographic Methods-Reviewer Guidance-Centre for drug evaluation and research (CDER) (1994).
 38. A. Demirbas, *Fuel Process. Technol.*, **88**, 591 (2007).
 39. P. Weerachanchai, C. Tangsathitkulchai and M. Tangsathitkulchai, *Korean J. Chem. Eng.*, **28**(12), 2262 (2011).
 40. B. Acharya, A. Dutta and P. Basu, *Int. J. Hydrogen Energy*, **35**(4), 1582 (2010).
 41. C. Franco, F. Pinto, I. Gulyurtlu and I. Cabrita, *Fuel*, **82**, 835 (2003).
 42. A. Inayat, M. M. Ahmad, S. Yusup, M. Ibrahim and A. Mutalib, *Energies*, **3**, 1472 (2010).
 43. B. Moghtaderi, *Fuel*, **86**(15), 2422 (2007).
 44. P. M. Lv, Z. H. Xiong, J. Chang, C. Z. Wu, Y. Chen and J. X. Zhu, *Bioresour. Technol.*, **95**(1), 95 (2004).
 45. A. Khor, C. Ryu, Y. Yang, V. N. Sharifi and J. Swithenbank, Clean Hydrogen Production via Novel Steam-Air Gasification of Biomass, in *Proceedings of the 16th World Hydrogen Energy Conference (WHEC)*, 1 (2006).
 46. Z. A. B. Z. Alauddin, P. Lahijani, M. Mohammadi and A. R. Mohamed, *Renew. Sustain. Energy Rev.*, **14**(9), 2852 (2010).
 47. N. Gao, A. Li and C. Quan, *Bioresour. Technol.*, **100**(18), 4271 (2009).
 48. J. Li, Y. Yin, X. Zhang, J. Liu and R. Yan, *Int. J. Hydrogen Energy*, **34**(22), 9108 (2009).
 49. N. Nipattummakul, I. I. Ahmed, S. Kerdsuwan and A. K. Gupta, *Int. J. Hydrogen Energy*, **35**(21), 11738 (2010).
 50. S. Uçar and S. Karagöz, *J. Anal. Appl. Pyrolysis*, **84**(2), 151 (2009).
 51. F. Yan, S. Luo, Z. Hu, B. Xiao and G. Cheng, *Bioresour. Technol.*, **101**(14), 5633 (2010).
 52. S. Rapagna, *Biomass Bioenergy*, **19**, 187 (2000).
 53. S. Portofino, A. Donatelli, P. Iovane, C. Innella, R. Civita, M. Martino, D. A. Matera, A. Russo, G. Cornacchia and S. Galvagno, *Waste Manag.*, **33**(3), 672 (2013).