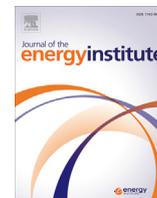




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Gasification of sugarcane bagasse in supercritical water; evaluation of alkali catalysts for maximum hydrogen production



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ABSTRACT

Sugarcane bagasse is one of the major resources of agricultural wastes in the Khuzestan Province of Iran. With the aim of maximum hydrogen production, supercritical water gasification of lignocellulosic feedstock was studied in a batch reactor at the constant pressure of 25 MPa. The effect of catalyst (five different alkali salts, Raney nickel, and activated carbon) and reaction temperature (400–800 °C) on gas yield and composition, gas heating value, carbon gasification efficiency (CGE), and hydrogen gasification efficiency (HGE) was investigated. An increase in reaction temperature led to significant improvement in hydrogen yield. The highest amount of hydrogen (75.6 mol kg⁻¹) was achieved at 800 °C with the presence of KOH as catalyst where the complete gasification of bagasse took place. The annual potential of hydrogen production in the Khuzestan Province of Iran was roughly estimated to be 470 millions of Nm³ and this calculation showed that this figure is capable of substituting the need of 6550 ha of sugarcane farms to chemical fertilizer.

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1. Introduction

Energy and environment protection are expected to remain two of the main challenges of the human life for the long-term future. Agricultural wastes have a great potential for energy production because of their non-food nature and renewability [1]. Sugarcane bagasse is an abundant source of lignocellulose [2]. Bagasse is the solid residue remaining after the process of juice extraction from sugarcane for sugar or ethanol production. Crushing of every 3 kg of sugarcane in sugar mills produces 1 kg of bagasse [3]. Currently, it is mainly used for combustion to produce heat and power required for the related sugar and ethanol factories [3] whilst it is known that with the technological improvements it is possible to supply the energy requirements of the plants with only half of the produced bagasse [4]. In Iran however, from the total annual production of 0.84 million tons of bagasse, only a small portion is being used for paper and medium-density fiberboard (MDF) production and the rest is usually disposed and causes environmental problems such as spontaneously ignition [5].

Conversion of biomass to fuel gases can reduce environmental issues [6] and progress its utilization [7]. Compared with conventional thermal gasification, supercritical water gasification (SCWG) is characterized by its high reaction efficiency and H₂ selectivity [8]. This technology benefits from the specific properties of water at supercritical conditions. With the operating temperature and pressure greater than its critical point (374 °C and 22.1 MPa for water) a fluid is termed as a supercritical fluid [9]. The density of water, above the critical point (0.2–0.7 g cm⁻³), is much lower than that at normal conditions and hydrogen bonds of water molecules are considerably weakened. The lower density leads to a decrease of the dielectric constant from 78 at normal conditions to the range of 2–20. This changes the water from a

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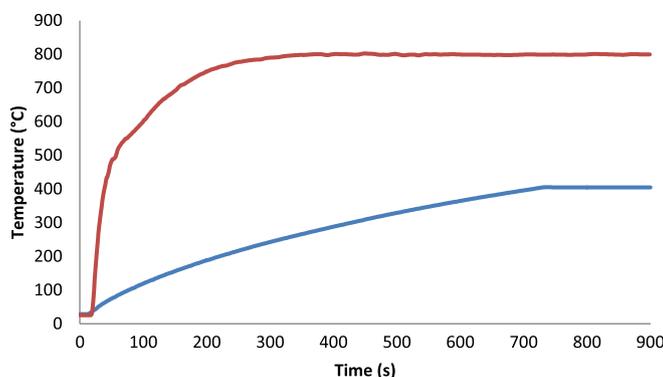


Fig. 1. A typical variation of the reactor temperature with time; red curve: GC oven, blue curve: electrical oven. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

highly polar solvent at an ambient condition to a non-polar solvent, like benzene, in a supercritical condition [10]. Such conditions enhance the solubility of organic substances and depress unwanted polymerization processes [11–14]. In addition, heat transfer is fast and the water molecule is still reactive which both supports fast reaction of the solved molecules [7]. Compared to conventional gasification, SWG is relatively efficient with no additional energy requirement for biomass drying. Lignocellulose biomass components can break down into simple molecules during SCWG to produce synthesis gas [9]. A variety of biomasses including lignocellulosic biomass from different sources such as manure [15–17], sewage sludge [18–20], food wastes [21], algae [22–24], and biorefinery residue [24] have been successfully gasified in SCW.

High moisture content of sugarcane bagasse makes it suitable for conversion in SCW [1] however, only a few reports on the treatment of sugarcane bagasse are available. Osada and his co-workers studied the effect of ruthenium catalyst on the gasification of bagasse at 400 °C and compared the results with those of cellulose and lignin [25]. They reported that without a catalyst, only 11.9% of bagasse converted to the gas. Barati and co-workers investigated the use of un-promoted and zinc promoted Ru/ γ -Al₂O₃ nanocatalysts on hydrogen yield from bagasse. They reported that the maximum hydrogen yield in their experiments was 15.6 mol kg⁻¹ [26].

Generally, there is a lack of knowledge about the role of alkali catalyst on gas yield from sugarcane bagasse. Moreover, the potential of hydrogen production from sugarcane bagasse in supercritical is unknown. We previously reported the effect of reaction time (RT) and pressure on gas yield and composition of sugarcane bagasse [27]. We also studied the SCWG of sugarcane bagasse in the present of some alkali catalysts (K₂CO₃, KHCO₃, NaHCO₃ and NaOH) in the reaction time of 45 min and pressure of 25 MPa at 400 °C [28].

In the present project, we designed a simple 3 stage framework in order to explore the highest possible hydrogen yield from supercritical water gasification of sugarcane bagasse. In this framework different alkali catalysts (KOH, NaOH, K₂CO₃, KHCO₃, NaHCO₃), Raney Nickel and activated carbon were applied. The effect of temperature on gas yield and composition was also investigated.

2. Experimental

2.1. Raw material

Sugarcane bagasse was obtained from a sugar mill of Debal Khazae Agricultural and Industrial Company in the Khuzestan Province of Iran. All experimental studies were performed in the laboratories of IKFT¹ at Karlsruhe Institute of Technology (KIT), Germany. The bagasse was milled and sieved to make the particle size of less than 180 μ m. The K₂CO₃, KHCO₃, Na₂CO₃, KOH and Raney Nickel were purchased from Merck Company (Darmstadt, Germany). The NaOH and activated carbon were purchased from VWR International Ltd. (UK) and applied in the amount of feed to catalyst (F/C) of 2. This amount of catalyst was chosen based upon literature [29–32].

2.2. Experimental procedure

The experiments were done in two batch autoclave reactors made of SS316 (for 400 °C) and Inconel alloy 625 (for the temperatures more than 500 °C) with the inner diameter of 11.5 mm and outer diameter of 13 mm and a volume of 5 ml. Before each experiment, the reactor was cleaned thoroughly with acetone to remove any residuals from the prior experiments [15]. The next step was to feed the reactor a mixture of sugarcane bagasse, water, and catalyst. Feedstock was prepared by bagasse powder loading of 9 wt%. In the experiments where a catalyst was applied, the mass ratio of 2:1 of F/C was taken into account. An exception was the case of a co-loading of Raney Nickel and K₂CO₃ where the amount of each catalyst was only half. For the experiments at the temperature of more than 400 °C, the feeding weight was decreased proportionally to keep the pressure constant at 25 MPa according to the steam table [33]. The heating source for the later experiments was an electrical oven while a gas chromatograph (GC) oven was used for the experiments at 400 °C. The typical temperature kinetics of the inside of the reactor in either of the ovens is shown in Fig. 1. The given reaction time does not include the heating up period.

After the certain reaction time, the reactor was cooled down rapidly by putting it into an ice-water bath. The reactor was then opened and the gas was quantified volumetrically. The gas was sampled by a 100 μ l syringe and injected into the GC. This was replicated for 3 times and the average was reported. Further details on experimental set up could be found elsewhere [28].

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2.3. Analytical procedure

Gaseous products were analyzed by two gas chromatographs; One GC specifically for hydrogen detection and the other for CO₂, CO, CH₄ and other hydrocarbons. The details for the two GC's could be found in [28,34].

Carbon gasification efficiency (CGE) and hydrogen gasification efficiency (HE) were defined according to the Formula (1) and (2);

$$\text{CGE}(\%) = (\text{Carboningasphase}/\text{carboninfeedstock}) \times 100 \quad (1)$$

$$\text{HGE}(\%) = (\text{Hydrogeningasphase}/\text{hydrogeninfeedstock}) \times 100 \quad (2)$$

The amount of carbon and hydrogen in the feedstock was calculated based upon ultimate analysis.

2.4. Three steps framework

At the first step, the effect of five alkali salts, Raney nickel, and activated carbon on gas yield and composition, carbon gasification efficiency and hydrogen gasification efficiency were investigated at 400 °C and 25 MPa and 75 min reaction time.

All data from this stage were subjected to analysis of variance (ANOVA) using SAS software (SAS Institute 2002). This technique was used to test the hypothesis that significant variation existed between different catalysts in the favor of hydrogen yield ($p < 0.01$). Actually, this stage determined the most effective catalyst in the favor of hydrogen. The identified catalyst was used to progress the work in the second and third stage where 8 different experiments were done separately (four experiments with the present of the identified catalyst and other without any catalyst). Temperatures of 500, 600, 700 and 800 °C were also tested. All these experiments had the same reaction time of 15 min and the same pressure of 25 MPa.

3. Results and discussions

The composition of sugarcane bagasse was 25.7% lignin, 46.6% cellulose, and 27.9% hemicelluloses and its elementary composition was 46.4% C, 5.69% H, <1% N, and 0.09% N.

The effect of catalyst on gas yield and composition is summarized in Table 1. The hydrogen yield with catalyst is higher than the case of without catalyst; therefore every catalyst seems to catalyze the gasification. In all experiments with the present of catalyst, there was not any trace of the CO while in the absence of catalyst, the fraction of CO was as high as 6.5 percent. Without catalyst, CO can be formed as a primary product of decarbonylation of aldehydes as confirmed by [35]. As a consequence of the high water content and in the presence of a catalyst, the water-gas shift reaction (Equation (3)) leads to very low CO content in the gas.



3.1. Effect of heterogeneous catalysts on gas yield and CGE

3.1.1. Raney nickel

Raney nickel which was applied in the experiment was a commercially available slurry grade and used without further treatment. The slurry contained 50 wt% of water and 50 wt% of solid catalyst. As was expected from the literature, Raney nickel directed the reactions to methane formation so as 10.11 mol kg⁻¹ of methane was produced [36,37]. Raney nickel has a strong ability in C–C breaking [38] which results in high carbon conversion. According to [29] before biomass can be gasified using a heterogeneous catalyst, it must be decomposed into smaller molecules. Only small molecules can access the catalytically active sites. Based on the report of [39] on a nickel catalyst, the small molecules such as carboxylic acids (acetic, formic, and levulinic), aldehydes (acetaldehyde, furfural, and formaldehyde), alcohols (ethanol and methanol), and ketones (acetone) can be reformed efficiently to CO₂, CO, H₂, and CH₄. Yu [40,41] proposed that acetic and formic acid decarboxylate directly to form CH₄, CO₂, and H₂ through the following equations;



Table 1
Mean comparisons of produced gas component under the effect of various catalysts.

Catalyst	Produced gas component mol kg ⁻¹			Carbon dioxide in gas + maximum carbon dioxide fixed by the catalyst
	Carbon dioxide	Hydrogen	Methane	
No catalyst	0.6 ^c	0.36 ^f	5.8 ^d	–
Raney-Ni	10.1 ^a	1.3 ^e	10.4 ^{abc}	–
KHCO ₃	0.45 ^c	5.3 ^b	12.1 ^{ab}	12.1
K ₂ CO ₃	0.39 ^c	5.6 ^b	7.6 ^{cd}	14.8
Raney-Ni + K ₂ CO ₃	5.1 ^b	4.8 ^c	11.7 ^a	18.9
NaHCO ₃	0.37 ^c	4 ^c	10.1 ^{abc}	10.1
KOH	0.45 ^c	6.6 ^a	5.5 ^{cd}	23.4
NaOH	0.39 ^c	5.6 ^b	0.3 ^e	25.3
Activated carbon	0.43 ^c	2.6 ^d	8.7 ^{bdc}	–

Means within each column of each section followed by the same letter are not significantly different ($p \leq 0.01$)

In addition, Nickel is an effective hydrogenation catalyst. It decomposes biomass to primary CO and H₂ which their reaction can form CH₄:



During methanation (Equation (6)), surface reactions of CO and H₂ lead to the hydrogenation of dissociated or molecular carbon monoxide. The rate of methanation depends directly on the hydrogen partial pressure [35] therefore, hydrogenation of carbon monoxide is a strongly inhibited reaction from a kinetics point of view. Only in the presence of an efficient hydrogenation catalyst the rather high CH₄ content in gas phase, as predicted by thermodynamics at this temperature [22,42], can be reached.

As could be estimated from Fig. 2, in the presence of this catalyst, CGE is higher than that of others, but not very high per se (only 53.1%). At similar conditions ($F/C = 2$, $T = 400$ °C, $P = 30$ MPa and Solid content = 10%), Waldner and Vogel reported complete gasification of wood with Raney nickel as catalyst [29]. Whereas the fraction of C, N and H in wood and sugarcane bagasse is almost the same, a reason of the lower conversion in the case of bagasse could be due to the high amount of sulfur in bagasse (0.09%) which is 4.5 times more than that of wood. It has previously been confirmed that sulfur has a poisoning effect in SCWG [43].

3.1.2. Effect of activated carbon

As could be found from Table 1, in contrast with Raney nickel, the effect of activated carbon on CH₄ and CO₂ yield was not significant. This catalyst improved the hydrogen yield but not as much as alkali ones. Generally, it seems that activated carbon did not improve the gasification. Yamaguchi and co-workers [44] reported that in low temperature SCW, activated carbon cannot enhance the rate of gasification. Although activated carbon is known to be the best heterogeneous catalyst for high temperature SCW in terms of cost, the exact role of carbon in SCWG reactions, particularly for tar cracking and water-gas shift reactions is still unknown [38]. It has to be pointed out that the type of activated carbon used here did not gasify at reaction conditions [45].

3.2. Effect of homogeneous catalysts on gas yield and CGE

In contrast with Raney nickel—as were expected, alkali catalysts improved the hydrogen yield. NaOH and K₂CO₃ had the same yield of hydrogen (5.6 mol kg⁻¹) which is not significantly more than the case of KHCO₃ (5.3 mol kg⁻¹) (Table 1).

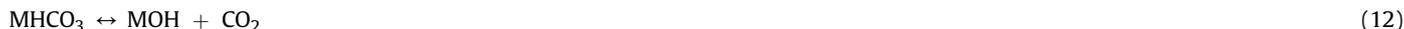
Generally, the CGE in the presence of alkali salts was small and the molar fraction and yield of hydrogen were improved noticeably. This indicates that the addition of alkali catalysts has a little effect on steam reforming reaction and more effect on the water-gas shift reaction [18].

According to many previously published reports, alkali catalysts degrade monomeric and dimeric carbohydrates at the temperatures of even below of 100 °C [46] and they also promote H₂ and CO₂ yield through water-gas shift reaction after the formation of gas [14,47–51] (Equation (5)).

Formation of HCOO–K⁺ in the presence of an alkali promoting the water-gas shift reaction are described according to the bellow equations [52]. However, the whole reactions are not as easy as detailed studies show [53].



In the presence of NaOH and KOH, the carbon dioxide fraction is low which resulted in a very low CGE (Fig. 2). The reason is that the added catalysts may react with the CO₂ and form carbonates (Equations. (11) and (12)):



where M = Na and K

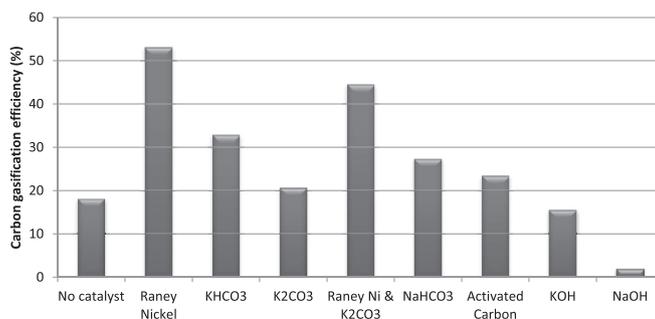


Fig. 2. Carbon gasification efficiency in different catalyst ($T = 400$ °C, $P = 25$ MPa, 9 wt% sugarcane bagasse).

According to Equations (11) and (12), every mol of MOH (here NaOH, or KOH) can fix up to 1 mol of CO₂. Therefore, one can conclude that in the presence of these catalysts, carbon was firstly gasified to CO₂ and then was captured in the aqueous phase. It is very difficult to determine how much CO₂ is fixed after reaction because according the authors experience; the equilibrium did not reach even after cooling down. After cooling down to room temperature the salts show too slow reaction to lead to the equilibrium with CO₂ content in the gas.

To consider this, in Table 1 a calculated CO₂ yield is given. This is the sum of the measured CO₂ yield and the maximum of CO₂ that could be adsorbed by the catalyst. The amount of absorbed CO₂ was calculated based upon Equations (11) and (12) considering the amount of catalyst and feedstock we used. The calculated CO₂ yield corresponds much better with the measured H₂ or CH₄ yield. This is because of this fact that a high gasification to H₂ or CH₄ leads to more CO₂ production.

Co-loading of Raney nickel and K₂CO₃ resulted in almost the same fraction of H₂ and CH₄. Since the amount of each catalyst was half the amount from the other experiments, it could be concluded that by a reduction of catalyst loading, the H₂ and CH₄ yield were likewise reduced.

Among all the catalysts used, KOH was significantly more effective on hydrogen yield where 6.64 mol kg⁻¹ was obtained (Table 1). This amount corresponds to 53% of the total produced gas. Schmieder and coworkers reported complete gasification of model and real biomass (wood sawdust) at 600 °C and 25 MPa in the presence of KOH where a H₂ rich gas containing CO₂ as the main carbon compound produced [54]. Here in this study, the contribution of the gas components is also free of other hydrocarbons with the exception of very small amount of ethane (0.4%). Gasification of glycerol by Guo and coworkers showed that NaOH acts better than KOH in a continuous reactor with the temperature of 526 °C and reaction time of seconds [31] which disagree with the results here. An important aspect here may be the phase behavior. On a molar base, dissolved potassium and sodium ion seems to behave similarly on the water-gas shift reaction [53]. On mass base, sodium salts should be more effective because they have a lower molecular weight. If the same mass is added, more sodium ions are in solution and more catalytic effect would be found, like found by Guo et al. [31]. Above the critical point of water, both hydroxides form a second liquid phase. Because of the existence of CO₂, carbonates are formed from the hydroxides so that K₂CO₃ forms a liquid phase and Na₂CO₃ a solid phase [55]. The experiments here are made in a batch experiments and the experiments of Guo at higher temperature and in a tubular reactor. Mixing is different in the different reactor types. The combination of the different phase behavior with less mixing in the case of the batch reactor might lead to the observed effect of higher catalytic effect of KOH/KHCO₃/K₂CO₃.

From the resultant data, the effectiveness of catalysts with respect to the hydrogen yield decreases in order of KOH > NaOH = K₂CO₃ > KHCO₃ > Raney-Ni & K₂CO₃ > NaHCO₃ > activated carbon > Raney nickel. Therefore, the KOH catalyst was chosen for further experiments utilizing higher temperatures and a lower reaction time.

3.3. Effect of catalyst on heating value of produced gas

Fig. 3 shows the effect of catalyst type on heating value of produced gas. Gas yield in the present of Raney nickel has the highest heating value. The maximum heating value (9.35 kJ kg⁻¹) was achieved with Raney nickel and the minimum was found in the experiment without catalyst. As was previously explained, Raney nickel directs the reaction to higher methane yields while alkali leads to more hydrogen production. In comparison with hydrogen, methane contains more heating value (889 kJ mol⁻¹), therefore the gas with more methane fraction corresponds to higher heating value.

3.4. Interaction effect of KOH and temperature

In order to study the effect of temperature and catalyst and to explore the highest possible hydrogen yield with the presence of KOH, 8 different experiments were done (four experiments with the present of KOH and other without any catalyst). Temperatures of 500, 600, 700 and 800 °C were applied. All these experiments had the same reaction time of 15 min and the same pressure of 25 MPa.

Fig. 4 shows the effect of temperature upon gas yield both with and without KOH. The overall trend in both cases seems to be more or less the same. The amount of hydrogen sharply increases when the temperature exceeds 600 °C while CO₂ and methane followed a smooth path in both situations.

This chart also emphasizes the effectiveness of temperature upon hydrogen yield even without catalyst. As the temperature increases, hydrogen yield in the presence of KOH increases more than situations void of catalysts. The resultant amount is 75.6 mol kg⁻¹ hydrogen, which is equal to 66% of the total produced gas. Fig. 5 depicts HGE as a function of temperature. As is clear from the figure, KOH made the

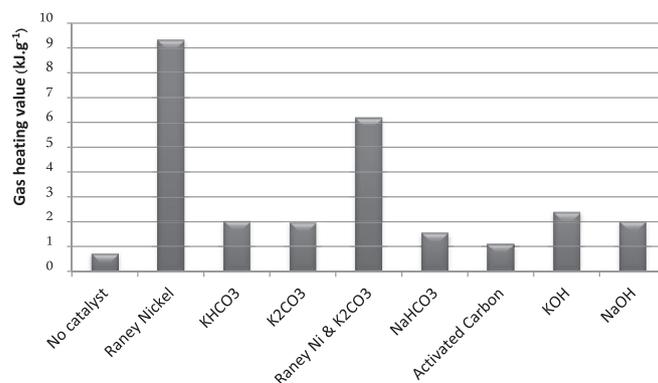


Fig. 3. Gas heating value in different catalyst ($T = 400$ °C, $P = 25$ MPa, 9 wt% sugarcane bagasse).

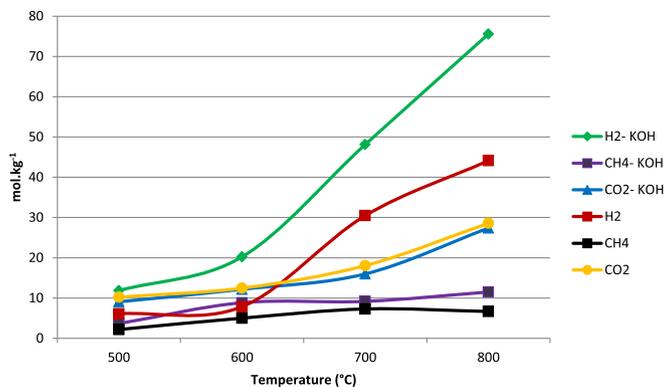


Fig. 4. Effect of temperature on gas product composition with and without KOH ($P = 25$ MPa, 9 wt% sugarcane bagasse, RT = 15 min).

HGE increase with higher rate though the trends are relatively similar. It can be concluded that by increasing the temperature over 650 °C, HGE exceeds 100%.

Antal and co-workers stated that “the higher temperatures drives the methane steam-reforming reaction to increase hydrogen yields at the expense of methane” [56]. Since the amount of methane is almost constant, we may conclude that the excess methane was being reformed to hydrogen, to maintain the thermodynamic equilibrium of the process.

Another reason could be the enhancement of water-gas shift reaction at high temperature. As confirmed by several studies, superheated water not only acts as a medium but also as a reactant [14,57,58]. In fact, heated compressed water can exchange hydrogen atoms [59] and hydrogen formed via this water-gas shift reaction can further react with other intermediates [60]. This reactive hydrogen may help in terminating free radical reactions and ultimately reduce formation of higher molecular weight species [61] which finally results in more gas formation.

HGE increases from 71% at 600 °C to 266% at 800 °C in the presence of KOH. It is worthy to state that since hydrogen from water are used during the water-gas shift, HGE based on the hydrogen content of feed biomass, may not be a reliable quantity for evaluating SCWG.

Yoshida and Coworkers showed that the hydrogen gasification efficiency of 89% is feasible from rice straw at 400 °C and 25 MPa with the presence of a sufficient amount of nickel. In the case of cellulose, they reached the efficiency of 123% [62]. Since the temperature in this study is doubled and an alkali catalyst was applied, this HGE is not surprising.

It has to be mentioned that at the supercritical conditions, the solubility of salts is limited. The reaction of KOH and carbon dioxide may result in formation of carbonates. KOH and carbonates are so-called type 1 salts which form a salt-rich phase. At the conditions of 400 °C and 25 MPa, the salts are likely dissolved but at 600 °C they would definitely precipitate [55,63,64]. Therefore it is generally problematic to directly compare experiments with salts as catalysts at different temperatures.

Fig. 6 shows CGE in different temperatures with and without catalyst. From this figure, increases in CGE by temperature in both cases are evident. Without a catalyst, CGE rose from 37% at 500 °C to 91% at 800 °C. Complete gasification of carbon occurred at a very high temperature of 800 °C with the presence of KOH. The most convincing proofs of the complete gasification were the clear remained water after this experiment and clean reactor wall, while brownish liquid and a thin white layer on the wall were observed in the cases of lower temperatures. The remained liquid was also free of black particulates (char). For those reasons probably KOH did not trap CO₂ at 800 °C. The remained liquid after high temperature experiments was too low to be used for further analysis.

Previous work indicated that in higher temperatures, the rate of steam reforming exceeds than char formation which lead to less char and higher gasification efficiency [65,66]. Waldner and Vogel reached complete gasification of wood biomass at 400 °C coupled with a 90 min reaction time in the presence of Raney nickel catalyst [29]. reported complete gasification of sawdust and potato-waste at the temperature of above 650 °C [56]. This rough comparison shows that though the temperature is effective in the conversion, the nature of biomass is also determinant factor. Another reason could be the type of catalyst employed. As depicted in Fig. 3, in comparison with alkali catalysts, Raney nickel leads to higher carbon conversion.

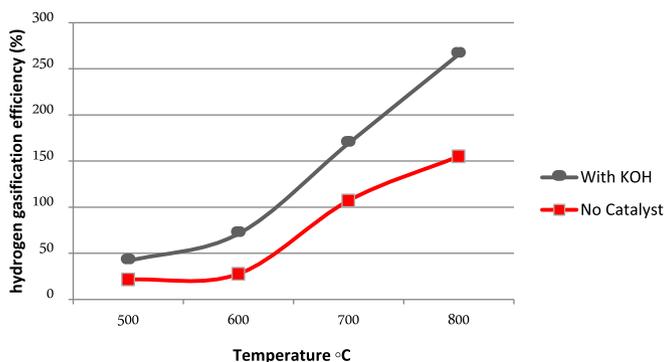


Fig. 5. Hydrogen gasification efficiency as a function of temperature with and without KOH ($P = 25$ MPa, 9 wt% sugarcane bagasse, RT = 15 min).

Table 2
Energy equivalent of the potential of hydrogen from sugarcane bagasse.

Fuel type	Million liters
Gasoline	39.1
Diesel	34
LPG	52.5
CNG	147.1

From a chemical point of view, Raney nickel and KOH have different functions. Nickel is a catalyst for methane formation and KOH for the water-gas shift reaction to form hydrogen. Therefore Nickel usually, as shown here, is used at near-critical conditions where methane is the thermodynamically-preferred product [63]. Therefore it is also more beneficial within this temperature range because it supports the formation of the “right” product.

In general, the temperature of 800 °C for complete gasification in supercritical water does not make sense from a practical point of view; while it is near to the common temperature for thermal gasification.

3.5. Potential of hydrogen production from sugarcane bagasse

It is not easy to accurately calculate the potential of hydrogen production from a process which is not fully developed. Moreover, SCWG has not yet been commercialized and there are big challenges regarding materials that are compatible with the extreme conditions. Maintenance cost, plugging due to salt precipitation and char formation are also considered as critical problems in SCWG of biomass [9]. However, based on the available feedstock and laboratory experiments, a satisfying estimation could be made.

The Khuzestan province of Iran is located in Southwest of the country. The climate of Khuzestan is generally hot and mostly humid, and due to the Karoun, Karkheh, Jarahi and Maroun rivers, it is the only region where sugarcane could be cultivated.

The annual sugarcane bagasse from 7 governmental sugarcane farms (totally 70,000 ha) is 0.84 millions of tones [5]. Considering 660 °C as the normal working temperature for large scale supercritical water gasification plants [67], from Fig. 4 we can estimate that 23.5 mol hydrogen per kg of bagasse can be produced without catalyst. Though the use of catalyst will improve the yield significantly however, we preferred not to include this option because of the catalyst cost and its problems associated with regeneration.

The total hydrogen potential is equal to 560 L in normal situation. Therefore the potential of annual hydrogen production in Iran is roughly 470 million Nm³. Considering the heating value of 2.5 MJ L⁻¹ for hydrogen at 148 bar, Table 2 shows the energy equivalent of this amount of hydrogen to other common vehicle fuels [68]. It has to be noted that including the energy input for pre-treatment of bagasse (grinding) and gasification process will definitely decrease the available yield.

3.6. Potential of fertilizer

Urea is the most widely used fertilizer in Iranian agriculture sector. The average urea utilization in sugarcane farms is 300 kg ha⁻¹. Currently, all chemical fertilizers are domestically produced in petrochemical factories from natural gas as the main feedstock. Hydrogen gas can be used for urea production through the Reactions (13),(14) and Reaction (15) [69].



Considering the conversion efficiency of 80% for each individual ammonia and urea formation process [70], 252,000 tons of urea would be theoretically obtainable. This amount can meet the need of 6550 ha of sugarcane farms.

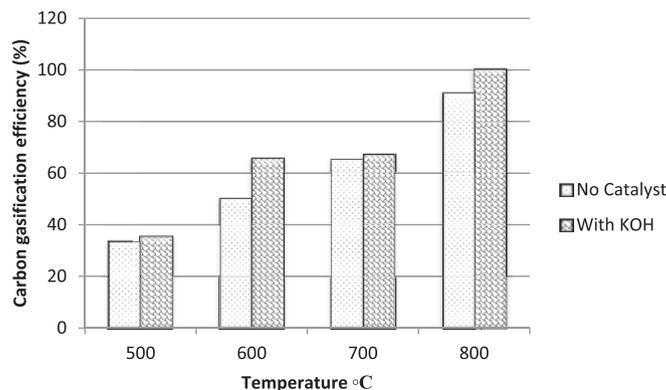


Fig. 6. Carbon gasification efficiency as a function of temperature with and without catalyst ($P = 25$ MPa, 9 wt% sugarcane bagasse, RT = 15 min).

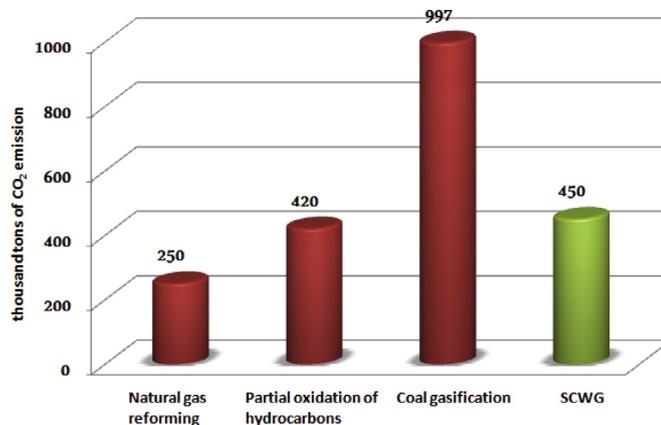


Fig. 7. CO₂ emission for 39.5 thousand tons of hydrogen production from various process.

3.7. Potential in CO₂ emission reduction

Regardless of what is intended to be produced from hydrogen, generation of such a huge amount from sugarcane bagasse contribute to great environmental benefits through prohibition of CO₂ emission and fossil fuel depletion. According to [71] production of 1 kg of hydrogen through natural gas reforming, partial oxidation of hydrocarbons, and coal gasification processes contribute to emission of 7.33, 12.35, and 29.33 kg carbon dioxide respectively. Fig. 7 shows the CO₂ emission for 39.5 thousand tons of hydrogen production from various processes. It is worthy to mention that we can optimistically consider the CO₂ emitted from sugarcane bagasse is environmentally neutral.

4. Conclusion

Supercritical water gasification of sugarcane bagasse was studied in a batch autoclave reactor at the constant pressure of 25 MPa.

The effect of catalyst and reaction temperature was investigated and the following major results were achieved: (1) the order of catalyst effectiveness in the favor of hydrogen production from bagasse is KOH > NaOH = K₂CO₃ > KHCO₃ > NaHCO₃ > activated carbon. (2) Temperature has a major effect upon hydrogen formation from sugarcane bagasse; at 700 °C even without catalyst, hydrogen gasification efficiency of more than 100% can be achieved. (3) The highest amount of hydrogen (75.6 mol kg⁻¹) was formed at 800 °C in the presence of KOH, where water-gas shift reaction donates an HGE of 266%.

The theoretical potential of annual hydrogen production in the Khuzestan Province of Iran is 470 million Nm³. It is worthy to emphasize that this figure is a rough estimation without considering the practical barriers such as maintenance cost, plugging and system failures.

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