

Preliminary Assessment of Synthesis Gas Production via Hybrid Steam Reforming of Methane and Glycerol

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ABSTRACT: In this article, hybrid steam reforming (HSR) of desulphurized methane, together with crude glycerol, in existing commercial steam reformers to produce synthesis gas is proposed. The proposed concept consists of a gasifier to produce vapors, gases, and char from crude glycerol, which is coupled with a pre-reformer to further convert the vapors into gases using a steam reforming catalyst. These gases are mixed with methane and subsequently reformed to synthesis gas ($\text{CO} + \text{H}_2$) in a primary reformer, using a steam reforming catalyst. In the present work, gasification, steam, and hybrid reforming of glycerol are reported. The total product distribution (gas, vapor, and char) of pure and crude glycerol gasification was quantified at different reaction temperatures at very high heating rates (atomization, $\sim 10^6$ °C/min). With pure and neutralized crude glycerol, no char formation was observed. However, with crude glycerol and pure glycerol doped with KOH, a significant amount of char on carbon basis ($\sim 10\%$) is produced. The results obtained here show that KOH present in glycerol was responsible for polymerizing higher molecular components formed during thermal degradation. Steam reforming of pure and neutralized crude glycerol was studied at different process conditions in the presence of commercial reforming catalysts. Pure glycerol was easier (in terms of catalyst activity) to reform when compared to neutralized crude glycerol at high temperature (800 °C). The results from the steam reforming of neutralized crude glycerol show that the loss of catalyst activity was due to the presence of organic impurities such as FAMES, diglycerides, and triglycerides. The proposed HSR concept was demonstrated using 28 wt % pure glycerol and 72 wt % methane (on C_1 basis) in a two-stage fixed bed reformer at 800 °C using commercial steam reforming catalyst.

INTRODUCTION

Over the past several years, there has been an increasing interest in the use of biodiesel as a supplement to the traditional fossil fuels. With the ever-increasing production of biodiesel, a surplus of crude glycerol, which is a byproduct from the transesterification process, is available for further processing. The crude byproduct stream typically comprises of a mixture of glycerol, methanol, inorganic salts (mainly catalyst residue), free fatty acids, and fatty acid methyl esters in varying quantities. Purification is required to transform the crude glycerol to a usable state for food and pharmaceutical applications. As a first step in purification, excess methanol is distilled and reused for the transesterification process. An acid neutralization step is required to purify crude glycerol further, to convert alkali hydroxide catalyst into its salts (e.g., chlorides), typically around 5% present in the crude.¹ The combination of high methanol prices and low crude glycerol prices has made the conversion of crude glycerol to methanol via steam reforming economically attractive.¹ To take advantage of the existing natural gas steam reformers, there is a possibility to replace natural gas by a fraction of crude glycerol on carbon basis. This concept is proposed here as “hybrid steam reforming” to utilize either a direct crude or purified/neutralized crude glycerol.

The hybrid steam reforming process consists of the following stages: (1) Gasification: the controlled atomization of crude glycerol into small droplets (~ 100 μm) in a gasifier around 500 °C. This leads to the production of vapor, gases, and char via thermal decomposition. (2) Steam reforming: the vapor produced from the gasifier can be pre-reformed using a commercial

reforming catalyst. Adhikari et al.² reported that a minimum temperature of ~ 600 °C is required to convert glycerol into gases. This step is similar to pre-reforming of naphtha/natural gas. In the case of naphtha and natural gas, higher hydrocarbons are partially reformed to produce gases whereas in the case of glycerol, vapors (oxygenates) are reformed to produce gases. (3) Hybrid steam reforming: the product gas obtained from the pre-reforming step can be mixed with desulphurized methane and reformed in the primary reformer. Because this is similar to natural gas reforming, a high temperature of ~ 800 °C is preferred for this step. The whole concept is summarized in Figure 1a.

Hybrid reforming can be beneficial in many ways:

- The steam necessary for the primary reforming (molar S/C ~ 3) can be completely/partly utilized in the pre-reforming step (S/C ~ 5 –15, depends on glycerol fraction). Here, S/C is defined as the ratio of the total moles of water added, including the water content of the glycerol, over the moles of carbon present in the glycerol. Therefore, no additional steam is required for the process.
- Figure 1b summarizes the S/C required for a specific fraction of crude glycerol (by wt % on C_1 basis) available for hybrid steam reforming. For instance, to process 30 wt % of glycerol on carbon basis, a S/C up to 10 is necessary in the

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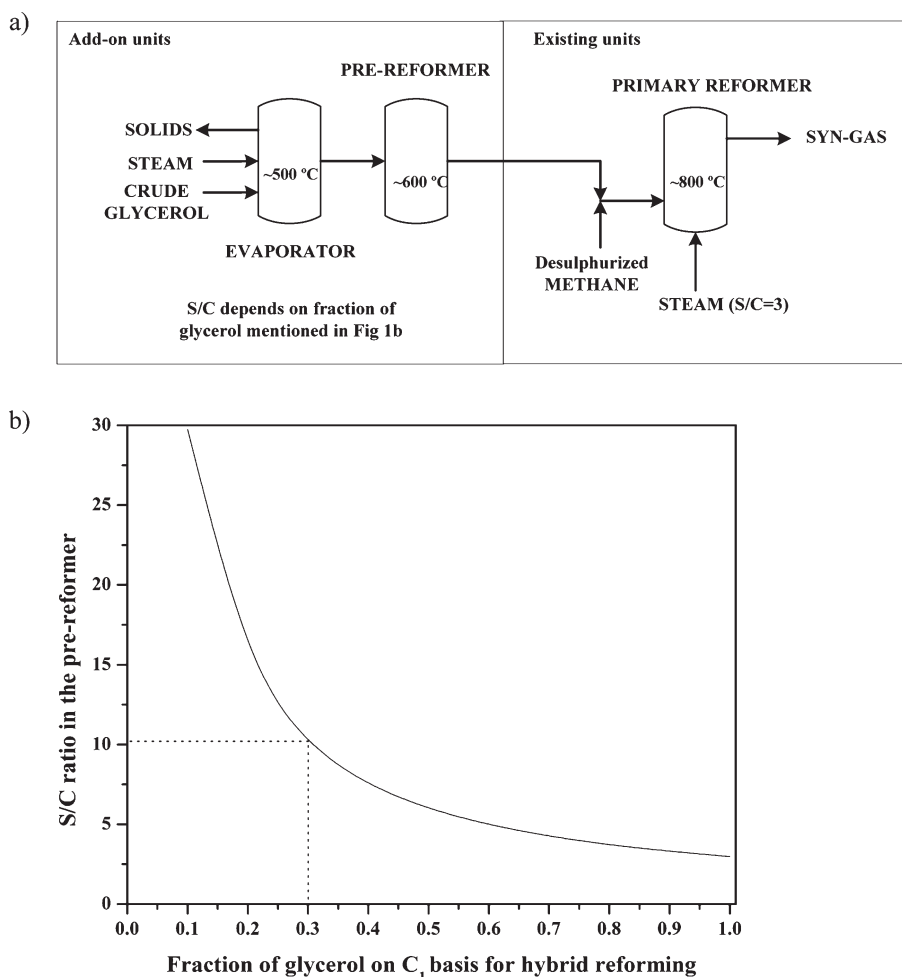


Figure 1. (a) Proposed concept for hybrid steam reforming of methane with glycerol. (b) Dependence of S/C ratio in the pre-reformer during hybrid steam of glycerol fraction with methane.

pre-reforming step, which makes $S/C = 3$ in the primary reformer, with 70 wt % of remaining carbon from methane.

- Adding steam to the glycerol reforming step may enhance char and coke gasification. Here, char is defined as the thermal degradation product from the feedstock and coke is defined as the carbon deposited on the catalyst.

A great deal of research has been carried out at the laboratory scale to obtain H_2 /synthesis gas from bioliquids such as glycerol, fast pyrolysis oil, or its fractions via steam reforming^{3–6} or partial oxidation⁷ or supercritical gasification.^{3,8–10} Several supports, such as Al_2O_3 , TiO_2 , SiO_2 , CeO_2 , MgO on nickel, and alumina support modifiers, such as ZrO_2 , CeO_2 , La_2O_3 , MgO , have been screened based on H_2 production via steam reforming of pure glycerol^{2,11} and model compounds.^{12–14} Adhikari et al.² reported that Ni/ CeO_2 catalyst has a better activity with >99% glycerol conversion at 600 °C and $S/C = 12$, whereas Ni/ Al_2O_3 catalyst has higher activity at 900 °C and $S/C = 9$. Czernik et al.¹⁵ produced H_2 -rich gas via steam reforming crude glycerol using a commercial steam reforming catalyst at 800 °C and $S/C = 2.6$. However, a gradual increase in the methane was reported. To the best of our knowledge, the quantitative information about the effect of alkali hydroxides or its salts and the organic impurities present in the crude glycerol during gasification and steam reforming is not available in the open literature.

In this article, various stages of hybrid steam reforming were tested. To clarify the effect of alkali hydroxide (e.g., KOH), the gasification of crude glycerol and pure glycerol with and without KOH was studied in TGA at a heating rate of 5 °C/min up to 600 °C. Visual observation tests during the gasification were performed to study the effect of KOH, which is present in the untreated crude glycerol and alkali salts (e.g., KCl), which is present in the neutralized crude glycerol. Gasification of crude glycerol, with and without KOH, is studied by atomizing it into fine droplets in the temperature range between 400 and 800 °C. The product distribution from the feedstocks to gas, vapor, and char has been studied in detail. Finally, the behavior of K, Mg promoted naphtha reforming catalyst, and unpromoted Ni/ Al_2O_3 natural gas reforming catalyst was studied on the basis of on their surface area, pore volume, and nickel particle size, using neutralized crude glycerol at steam reforming conditions. Several implications of the overall concept are discussed at the end of the article.

EXPERIMENTAL SECTION

Materials. Pure glycerol (Sigma Aldrich), in-house produced crude glycerol 1 obtained from transesterification of waste cooking oil, crude glycerol 2 (neutralized feedstock; BioMCN, Delfzijl, The Netherlands),

Table 1a. Elemental Analyses (Wet) and Water Content Determination of Different Glycerol Feedstocks (As Received)^a

feedstock ^b	C (wt %)	H (wt %)	rest (wt %)	water (wt %)
pure glycerol	39.1	8.7	52.2	0
crude glycerol 1	45.5	7.7	46.8	0
crude glycerol 2	31.9	8.6	59.5	11

^aThe rest is mainly oxygen but also with other elements such as sulfur and nitrogen. ^bThe ash content of crude glycerol 1 is 6.6% (consists of K₂O and trace amounts of CaO and Fe₂O₃), and the ash content of crude glycerol 2 is ~4.3% (consists of Na₂O).

Table 1b. Composition of Crude Glycerol 2

component	wt %
glycerol	83
water	11
organics ^a	1.78
inorganics ^b	4.4

^aConsists of diglycerides (0.78%), triglycerides (0.5%), FAME (0.3%), free fatty acids (0.2%), methanol (0.01%), and trace amounts of citric acid and acetic acid. ^bConsists of 4.3% sodium chloride, 0.09% magnesium sulfate, and 0.01% calcium sulfate.

and pure glycerol doped with KOH, NaOH, and KCl (NaOH and KOH from Merck; KCl from Sigma Aldrich) were used in this study. Elemental compositions were analyzed with an EA 1108 (Fisons Instruments). The water content of the glycerol was determined by Karl Fischer titration (titrant: hydranal composite 5, Metrohm 787 KFTitrino). The as-received elemental composition and the water content of the feedstocks are presented in Table 1a. The composition of crude glycerol 2 is given in Table 1b. An organic concentration of 62.5% by weight (rest: water) was prepared to facilitate atomization for continuous gasification experiments. Prior to the addition of water, methanol was removed from the crude glycerol 1 via vacuum distillation. The molecular mass distribution of the condensed liquid obtained after the vaporization of glycerol was measured using a gel permeation chromatography (GPC, Agilent Technologies, 1200 series RID detector, 1 mL/min eluent). The solvent used was dimethyl sulfoxide (DMSO; 10 mg sample/mL DMSO). The columns used were 3 PLgel 3 μ m MIXED-E placed in series. The RID signal is calibrated with polystyrene standards (MW) 162–30 000. Two Ni/Al₂O₃-based commercial steam reforming catalysts (catalyst A: NiO ~23%, promoted using MgO and K₂O. Catalyst B: NiO ~ 18%, here termed as unpromoted) were used in this study. The catalyst pellets were crushed and sieved between 3 and 5 mm particle sizes. The catalyst was mixed with quartz particles of similar particle size range to have a reasonable bed height of ~100 mm.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out in aluminum cups using a NETZSCH STA 449 F3 instrument. The heating rate for all the samples was 5 °C/min from 25 °C to a maximum temperature of 600 °C using N₂ flow of 20 mL/min together with a protective flow of 40 mL/min. The initial mass of the samples was determined using an external weighing balance.

The mass rate loss is defined as

$$r_{\text{wt}} \equiv \frac{dX}{dT} = -\frac{(m_{\tau} - m_{\tau+1})}{m_0(T_{\tau} - T_{\tau+1})} (1/^{\circ}\text{C})$$

where τ and $\tau+1$ are logged times, T (°C) is the temperature of the sample cup and m_0 (mg) is the initial amount of glycerol, as weighed with the external balance.

Batch-Wise Gasification. A fixed amount of glycerol solution (2 g) was added to the bottom of a glass tube (\varnothing 10 mm). The glass tube was placed inside an electrically heated oven and the temperatures were measured in the solution itself. A heating rate of ~50 °C/min was applied to the oven. A small nitrogen flow was placed just above the glycerol to avoid direct contact with air and to remove the vapors, which were released during gasification. Snapshots were taken during the gasification tests. A brief description of the procedure was given by Rossum et al.¹⁶

Gasification of Glycerol via Atomization. To quantify the distribution of glycerol during gasification (atomization) over the gas, vapor, and char, prior to the reforming step and to measure individual gas yields, a dedicated continuous gasification setup was constructed. About 1.7 mL/min of glycerol was sprayed onto an empty electrically heated stainless steel tube (40 mm inner diameter, 400 mm length) using an externally cooled atomizer that produced droplets of ca. 100 μ m. A detailed description of the setup was given by Ramachandran et al.¹⁷

Steam and Hybrid Steam Reforming—Experimental Setup. A schematic overview of the hybrid reforming setup is shown in Figure 2. The setup consists of three stages: gasification of glycerol, followed by catalytic pre-reforming of vapors, and catalytic reforming of methane, together with the gas/vapor produced from the pre-reforming. All the equipment components were made of stainless steel (type R543). The setup was operated at near atmospheric pressure.

Gasification Section. The gasifier has an inner diameter of 40 mm and a height of 350 mm. It consists of an ultrasonic atomizer that sprays droplets of ~100 μ m with a liquid flow rate ranging from 0.2 to 0.4 mL/min, using a HPLC pump (Instrument Solutions). Nitrogen stream (0.2 NL/min flow rate) was used to facilitate atomization. The atomizer was fitted in a copper ring in which water was circulated to keep the temperature below 70 °C. This is to protect the piezo-electric parts of the atomizer from thermal damage. A preheater (450 °C) was attached to the top of the gasifier to supply additional nitrogen (0.4 NL/min flow rate) and steam required for the reaction. This added stream kept the top of the gasifier at ~400 °C to minimize vapor condensation at the upper part of the gasifier. A filter was placed at the bottom of the gasifier to collect the solids. Temperatures were measured at the top, middle, and bottom sections of the gasifier. The reported gasification temperature was the average temperature of the middle and the bottom section of the gasifier.

Pre-Reforming Section. Beneath the evaporator, the pre-reformer (40 mm inner diameter and 150 mm height) was placed, where the gas/vapor mixture from the gasifier is catalytically converted using a commercial steam reforming catalyst. The catalyst was placed in an inconel distribution plate at the bottom of the pre-reformer. The temperature of the pre-reforming section was kept at ~600 °C and measured at the middle. Methane was supplied at the exit of the pre-reformer for hybrid steam reforming experiments.

Primary Reforming Section. The primary reformer (35 mm inner diameter and 300 mm height) was fitted with an inconel distribution plate at the middle of the reactor. The bed consists of a mixture of quartz and catalyst particles (3:1, quartz/catalyst), which was placed over the plate with a bed height of ~100 mm. Both the pre-reforming and primary reforming catalyst beds were fixed. The catalyst bed and the exit gas temperatures were ~800 °C respectively. Both the pre-reforming and the primary reforming catalyst were reduced in situ with hydrogen (0.2 NL/min) and diluted with nitrogen (0.4 NL/min) at 800 °C for ~8 h before each experiment. Temperatures of the primary reformer were measured at the bottom (product gas from pre-reformer) and also at the middle of the catalyst bed, which was the reported temperature.

For hybrid reforming experiments, the pre-reformer was used together with the primary reformer, whereas for the “stand alone” low temperature reforming of glycerol (LTR, single catalyst bed) and steam

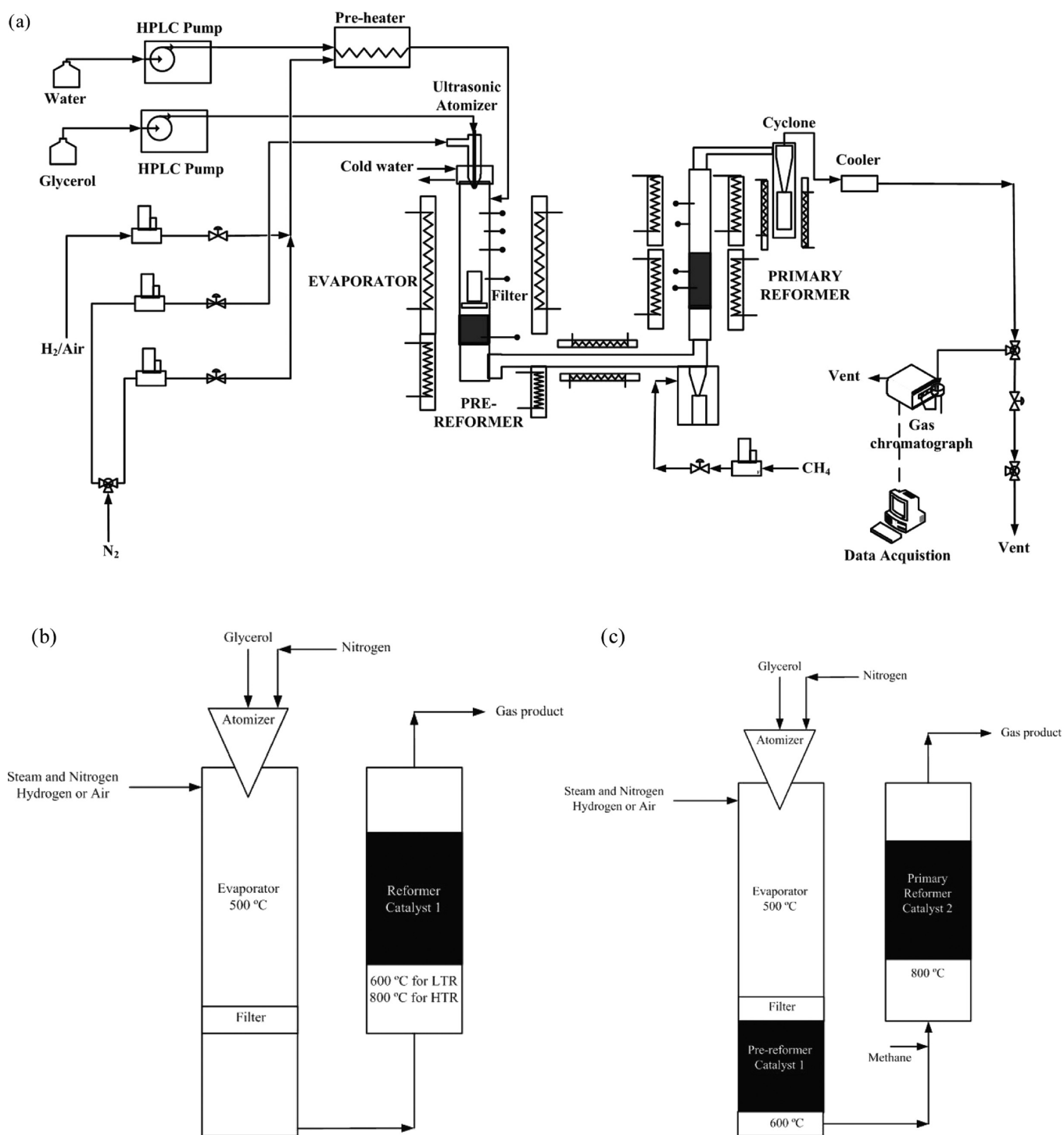


Figure 2. (a) Schematic overview of the hybrid steam reforming setup. (b) Representation of a "stand alone" reforming reactor configuration in which catalyst A or B used. (c) Hybrid reforming configuration (catalyst A used as both pre-reforming and primary reforming catalyst).

reforming or high temperature reforming of methane or glycerol (HTR, single catalyst bed), the catalyst was placed in the primary reformer. Representations of the experimental setup configurations are shown in parts b and c of Figure 2. Performance of catalysts A and B were screened based on configuration, as shown in Figure 2b. Catalyst A was used as both the pre-reforming and the primary reforming catalyst for hybrid steam reforming experiments. The products from the reformer were immediately cooled after the cyclone to collect the condensables. A micro-GC (Varian CP-4900; 10 mmol sieve 5A Ar, 10 mmol sieve

5A He, 10 m PPQ He, 8 m Sil-5CB He) was used to detect H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈. The integral carbon balance and gas production for both the gasification and catalytic reforming experiments were made based on nitrogen as an internal standard, which was fed to the atomizer and preheater. The gas production from the primary reformer is reported as Nm³ of H₂ or CH₄ or CO or CO₂ per kilogram of the dry feedstock.

The catalysts were regenerated using 200 mL/min of air diluted with 100 mL/min of nitrogen to estimate the amount of carbon deposited

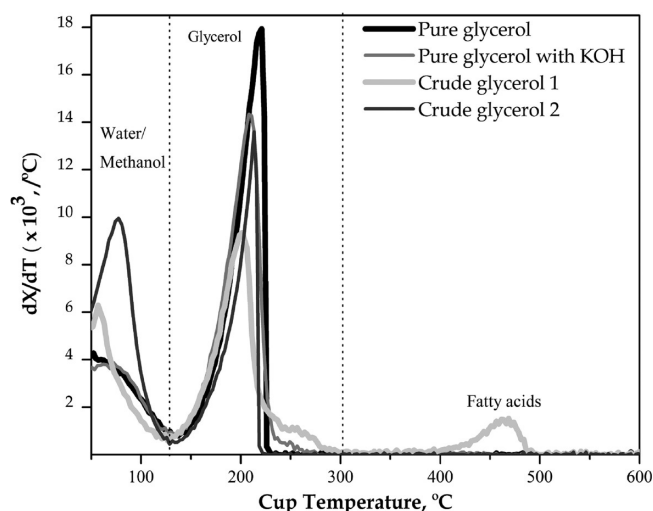


Figure 3. TGA of crude glycerol and pure glycerol with and without KOH at 5 °C/min heating rate in inert N₂ gas.

(coke) on the catalyst. The carbon to gas conversion or fraction of carbon converted to gases was calculated at the steady-state operation that excludes the start-up profile. Gas hourly space velocity on C₁ basis is defined as the volume of C₁ equivalent species in the feed at the STP (standard temperature and pressure) per unit volume of the catalyst. C₁ equivalent is used to compare feedstocks containing different number of carbon atoms per molecule. The carbon closure of experimental setup was found to be adequate (i) 100 ± 3%, using methane and steam at 795 °C, S/C = 3, (ii) 99 ± 3%, using pure glycerol at 805 °C, S/C = 3. There is a slight degree of fluctuation in the gas production due to glycerol, steam, and nitrogen flows.

Catalyst Characterization. Commercial steam reforming catalysts (promoted and unpromoted) were characterized for their surface area, pore volume, and active metal dispersion before and after the steam reforming of crude glycerol 2. Specific surface area measurements were carried out by the BET method (Micromeritics Tristar). H₂ chemisorption (Chemisorb 2750, Micromeritics) measurements were carried out to determine Ni dispersion, particle size, and the metal surface area. Prior to the measurement, the catalyst was reduced at a heating rate of 5 °C/min up to 800 °C in a 5% H₂/Ar flow (30 mL/min).

RESULTS AND DISCUSSION

Batch Gasification of Glycerol. *TGA Measurements.* TGA results for glycerol solution with and without KOH (KOH ~ 3% on glycerol mass basis) and crude glycerol 1 and 2 at 5 °C/min up to 600 °C are shown in Figure 3, where the rate of gasification and mass loss is plotted versus the temperature trajectory. The gasification rate for each sample is expressed on the initial mass basis, excluding the amount of KOH added. From the TGA measurements, the following observations were made:

- A peak around 100 °C is observed for all feedstocks, which is due to the evaporation of water. From Figure 3, it can be observed that the gasification rate of crude glycerol 1 and glycerol with KOH proceeds at a slower rate than pure and crude glycerol 2 in the temperature range between 200 and 270 °C.
- It is also observed that the rate of gasification for the pure glycerol and the crude glycerol 2 is ceased completely at a temperature around 230 °C, whereas the conversion rate for

crude glycerol 1 and glycerol with KOH proceeds slowly above 230 °C.

- At temperature between 400 and 450 °C, a peak was observed for crude glycerol 1, which is presumably due to the presence of fatty acids in the crude. This peak is not observed for crude glycerol 2 due to low amount of FAMES, diglycerides, and triglycerides (1.78%) present in it.
- Crude glycerol 1 gives ~10% residue on mass basis, glycerol with KOH gives ~6–7% residue, pure and crude glycerol 2 gives ~3% of residue at 600 °C. Similar results for pure and crude glycerol were obtained at 5 °C/min by Dou et al.¹⁸ To clarify the observed phenomena from the TGA measurements, visual observation tests were performed.

Visual Study in Batch Tubes. Figure 4 shows the snapshots taken during the gasification of glycerol with and without KOH, NaOH, and KCl and crude glycerol 1 and 2. The glass tubes were heated at a heating rate of ~50 °C/min to 400 °C. Figure 4a shows that the pure glycerol was almost completely evaporated above the boiling point (290 °C), leaving no solid residue in the glass tube. Pure glycerol with 1% KOH polymerized above ~350 °C, which resulted in ~10% char on carbon basis. This is illustrated in Figure 4b. To crosscheck the effect of KOH, 1% NaOH was added to pure glycerol. An effect similar to that for KOH was observed for NaOH (not shown in Figure 4). However, KCl did not polymerize pure glycerol above 350 °C. Figure 4c and d illustrates the gasification of crude glycerols. The visual study suggests that crude glycerol 1 has a similar effect on polymerization, as glycerol with KOH and crude glycerol 2 showed similar behavior as glycerol with KCl. Table 2 summarizes the char yield on carbon basis. It has been visually observed that, at the boiling point (290 °C), the solution behaves like a boiling liquid and an increase in temperature resulted in polymerization in the liquid phase. The visual tests indicate that the formation of char via polymerization is due to the presence of hydroxides and not because of its salt present in the pure glycerol or crude glycerol 2. GPC analysis of liquids obtained after the vaporization of glycerol with and without KOH and crude glycerol 1 and 2 was performed to confirm the causes of polymerization.

Molecular Mass Distribution. The feedstocks were heated in the batch tubes, and when the temperature reached near to glycerol boiling point (290 °C), the remaining liquids were cooled before the polymerization began. Figure 5 shows the molecular mass distribution of liquids obtained from the crude glycerol 1 and 2 and glycerol with and without KOH. From Figure 5, it can be observed that no larger molecules are formed during the vaporization of pure glycerol, whereas with the addition of KOH to glycerol, a single peak of molecules twice that of glycerol is formed. To differentiate the temperature effect, the liquids were collected before the boiling point of glycerol (~275 °C) with KOH. It is clearly observed that the larger molecules formed before the boiling temperature of glycerol itself. This indicates that the intermediates that have higher molecular mass than glycerol are formed in the liquid phase in the presence of KOH. This may be due to glycerol dimerization in the presence of KOH.¹⁹ Crude glycerol 1 showed three prominent peaks between 250 and 500 g/mol. This may be due to the presence of fatty acids, diglycerides, and triglycerides in crude glycerol 1. Because the amount of aforementioned compounds is small in crude glycerol 2, the peaks are not identified.

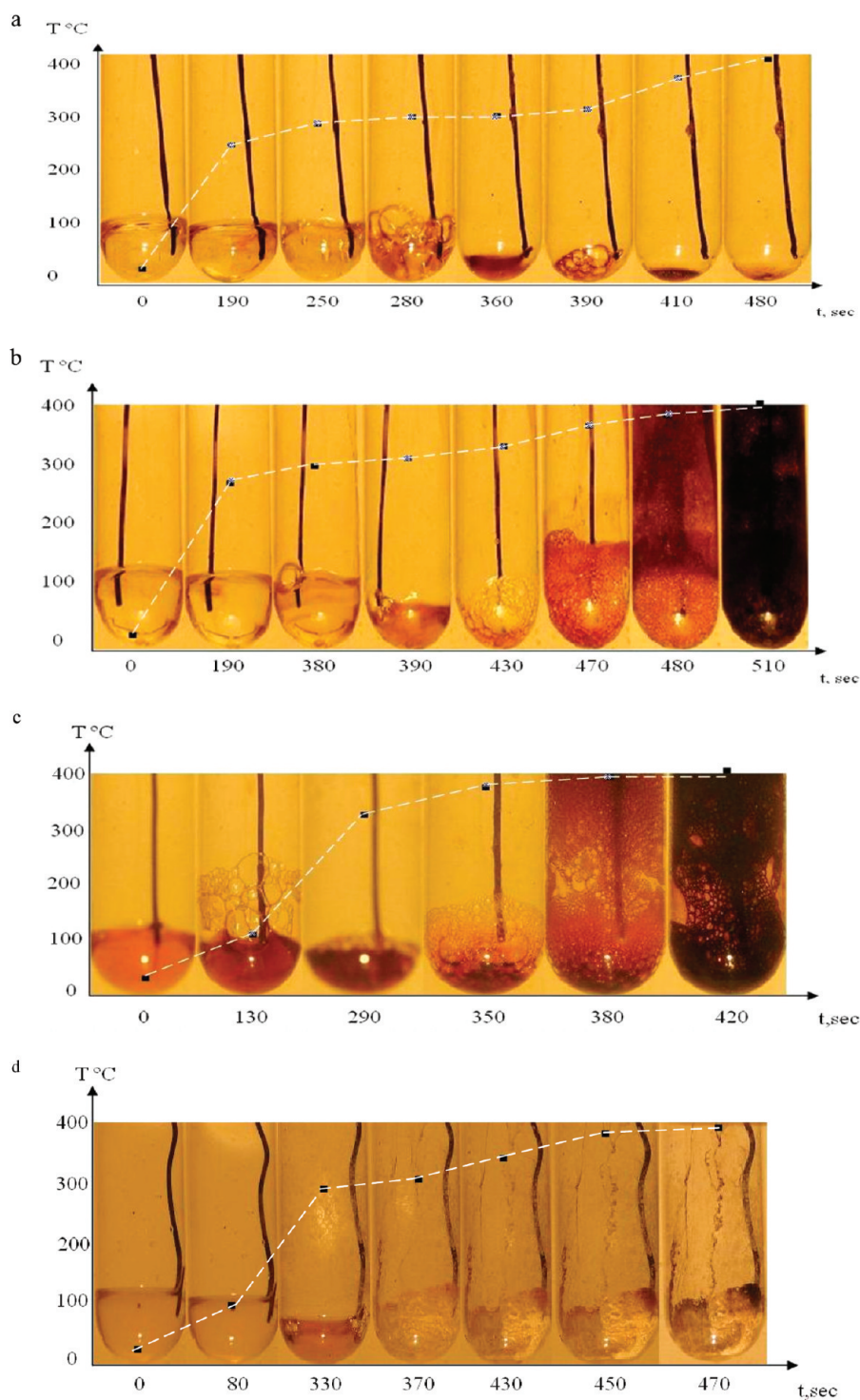


Figure 4. Snapshots of batch tubes during gasification of (a) glycerol, (b) glycerol with KOH, (c) crude glycerol 1, and (d) crude glycerol 2.

Continuous Gasification by Atomization. The effect of the evaporator temperature (400–800 °C, vapor residence time = 2–3 s) on the amount of char, gas, and vapor produced from the gasification of crude glycerol 1 and 2 and glycerol with and without KOH by controlled atomization (heating rate $\sim 10^6$ °C/min as described by Rossum et al.¹⁶) is showed in Figure 6. Over the whole temperature range studied, the amount of the char produced from the crude glycerol 1 (Figure 6c) and glycerol with KOH (Figure 6b) is nearly constant. This indicates that the initial distribution of carbon

from the glycerol to the vapor/gas and char has already attained well before the gasifier temperature of 450 °C. This is an observation in line with the gasification of pyrolysis oil.¹⁶ It is observed from Figure 6a and d that glycerol and crude glycerol 2 do not form any char at the temperature range studied. The amount of char formed on the carbon basis for pure glycerol with $\sim 3\%$ KOH was in the range 8–10%, whereas for crude glycerol the amount was found to be between 5 and 7%. Above ~ 600 °C, for all the feedstocks, vapor cracking reactions to gases were found to be predominant.

Table 2. Char Productions from Batch Gasification of Glycerol^a

feedstocks	salt % (on dry basis)	residue, wt %	char yield, %
pure glycerol	0	0.85	No solid residue
pure glycerol with KOH	0.90	6.10	9.6
pure glycerol with NaOH	0.94	7.51	11.1
pure glycerol with KCl	1.22	3.83	0
glycerol (62.5%)	2.91	4.81	10.9
crude glycerol 1	n.m. ^b	10.2	15.9
crude glycerol 2	n.m.	4.8	0

^aThe amounts are given both on mass and carbon to char basis. The sample was heated to 400 °C with a heating rate of ~50 °C/min. ^bn.m. = not measured.

The formation of char for glycerol with KOH and crude glycerol 1 signifies that the presence of KOH accelerates the formation of char even at high heating rate. By comparing the batch and continuous tests, it is observed that the heating rate does not have a significant effect on the polymerization, as these reactions happen extremely fast at temperatures <350 °C. However, for pyrolysis oil gasification, the heating rate has a tremendous effect in controlling the char formation.¹⁶ The gasification experiments from both batch and continuous processes indicate that, to prevent polymerization or carbon leading to char, potash free glycerol has to be processed in the reformer. However, solids handling either as char and salts (in the case of crude glycerol 1 and glycerol with KOH) and salts (for crude glycerol 2) become mandatory in the gasifier.

Pre-Reforming and Steam Reforming of Pure Glycerol Using Catalyst A. To evaluate the process conditions of steam reforming, pure glycerol was reformed at LTR and HTR conditions. Figure 7 shows the gas production (Nm³/kg dry glycerol) obtained at two different reaction conditions using catalyst A: (a) LTR at S/C = 3 and (b) HTR at S/C = 3. The results are summarized in Table 3. In both cases, the carbon recovery to gases was ~100%. In the first 7 h, pre-reforming of glycerol (LTR; Figure 7a; 588 °C, S/C = 3) was performed. The gas production was constant and carbon to gas conversion was ~103%. During the next 3 h, temperature was increased to ~788 °C and S/C was kept constant. In both cases, the gas production was close to the equilibrium values, as shown in Table 3. At high temperature reforming conditions (HTR; Figure 7b), almost no methane and C₂₋₃ were observed, whereas at low temperature conditions, a considerable amount of methane and low amounts of C₂₋₃ were observed in the product gas.

LTR was carried out over a long duration run of 25 h under similar conditions ($T = 590$ °C, $S/C \sim 3.5$, $GC_1HSV = 543$ h⁻¹) in order to investigate the performance of catalyst A. Figure 8 shows the effect of time on-stream on the gas production. For the first 10 h, H₂, CO, and CO₂ gas production was constant. For the next 5 h, a slight decrease in gas production was observed. There is a drop in the initial activity of the catalyst. Initially, the average carbon to gas conversion was ~100%, which decreased to ~90% at the end of the run. Carbon deposited on the catalyst was estimated to be 0.024 g/g of catalyst. The gas productions from the catalytic reforming and gasification of pure glycerol are given in Table 3. Selectivity (moles of methane/total moles of product gases) toward methane for LTR and gasification was found to be ~12%. This indicates that, at LTR, hydrocarbons

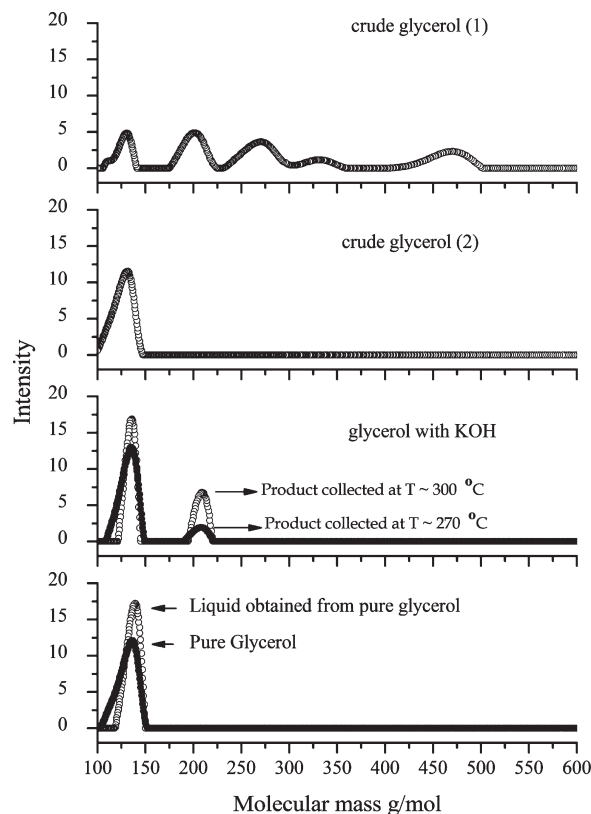


Figure 5. Molecular mass distribution of liquid products obtained after gasification from different glycerol feedstocks.

produced from the gasification of glycerol are not reformed, as it is limited by thermodynamics.

Evaluation of Catalysts Performance on Steam Reforming of Crude Glycerol 2. HTR conditions were chosen to evaluate the catalysts performance on steam reforming of crude glycerol 2 because

- it contains ~2% of organic impurities which may be easier to reform at HTR conditions.
- no loss of activity or no CH₄ was observed from the gaseous product obtained from steam reforming of pure glycerol using catalyst A at HTR conditions.

Two nickel-based commercial steam reforming catalysts (catalysts A and B) were chosen for the steam reforming of crude glycerol 2. Figure 9 shows two consecutive runs of crude glycerol 2 and pure glycerol (with 4 wt % KCl) steam reforming, which were done at similar process conditions ($T = 800$ °C, $S/C = 3$, $GC_1HSV = 600$ h⁻¹). KCl was added to pure glycerol (~4 wt % KCl) to study the effect of inorganic impurities during steam reforming. This is to differentiate the effect of organic and inorganic impurities present in the crude glycerol 2.

In the first run for catalyst A, a high gas production for H₂ = 1.25 Nm³/kg dry feed, CO = 0.28 Nm³/kg dry feed, and CO₂ = 0.38 Nm³/kg dry feed was reached. The gas production was slowly decreased at the end of 25th hour to H₂ = 1.10 Nm³/kg dry feed, CO = 0.23 Nm³/kg dry feed, and CO₂ = 0.37 Nm³/kg dry feed. CH₄ was continuously increased and reached a steady-state value of 0.044 Nm³/kg dry feed. A similar trend was also observed for C₂₋₃ gases. It should be noted that, from the gasification of crude glycerol 2, CH₄ and C₂₊ were found to be 0.067 Nm³/kg dry feed and 0.013 Nm³/kg dry feed, respectively,

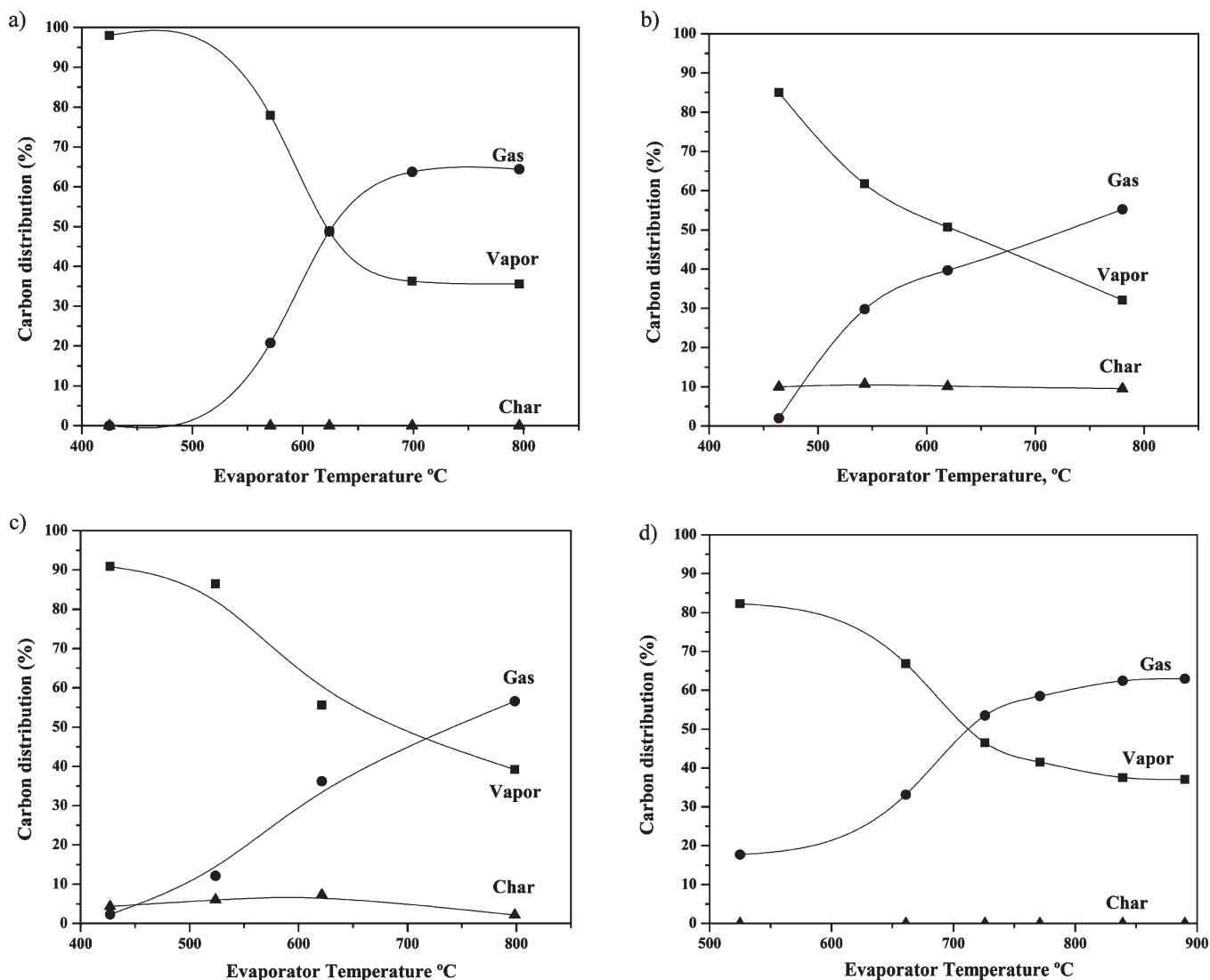


Figure 6. Carbon distribution over the gas, vapor, and char during the gasification of glycerol: (a) pure glycerol, (b) glycerol with KOH, (c) crude glycerol 1, and (d) crude glycerol 2.

at 770 °C and $S/C = 1$ and $C/\text{gas} = 62\%$. This indicates that catalyst A still has reasonable oxygenates reforming activity; nevertheless, its hydrocarbon reforming activity has been lost to a certain extent. By comparing the gasification (given in Table 3) and the reforming of crude glycerol 2, it is observed that methane obtained from the gasification is converted 68% at the end of 25th hour.

Crude glycerol 2 flow was stopped, and catalyst A was regenerated using a mixture of air and nitrogen at 800 °C and reactivated using H_2 at 800 °C. No appreciable amount of coke on catalyst A was measured. In the second run, the activity of catalyst A was not retained at its initial high activity. CH_4 production was raised rapidly, as compared to the first run. The average carbon to gas conversion dropped from 98 to 91% at the end of the second run. No CH_4 was observed for 3 h for catalyst A when pure glycerol was used as feedstock, whereas for crude glycerol 2, CH_4 increased linearly initially and stayed constant after 20 h.

For catalyst B, gas production similar to that of catalyst A was attained, except that no CH_4 was observed in the first 10 h. CH_4

and C_{2-3} compounds were increased rapidly and reached a steady-state value of $0.018 \text{ Nm}^3/\text{kg}$ dry feed for CH_4 and $0.0018 \text{ Nm}^3/\text{kg}$ dry feed for C_{2+} compounds, which is almost three times less than that obtained for catalyst A; that is, $\sim 88\%$ conversion of methane based on its selectivity from reforming and gasification experiments was obtained. After burnoff and reactivation, the activity of the catalyst was retained; nevertheless, CH_4 and C_{2-3} compounds were rapidly increased. Average carbon to gas conversion trends similar to those for catalyst A were noticed for catalyst B. As shown in Figure 9c, no CH_4 was observed for catalyst A when KCl was added to pure glycerol, whereas for crude glycerol 2, CH_4 was linearly increased from the beginning of the experiment. This indicates that the organic impurities present in crude glycerol 2 are solely responsible for reducing the initial activity of catalyst A.

Catalyst Analysis. The BET surface area, pore size distribution and Ni dispersion by chemisorption of fresh and used catalyst A are reported in Table 4.

There is a progressive drop in the BET surface area of catalyst A from 19.9 to $6.5 \text{ m}^2/\text{g}$. However, it is noticeable that surface

area reduction also takes place during methane steam reforming at similar conditions. The surface area after methane steam reforming is comparable with low temperature reforming of glycerol. Because a reduction in the measured BET surface area might also be caused by obstruction in the pore system, the pore volume of the catalysts was determined before and after the reaction. No appreciable loss in pore volume was observed for used catalyst after steam methane reforming. However, there is appreciable loss in volume after steam reforming of crude glycerol 2 and low temperature reforming of pure glycerol. The pore volume was reduced further after the catalyst is regenerated. Because there is a considerable decrease in pore volume, the blockage of pores contributes to the reduction in surface area. The properties of the support and choice of promoters may also have an influence on pore volume reduction on the catalyst.²⁰

The Ni surface area, metal dispersion, and Ni particle size were found from the hydrogen chemisorption measurements before and after the steam reforming of glycerol. It is observed that the quantity of hydrogen adsorbed, metal dispersion, Ni metal surface area, and Ni particle diameter were found to be similar

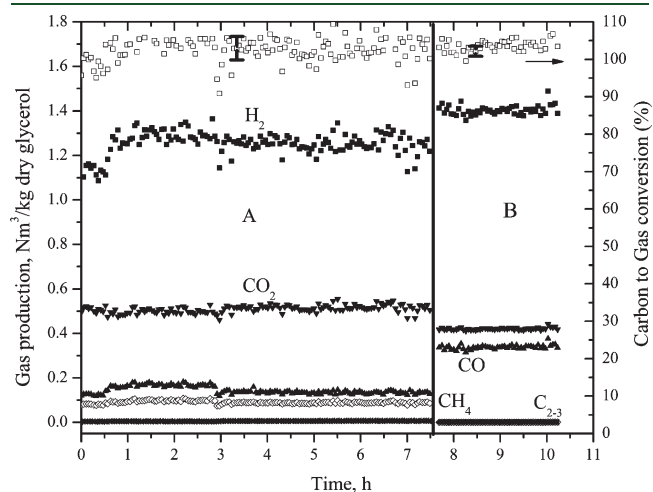


Figure 7. Pre-reforming and steam reforming of glycerol (a) LTR, S/C = 3, $T_{\text{cat}} = 588$ °C and (b) HTR, S/C = 3, $T_{\text{cat}} = 787$ °C. For all cases, $GC_1\text{HSV} = 838$ h⁻¹.

between steam methane reforming and low temperature reforming of glycerol. However, there is a drastic reduction in the metal dispersion, quantity of hydrogen adsorbed, and Ni metal surface area when crude glycerol 2 was used as a feedstock. Ni particle size has grown from ~349 to 801 nm. The increase in Ni particle size is attributed to sintering that depends on Ni loading and support properties. After regeneration, catalyst A never retained its high initial activity. This may be due to the following reasons:

- obstruction in the pore system of the catalyst caused by coke deposition.
- coke deposited as a result of the presence of impurities present in the crude glycerol 2.

This gives an indication that catalyst A is designed to work effectively either at low temperature (<600 °C) or for high purity feedstocks or a combination of both.

For catalyst B, BET surface area and pore volume remained constant; however, the quantity of hydrogen adsorbed and Ni metal surface area reduced drastically. Ni particle diameter is increased from 199 to ~4000 nm. After regenerating the catalyst, the initial activity of unpromoted catalyst is retained. Therefore, sintering is not considered to be important, whereas coke deposition due to organic impurities on the catalyst is a critical design parameter.

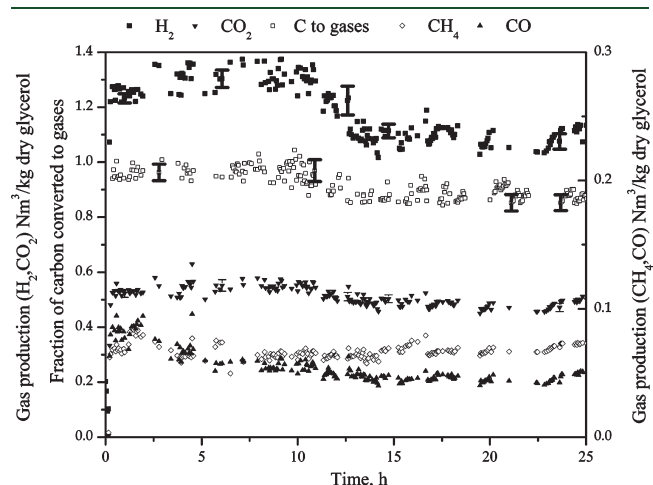


Figure 8. Long duration pre-reforming of glycerol at $T = 590$ °C, S/C = 3.5, $GC_1\text{HSV} = 543$ h⁻¹.

Table 3. Comparing Reforming and Gasification of Pure and Crude Glycerol 2

feedstock	pure glycerol	pure glycerol	pure glycerol	pure glycerol	crude glycerol 2
expt	LTR ^a	HTR ^b	gasification	gasification	gasification
S/C	3	3	1	1	1
gasification temp. (°C)	526	548	570	796	839
reactor temp. (°C)	588	787			
$GC_1\text{HSV}$ (hr ⁻¹)	838	838			
	gas prod. (Nm ³ /kg dry feed) at steady state ^c				
H ₂	1.26 (1.38)	1.40 (1.40)	0.05	0.63	0.41
CH ₄	0.09 (0.05)	0 (5e-4)	0.02	0.06	0.067
CO	0.14 (0.15)	0.34 (0.31)	0.09	0.22	0.28
CO ₂	0.51 (0.54)	0.42 (0.43)	0.014	0.18	0.06
C ₂₊	0.0055 (0)	0	0.017	0.01	0.01
C _g (%)	103	104	20	64	62

^aLTR, low temperature reforming (pre-reforming). ^bHTR, high temperature reforming (primary reforming). ^cEquilibrium values are given in parentheses for the respective process conditions.

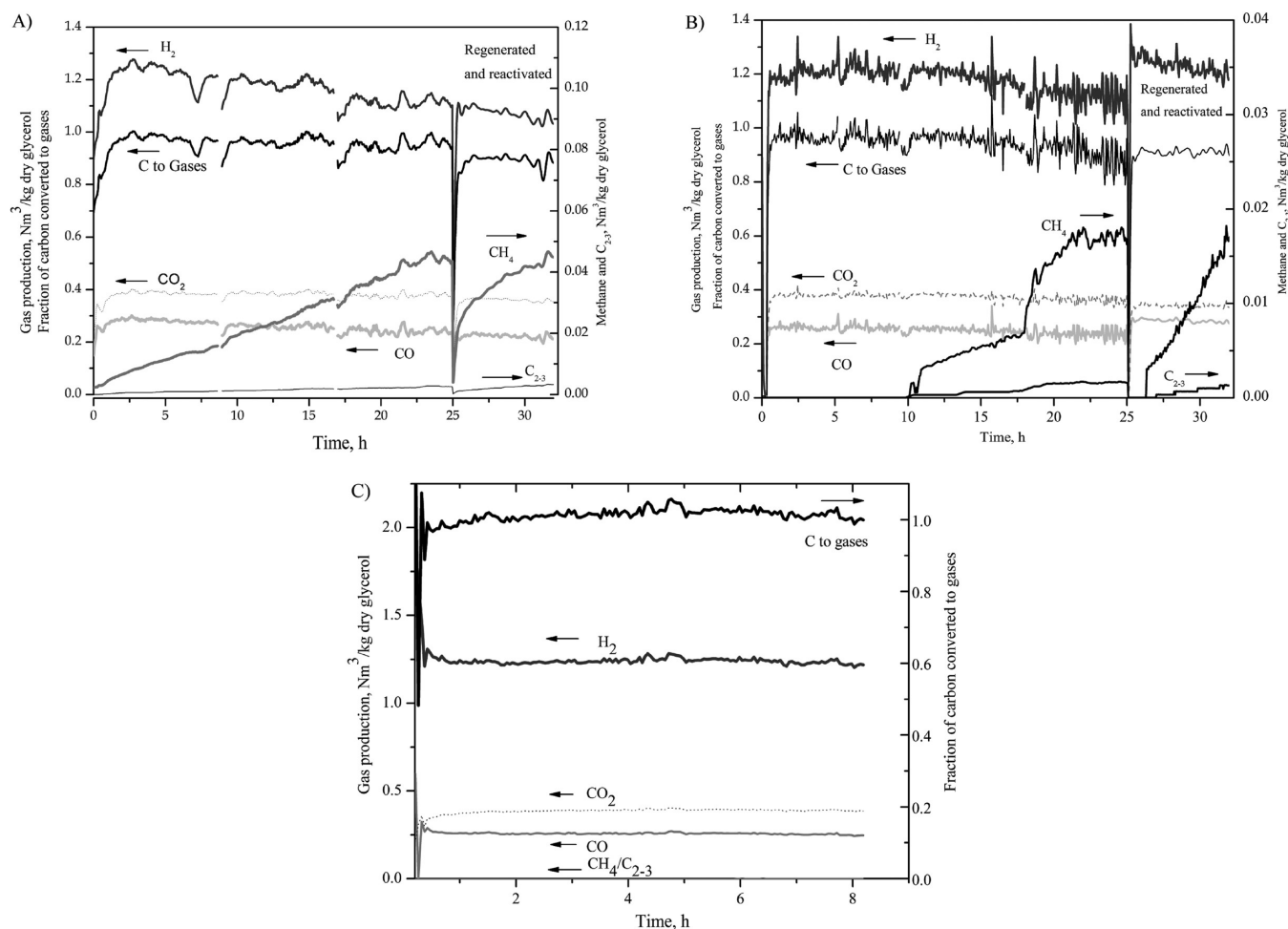


Figure 9. Steam reforming of crude glycerol 2: (a) catalyst A, $S/C = 3$, $T_{\text{cat}} = 804$ °C, and (b) catalyst B, $S/C = 3$, $T_{\text{cat}} = 795$ °C. (c) Pure glycerol with 4% KCl by weight, catalyst A, $S/C = 3$, $T_{\text{cat}} = 803$ °C. For all cases $GC_1\text{HSV} = 600$ h⁻¹.

Table 4. Surface Area, Pore Size and Chemisorption Measurements of Fresh and Used Catalysts

catalyst	feedstock	BET (m ² /g)	pore volume (cm ³)	H ₂ adsorbed (cm ³ /g)	metallic surface area (m ² /g metal)	nickel particle size (nm)
catalyst A, fresh		19.9	0.049	0.089	1.93	349
catalyst A (25 h)	crude glycerol 2	7.3	0.034	0.048	1.03	653
catalyst A (after regeneration, 8 h)	crude glycerol 2	6.5	0.030	0.039	0.84	801
catalyst A (25 h, LTR)	pure glycerol	6.83	0.029	0.061	1.33	508
catalyst A (SMR)	methane	8.66	0.040	0.061	1.33	508
catalyst B, fresh						
catalyst B (25 h)		3.4	0.011	0.14	3.39	199
catalyst B A (after regeneration, 8 h)	crude glycerol 2	3	0.011	0.006	0.15	4458
	crude glycerol 2	2.1	0.006	0.007	0.17	3983

Hybrid Steam Reforming of Methane and Glycerol. In the hybrid reforming experiment, 28 wt % glycerol was co-reformed with 72 wt % methane on C₁ basis. The test was carried out for 4 h. Figure 10a shows the gas production obtained from the hybrid reforming experiment. Initially, there is a slight fluctuation in the gas productions due to the addition of hydrogen to keep the catalyst active. The gas production was almost constant over the period of 4 h. An average carbon recovery of ~97% was obtained.

Figure 10b shows the gas production obtained from three cases: (1) methane steam reforming; (2) hybrid reforming, and (3) glycerol steam reforming. The line indicates the equilibrium gas production obtained at 800 °C and $S/C = 3$. The gas production is expressed in mol of gas produced per carbon atom. For all the cases, the experimental values almost reached the equilibrium gas productions.

Implications on Glycerol Steam Reforming. The gasification of crude glycerol is summarized in Figure 11. Crude glycerol

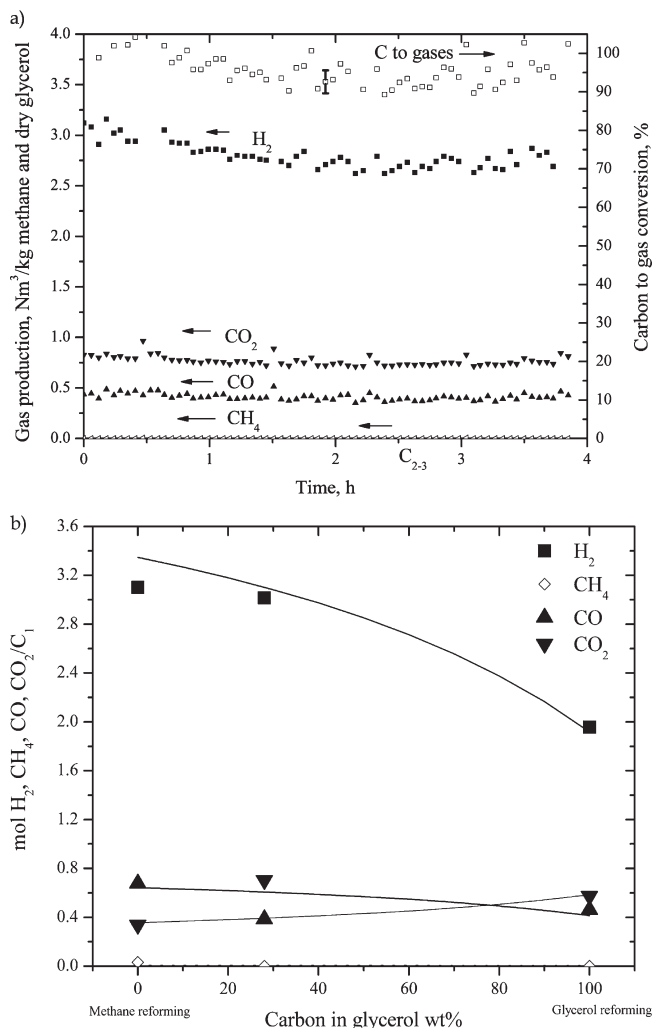


Figure 10. (a) Hybrid reforming of methane with pure glycerol, glycerol 28%, methane 72%. Pre-reformer: S/C \sim 15, $T = 590$ °C, GC1HSV = 516 h^{-1} . Primary reformer: S/C \sim 3, $T = 791$ °C, GC1HSV = 958 h^{-1} . (b) Comparison of methane, hybrid, and glycerol steam reforming with thermodynamic equilibrium. (Line represents thermodynamic equilibrium; points represent experimental values).

1 from the transesterification unit can be directly vaporized above 300 °C to produce vapors/gases. Due to the presence of KOH in the crude, carbon loss in the form of char \sim 10% is inevitable. The solid residue primarily consists of char and inorganics. On the other hand, crude glycerol 1 can be neutralized using an acid and evaporated further to prevent polymerization. In both the options, solid handling becomes mandatory; nevertheless, in option 1, there are possibilities of converting the char by steam gasification, because the activity of char may be high as a result of the presence of salts^{21,22} or it can be combusted to produce energy. To avoid solid handling in the steam reformer, the catalyst for transesterification has to be changed to a heterogeneous catalyst instead of KOH.

Based on the process conditions used (1 bar, \sim 800 °C, and $\tau \sim$ 3 s) for gasification experiments, the complete conversion of glycerol to gases is possible only at higher temperatures (\sim 800 °C). Therefore, in the hybrid reforming process, the gasification of glycerol can be combined with a primary reformer, where methane is co-reformed with gases produced from the gasification step,

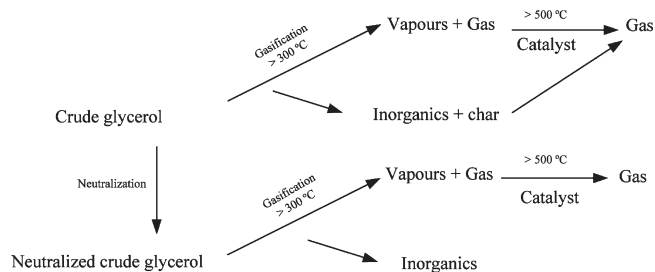


Figure 11. Mechanism of glycerol gasification.

only when complete conversion is achieved via gasification. This may eliminate the pre-reforming process. Therefore, the choice should be made between the high temperature gasification or low temperature steam reforming. However, results from pre-reforming at low temperature using commercial steam reforming catalyst were promising to use as an upstream step for primary reforming. Moreover, the catalyst in the pre-reformer acts as a “guard bed” and may protect the primary reforming catalyst. To utilize these liquids on a larger scale, a flexible pre-reformer that handles crude glycerol (treated or untreated) is required.

From the catalyst point of view, the promoted Ni/Al₂O₃ catalyst suffers initial activity loss, which was not retained after regeneration. However, the unpromoted catalyst has retained its activity after regeneration. The dominant impurities present in the crude glycerol are FAMES, diglycerides, triglycerides, and alkali salts. Our experimental results indicated that reforming pure glycerol or glycerol with chlorides does not affect the activity of the catalyst, whereas organic impurities affected the initial activity of commercial promoted Ni/Al₂O₃ catalyst. However, commercial unpromoted Ni/Al₂O₃ catalyst also loses its activity. Therefore, a frequent regeneration step is necessary to utilize crude glycerol for methanol production. However, the role and choice of promoters on the commercial catalyst to reform crude glycerol has to be investigated further.

CONCLUSIONS

The various stages of hybrid steam reforming such as gasification of crude glycerol, low temperature steam reforming (pre-reforming), and co-reforming glycerol with methane were studied. The main conclusions can be summarized as follows:

- The presence of alkali hydroxides (NaOH and KOH) in the glycerol enhances the char formation via polymerizing the intermediates in the liquid phase. Higher molecular mass intermediates formed near the boiling point of glycerol are responsible for char formation.
- Pure glycerol and neutralized crude glycerol can be gasified with no loss of carbon as char. Solid handling, in processing neutralized glycerol (salts) and untreated glycerol (inorganics and char), becomes mandatory to scale up evaporator/gasifier.
- To upgrade realistic feedstocks, such as crude glycerol, to produce synthesis gas via steam reforming, a flexible steam reformer is required.
- Pure glycerol can be reformed using a commercial catalyst with no loss in the activity. For a realistic feedstock such as crude glycerol, organic impurities such as FAME, diglycerides, and triglycerides deteriorate the initial activity of the commercial steam reforming catalyst.

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