

Production of hydrogen-rich gas via reforming of iso-octane over Ni–Mn and Rh–Ce bimetallic catalysts using spray pulsed reactor

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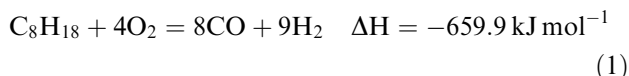
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The conversion of hydrocarbon fuels such as gasoline and diesel is a potential source for hydrogen production towards various fuel cell systems. A novel spray pulsed mode reactor to create alternate wet and dry conditions on the catalyst surface has been used in this study to enhance the rates of hydrogen production compared with the solid-gas phase reaction due to the improvement of the catalyst reactant contact. The production of hydrogen-rich gas by reforming of iso-octane (2,2,4-trimethylpentane) in the presence of steam and air has been studied at 600 and 700 °C over Ni–Mn and Rh–Ce bimetallic catalysts supported on alumina mesh. The feed rate of iso-octane was varied from 0.553 to 5.53 m mol min⁻¹ by controlling pulse injection in terms of the width and frequency of injection of iso-octane. Based on the product analysis optimized condition for higher hydrogen production and high H₂/CO ratio has been deduced.

KEY WORDS: iso-octane reforming; hydrogen production; bimetallic catalysts; pulse spray injection.

1. Introduction

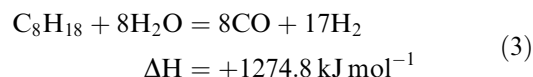
The reforming of fuels such as gasoline and diesel to produce hydrogen-rich gas leads to the possibility of on-board production of hydrogen for automobile emission reduction applications [1]. The iso-octane closely represents gasoline and has been used in several studies as a model hydrocarbon for reforming reactions [2–4]. The catalyst assisted conversion of iso-octane to produce hydrogen is possible via, partial oxidation, steam reforming or CO₂ reforming [5–7]. The type of reaction depends on the equivalence ratio and steam to carbon ratio used in the reaction. This in turn governs the product formation.



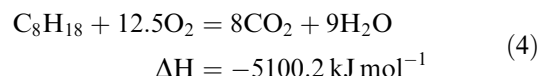
The Partial oxidation of iso-octane produces H₂ and CO (reaction 1). The formation of CO is not desirable for hydrogen production for fuel cell applications therefore the reaction of partial oxidation is coupled with water gas shift (WGS) reaction (reaction 2). The steam to carbon ratio governs the possible extent of the WGS reaction and thus production of additional hydrogen. However introduction of larger quantities of water into the reaction is energy intensive and thus a proper steam to carbon ratio is very important.



Where as the steam reforming reaction proceeds as;



Since the steam reforming is endothermic reaction the exothermic reactions of partial oxidation or complete oxidation (reaction 4) of part of the iso-octane may be used for generating the required energy.

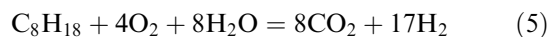


Steam reforming shows the highest hydrogen production efficiencies but the requirement of large energy input due to the endothermic nature of the reaction is considered to be the major drawback. Partial oxidation needs external cooling and generates a high concentration of CO. The autothermal reforming of hydrocarbon with air in the presence of steam proceeds in two different reactions at particular conditions. The exothermic reaction of partial oxidations forms H₂ and CO as products while providing energy for the endothermic steam reforming reaction. Two side reactions that may occur are water gas shift reaction to produce more H₂ and consume the CO generated and the methanation reaction. Thus autothermal reforming provides hydrogen-rich gas with lower concentrations of CO [8]. The various reforming reactions are generally carried out separately, some of the recent studies reported the reforming of hydrocarbons in simultaneous presence of steam, air and/or CO₂ [9,10]. The targeted reaction in this study is autothermal reforming (reaction 5) which is

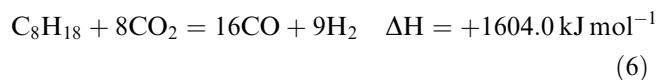
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a combination of partial oxidation and steam reforming reaction. The steam to carbon ratio was kept at 1 and the equivalence ratio of 0.32 was used in the reaction with simultaneous feeding of steam and air to the reactor. The reaction is expected to be autothermal with no net energy change.



Iso-octane may also be converted to hydrogen using carbon dioxide reforming (reaction 6). The steam reforming is generally preferred as it is relatively fast reaction than CO_2 reforming.



The product distribution of the conversion of iso-octane depends on the catalyst used and varies with parameters such as steam to carbon ratio, carbon to oxygen ratio and the reaction temperatures. These parameters are generally selected in such a way that to avoid formation of coke on catalyst and also to minimize the methane production [11–14]. Since in this study a pulsed feed mode was used for iso-octane the steam/carbon and equivalence ratios may be slightly differing at the catalyst surface during alternate wet and dry conditions. This may have some effect on product distribution. In this paper we have discussed the product distribution at various feed conditions.

In the case of a liquid reactant such as iso-octane and solid catalyst, the contact between catalytic sites and reactant is difficult to achieve. The catalyst–reactant contact may be improved by vaporizing the liquid and

introducing it with a carrier gas. When liquid reactant is directly injected in atomized form on the catalyst surface the catalyst gets enriched with reactant and results in a better contact. However there is a possibility of forming wet conditions due to liquid pools on the catalyst surfaces. Feeding of atomized liquid reactant in pulses and alternatively creating wet and dry conditions on heated solid catalyst surface improves the yield of the reaction. Use of the unsteady state pulse spray has been demonstrated for improving the rate of reaction by a magnitude higher than the rate for conventional flow reaction conditions [15,16]. A spray pulse reactor has been used in this study for atomization of iso-octane and for improving the contact between reactant and the catalyst.

In this paper we report the experimental findings obtained for promoting of the reforming of iso-octane over Ni–Mn, and Rh–Ce bimetallic catalysts with a spray pulse reactor by the controlled pulse width and period of iso-octane injection.

2. Experimental setup

The details of the experimental set-up are shown in figure 1. The main reactor is a vertical cylinder made of stainless steel. Iso-octane (2,2,4-trimethylpentane, 99% pure, Wako Pure Chemicals, Japan) was introduced into the reactor through an atomizer fitted at the top end. The pulse width and the frequency for supply of iso-octane through atomizer were controlled by a frequency generator and pulse width controller. Pressure in the fuel supply line for a desired spray pattern was maintained by a high-pressure supply system. The fuel

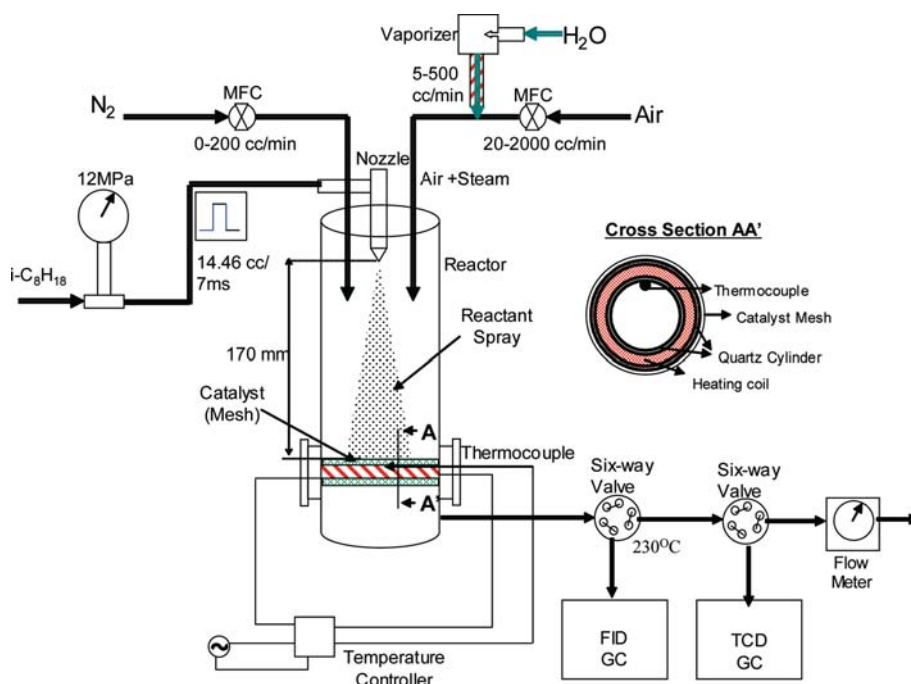


Figure 1. Experimental setup for spray-pulse catalytic reactor system.

pressure maintained in the fuel supply line was 12 MPa. Carrier gas (N_2) and oxidizer (Air) were introduced from separate inlet tubes from the top of the reactor. Mass flow controllers maintain the flow rates of all gases. Steam was added through a micro-feeder pump and a vaporizer.

The bimetallic catalysts Ni–Mn (10:1 wt basis) and Rh–Ce (6:1 wt basis) were proprietary catalysts supplied by DENSO Corporation Japan. The catalyst were supported on alumina mesh and wrapped over a quartz tube. A tungsten wire coil was used to provide heating to the catalyst. The thermocouple and temperature controller maintained the temperature of the catalyst. Fuel was sprayed over the catalyst mesh while maintaining the flow of feed gases. N_2 was used as swept gas and the flow was maintained at 200 mL min^{-1} . Reforming of iso-octane was studied by monitoring the concentration of outlet gases. Hydrocarbon analysis was conducted using FID GC (Shimadzu GC-14B) and H_2 , CO, and CO_2 were monitored using TCD-GC (Shimadzu GC-8A). The packed column used in TCD GC was Shin-carbon–ST obtained from Shimadzu; the column in FID GC was Porapack-P. A micro GC (model HP G2890A) was used for rapid analysis of products. Micro GC has Molecular Sieve 5A, 10 m column.

3. Results and discussion

3.1. Hydrogen production rates

The iso-octane was injected into the reactor as an atomized spray using a fine nozzle and by maintaining a pressure of 12 MPa in the fuel supply line. Controlling the pulse injection frequency and pulse width dose of iso-octane was varied. The catalyst was heated at 600 and 700 °C to maintain the reaction temperatures. The hydrogen production rates were observed for about 2.5 h with analysis at the intervals of 3 min. The average hydrogen production rates at equilibrium on Ni–Mn (10:1 wt basis) bimetallic catalyst with varying feed rates of iso-octane have been shown in figure 2. At the reaction temperature of 600 °C as the feed rate of iso-octane

is increased from 0.553 to $3.32 \text{ m mol min}^{-1}$ the average rates of hydrogen production observed to be increasing from 1.53 to $7.31 \text{ m mol g}^{-1} \text{ min}^{-1}$. Further increase in feed rate of iso-octane to $5.53 \text{ m mol min}^{-1}$ caused the rate of hydrogen production to decrease to $4.32 \text{ m mol g}^{-1} \text{ min}^{-1}$. The increase in the rate of hydrogen production till iso-octane dose of $3.32 \text{ m mol min}^{-1}$ is due to the increase in amount of iso-octane injected which still could evaporate quickly at the heated catalyst surface and may have formed vapor phase with high partial pressure of iso-octane in the catalyst vicinity. After the reforming reaction and during the interval between pulse injections the products and unreacted iso-octane is removed easily due to the high temperature of the catalyst surface. Thus during the dry condition on catalyst surface, it becomes dry and clean. The easy removal of unreacted iso-octane and product gases helps in higher hydrogen production rate. However at higher feed rate may be the rate of the evaporation of iso-octane is not quick enough and may have led to formation of liquid pool. This might be the reason of decreasing the rate of hydrogen production at the feed rate of $5.53 \text{ m mol min}^{-1}$. When the reaction temperature was increased to 700 °C the rate of hydrogen production observed to be higher at all feed rates as compared to the hydrogen production rates at 600 °C. A rate of $22.5 \text{ m mol g}^{-1} \text{ min}^{-1}$ of hydrogen production was observed at the feed rate of $0.553 \text{ m mol min}^{-1}$ of iso-octane, where as the rate was increased to $68.28 \text{ m mol g}^{-1} \text{ min}^{-1}$ at the feed rate of $1.66 \text{ m mol min}^{-1}$ of iso-octane. Increase in feed rate to $3.32 \text{ m mol min}^{-1}$ and further to $5.53 \text{ m mol min}^{-1}$ of iso-octane resulted in the decrease of the rate of hydrogen production at 700 °C.

When, hydrogen production rates were compared on different feed conditions in terms of partial pressure of iso-octane and partial pressure of steam as shown in table 1. At the heating temperature of 600 °C the hydrogen production rate was observed to be increasing with increase in iso-octane partial pressure. The hydrogen production rate at iso-octane partial pressure of

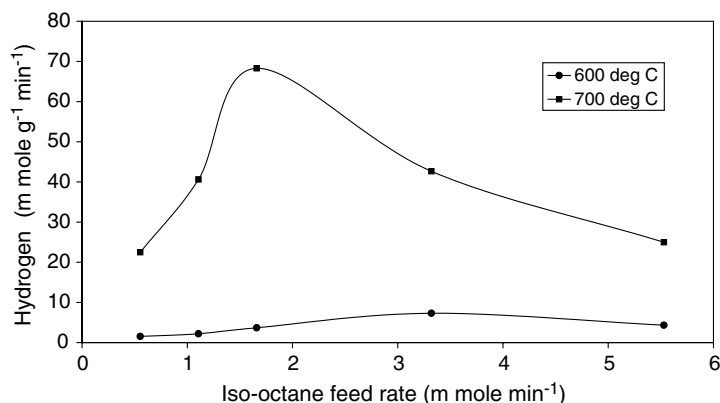


Figure 2. Hydrogen production rate at various feed rates of iso-octane over Ni–Mn at 600 °C and 700 °C.

2.34 kPa (steam partial pressure 13.88 kPa) was $1.53 \text{ m mol g}^{-1} \text{ min}^{-1}$ and at iso-octane partial pressure of 3.42 kPa (steam partial pressure 20.06 kPa) was $7.31 \text{ m mol g}^{-1} \text{ min}^{-1}$. At 700 °C and at the partial pressure of iso-octane 3.13 kPa with corresponding steam partial pressure of 18.38 kPa the hydrogen production rate was maximum over Ni–Mn catalyst i.e. $68.27 \text{ m mol g}^{-1} \text{ min}^{-1}$. The corresponding iso-octane feed rate was $1.66 \text{ m mol min}^{-1}$ (0.552 m mol pulse, 20 s intervals). The catalysts activity was compared with the steam reforming of the iso-octane using Ni or Rh based monometallic or bimetallic catalysts reported in the literature. Prahars et al. [2] reported H_2 production of 0.207 and $0.32 \text{ m mol g}^{-1} \text{ min}^{-1}$ over Ni/ α - Al_2O_3 catalyst at 350 °C for varying steam partial pressure 23.77 kPa (corresponding iso-octane partial pressure 1.23 kPa) and 53.86 kPa (corresponding iso-octane partial pressure 1.27 kPa) respectively. Murata *et al.* [3] reported H_2 production of 0.1, 0.092 and $0.23 \text{ m mol g}^{-1} \text{ min}^{-1}$ at 550 °C over Rh/ Al_2O_3 , Rh–Pt/ Al_2O_3 , Rh–Fe/ Al_2O_3 catalysts respectively. The bimetallic catalysts used under the pulsed spray condition in this study have exhibited higher rates of hydrogen production.

At the iso-octane feed rate of 0.553 and $1.107 \text{ m mol min}^{-1}$ the catalyst activity was observed to be higher initially over Ni–Mn catalyst and subsequently after about 20 min from the start of the reaction remained constant for about 2.5 h. On the same feed rate the hydrogen production rate for Rh–Ce remained constant. Thus the catalyst shows a good stability for the iso-octane reforming at the lower feed rates. At higher feed rates the hydrogen production was observed to be steadily decreasing.

The pulse mode of injection of iso-octane used in this study has created the alternate wet and dry conditions on the catalyst surface and has promoted the hydrogen production. The period of wet condition and subsequent dry condition not only depends on the injection frequency but also on the control of the dose of iso-octane

in one pulse by changing pulse injection width. The variation in the catalyst activity at the different reaction temperatures may further be explained using the product analysis at various operating conditions as discussed in the later sections.

3.2. Iso-octane conversion

The iso-octane conversion was monitored during the reaction at the time interval of about 25 min and the average conversions at varying feed rates of iso-octane are shown in figure 3. With increase in the feed rate of iso-octane by ten times from $0.553 \text{ m mol min}^{-1}$ the conversion of iso-octane was decreased from 38 to 31% (carbon balance 98.5%) at the reaction temperature of 600 °C. The percentage conversion was 36% (carbon balance 98%), 37% (carbon balance 98.5%) and 34% (carbon balance 99.8%) at the iso-octane feed rate of 1.107, 1.66 and $3.32 \text{ m mol min}^{-1}$ respectively. At the higher reaction temperature of 700 °C the percentage conversion of iso-octane was considerably high and was in the range of 81–87% and the carbon balance was on the lower side i.e. at 0.553, 1.107, 1.66 and $3.32 \text{ m mol min}^{-1}$ of iso-octane feed rate its was 80.5, 80.7, 87.8 and 88% respectively. The lower carbon balance particularly at higher temperature may be because of possible carbon formation on the catalyst surface. The conversion of iso-octane appears to be slightly dependent on the feed rate with a small change in conversion by increase in feed rates.

3.3. Effect of spray pulsed feed conditions on product distribution in the iso-octane reforming reaction over Ni–Mn

The reforming of higher hydrocarbons such as iso-octane is a complex phenomenon and involves several reactions (reaction 1–6) based on the steam to carbon ratio and equivalence ratio. One of the approaches for hydrocarbon reforming given by Savage [17] proposes that the hydrogen production from hydrocarbon occurs

Table 1
Dependencies of hydrogen production rate on partial pressure of iso-octane and partial pressure of steam

Catalyst	Iso-octane partial pressure (kPa)	Steam partial pressure (kPa)	Temperature (°C)	Hydrogen production rate ($\text{m mol g}^{-1} \text{ min}^{-1}$)
Ni–Mn	2.34	13.88	600	1.53
Ni–Mn	3.21	19.03	600	2.18
Ni–Mn	3.13	18.38	600	3.68
Ni–Mn	3.42	20.06	600	7.31
Ni–Mn	2.34	13.88	700	22.50
Ni–Mn	3.21	19.03	700	40.62
Ni–Mn	3.13	18.38	700	68.27
Ni–Mn	3.42	20.06	700	42.64
Rh–Ce	2.34	13.88	600	83.79
Rh–Ce	3.21	19.03	600	129.77
Rh–Ce	2.34	13.88	700	113.23
Rh–Ce	3.21	19.03	700	176.50

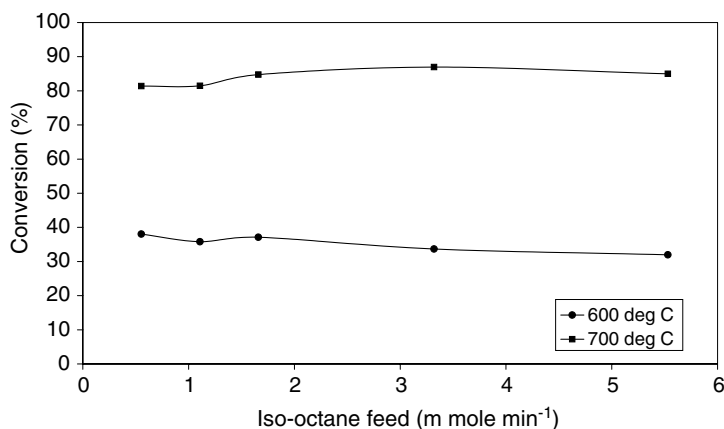


Figure 3. Iso-octane conversion at various feed rates of iso-octane over Ni–Mn at 600 °C and 700 °C.

through a number of pyrolysis reactions of the hydrocarbon includes homolytic dissociation of C–C bond, radical recombination, β -scission, isomerization, and hydrogen abstraction amongst the others. The magnitude of the C–H and C–C bond energies of the different bonds of the reactant molecule determines the kinetics and product distribution of pyrolysis reaction. Pyrolysis then may be followed by hydrogen desorption and carbon oxidation. In another approach by Kopasz *et al.* [18] it is thought that the iso-octane breaks into a string of lighter hydrocarbons from C1 to C4 by thermolysis and then the steam reforming of these lighter fractions occur on the catalyst surface.

In the present study although the feed flow of steam and air was maintained for set conditions (steam/carbon ratio 1, equivalence ratio 0.32), the iso-octane was injected in a pulsed mode. The pulsed injection of iso-octane creates a wet condition on catalyst surface with delivery of iso-octane followed by formation of a high partial pressure vapor phase in the vicinity of catalyst

surface and subsequently a dry condition on the catalyst surface. We have observed different product distribution at different feed conditions of iso-octane. The product distribution on Ni–Mn catalyst at the reaction temperature of 600 °C and 700 °C and at a feed rate of iso-octane equal to 0.553 m mol min⁻¹ (0.184 m mol pulse, 20 s intervals) is shown in figure 4. At 600 °C very small amount of hydrogen, methane and CO has been observed with the about 7 mol% of CO₂ (carbon balance 98.5%). The concentration of nitrogen and unreacted iso-octane in reactor outlet flow is not shown in product distribution and water quantities were not analyzed. The product distribution suggests that since oxygen is consumed probably partial or complete oxidation of iso-octane has occurred and resulted into production of hydrogen at 600 °C. Also there may some contribution from WGS reaction at this temperature of 600 °C as H₂/CO ratio observed was as high as 5.5 as shown in figure 5(a). Since practically no other hydrocarbons C2 to C4 have been observed it may be assumed

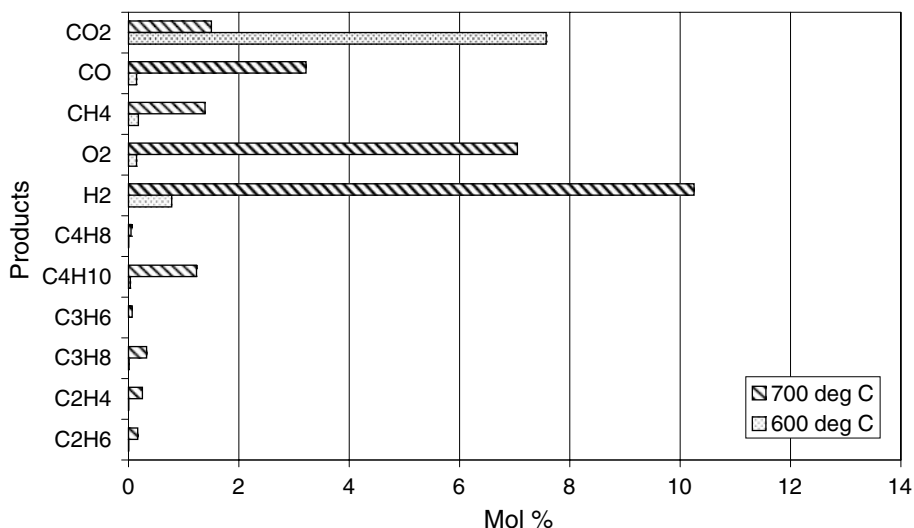


Figure 4. Product distribution over Ni–Mn at 600 °C and 700 °C at iso-octane feed rate of 0.553 m mol min⁻¹.

that the thermolysis of the iso-octane has occurred only to a small extent at 600 °C and the smaller fractions formed has undergone the steam reforming. Since the steam reforming is favorable at higher temperature at reaction temperature of 700 °C hydrogen was the major product. Observed increase in amount of CO at 700 °C as compared to at 600 °C indicates that the reaction may have proceeded following partial oxidation and steam reforming. The H_2/CO ratio has been lowered at the higher temperature may be attributed to suppression of WGS reaction. The appearance of C2 to C4 hydrocarbons suggest that as proposed by Kopasz [19] the part of iso-octane undergone thermolysis and followed by steam reforming. The primary reforming products such as methane and butane are major in these lighter hydrocarbons as compared to small amounts of secondary reforming products such as ethane, ethylene or propane.

Similar trend for product distributions has been observed when the iso-octane dose was increased to $1.107 \text{ m mol min}^{-1}$ (0.184 m mol pulse, 10 s intervals) and $1.66 \text{ m mol min}^{-1}$ (0.552 m mol pulse, 20 s intervals) as shown in figures 6 and 7 with corresponding increase in hydrogen production rate (figure 2). The highest activity of the hydrogen production of $68 \text{ m mol g}^{-1} \text{ min}^{-1}$ was observed at the iso-octane feed

rate of $1.66 \text{ m mol min}^{-1}$ and the reaction temperature of 700 °C. The hydrogen selectivity observed was also highest at about 70% at this feed rate as shown in figure 5(b). The H_2/CO ratio was observed to be increasing with feed rate upto $3.32 \text{ m mol min}^{-1}$ and was highest at this feed rate for reaction temperatures of 600 °C and 700 °C. However the lower hydrogen selectivity indicates that the CO may have also been oxidized to CO_2 , which may also be evident from the nearly complete consumption of oxygen. About 100% consumption of oxygen is reported in autothermal reforming with steam to carbon ratios more than 1.5 or 2 [10]. In this study the steam to carbon ratio is equal to 1 and therefore may some amount of oxygen is consumed towards CO oxidation. Since the hydrogen selectivity has been decreased there may be the possibility of methanation reaction at this feed condition of $1.107 \text{ m mol min}^{-1}$ (figure 6). However the concentration of methane is not very high as compared to other conditions and therefore methanation may not be very significant. At the reaction temperature of 700 °C and feed rate of $1.66 \text{ m mol min}^{-1}$ the H_2/CO ratio is nearly same as the stoichiometric H_2/CO ratio of 2.1 in steam reforming (reaction 3) which indicates that steam reforming may have been prevalent reaction at 700 °C and at this particular feed rate.

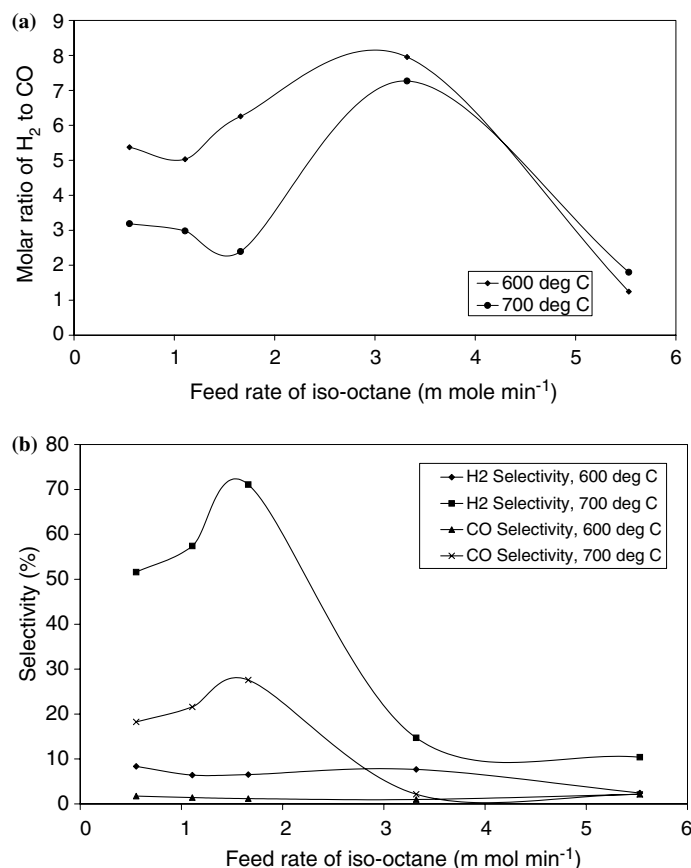


Figure 5. Effect of feed conditions on selectivities, (a) Molar ratio of H_2 to CO , (b) H_2 and CO selectivities.

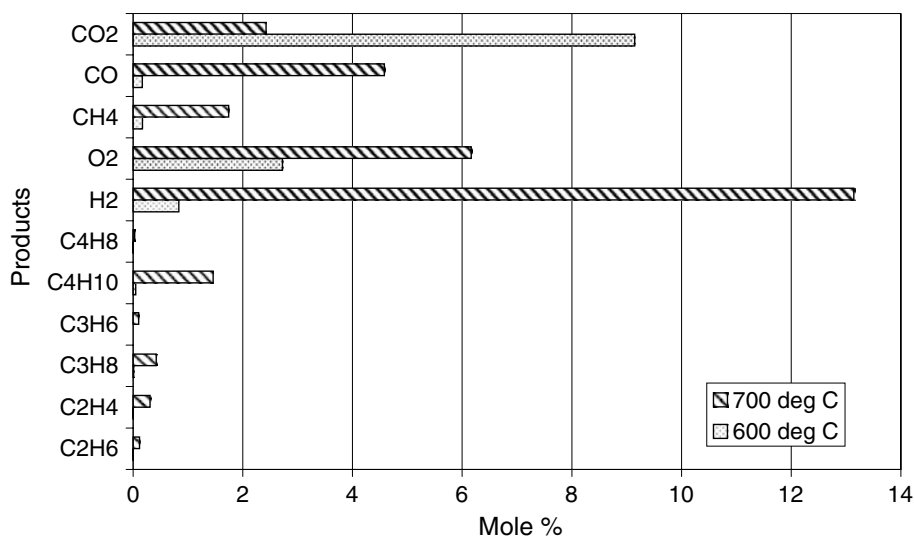


Figure 6. Product distribution over Ni-Mn at 600 °C and 700 °C at iso-octane feed rate of 1.107 m mol min⁻¹.

When the feed rate of iso-octane further increased to 3.32 m mol min⁻¹ (0.552 m mol pulse, 10 s intervals) the concentration of hydrogen in product decreased considerably and CO₂ levels have been observed to be increased at both the temperatures as shown in figure 8. There was a very small amount of oxygen observed suggesting under this feed condition the autothermal reforming has not occurred and mostly there could be oxidation of iso-octane followed by WGS reaction, as at these feed rates there is possibility of reduction in catalyst surface temperature due to liquid pool formation. The conversion of iso-octane to hydrogen is possible via pyrolysis and subsequent desorption of hydrogen and carbon oxidation. In case of figure 8, when feed rate of iso-octane was 3.32 m mol min⁻¹ we observed methane and also in small amount C₂, C₃ and C₄ hydrocarbons. Therefore although pyrolysis may also be the possible reaction since

higher CO₂ concentrations was observed we consider that at this particular feed rate oxidation of iso-octane might have occurred. The possible liquid pool formation might have caused resistance to mass transfer and the contact of oxygen and steam with catalyst might be difficult. Therefore catalyst activity was observed to be decreased at the higher feed rate of iso-octane. It suggest that the alternate wet and dry conditions created on catalyst surface using spray pulsed injection was having the effect on hydrogen production rate and product distribution. It may be possible to control the H₂/CO ratio and H₂ selectivity by manipulating feed conditions with respect to pulse injection frequency and width in pulse spray mode reactor. The feed rate of 1.66 m mol min⁻¹ (0.552 m mol pulse, 20 s intervals) and the reaction temperature of 700 °C are the optimum conditions for reforming of iso-octane over Ni-Mn to produce hydrogen.

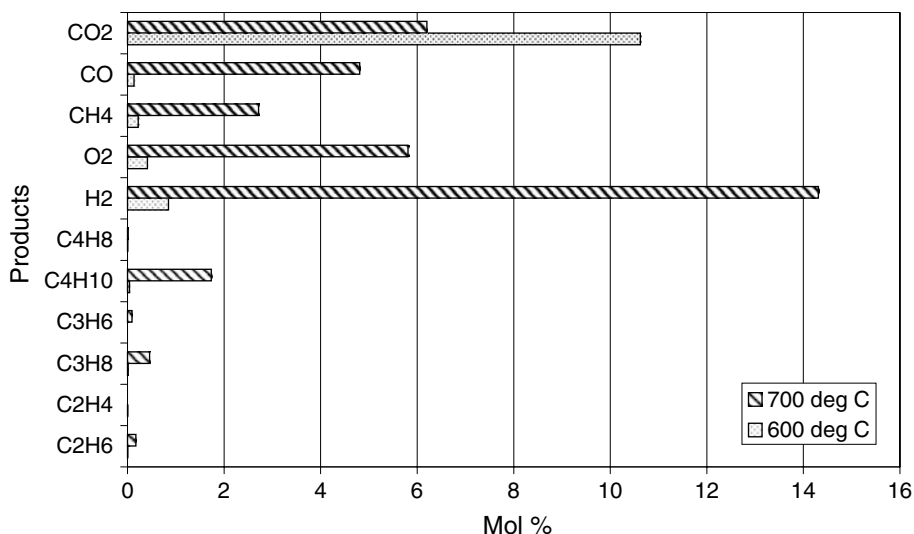


Figure 7. Product distribution over Ni-Mn at 600 °C and 700 °C at iso-octane feed rate of 1.66 m mol min⁻¹.

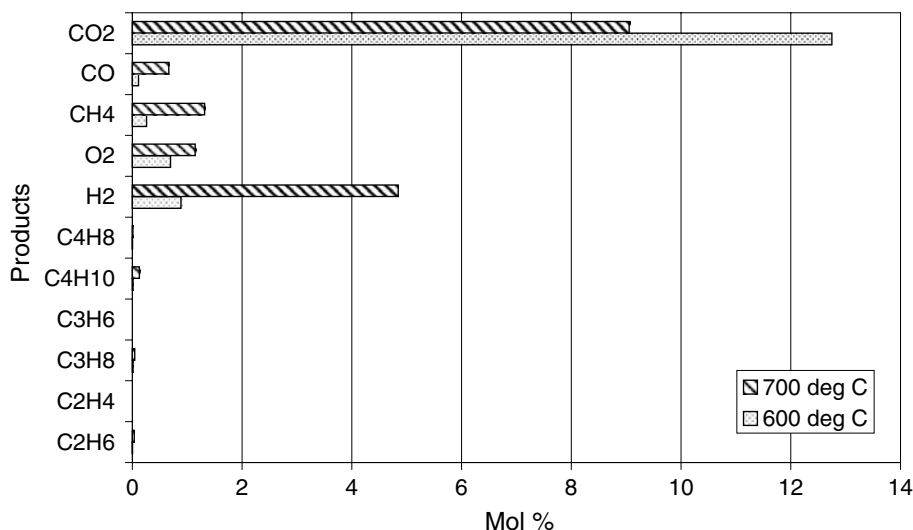


Figure 8. Product distribution over Ni-Mn at 600 °C and 700 °C at iso-octane feed rate of 3.32 m mol min⁻¹.

3.4. Product distribution over Rh-Ce

The product distribution observed for reforming of iso-octane over Rh-Ce catalyst under same conditions i.e. steam to carbon ratio equal to 1 and equivalence ratio 0.32 is depicted in figures 9 and 10 for iso-octane feed rates of 0.553 and 1.107 m mol min⁻¹ respectively. The hydrogen production at both the temperatures of 600 and 700 °C over Rh-Ce catalyst was higher than the rates of hydrogen production over Ni-Mn catalyst. No C₂ to C₄ hydrocarbons were practically observed the outlet stream contains methane, hydrogen, CO, CO₂, O₂ and unreacted iso-octane. At 600 °C the hydrogen production activity was 84 m mol g⁻¹ min⁻¹ (85% conversion, 39.55% selectivity) and 130 m mol g⁻¹ min⁻¹ (81% conversion, 32.69% selectivity) for iso-octane feed of 0.553 and 1.107 m mol min⁻¹ respectively. Whereas at 700 °C the hydrogen production was enhanced to 113 m mol g⁻¹ min⁻¹

(94% conversion, 48.37% selectivity) and 176 m mol g⁻¹ min⁻¹ (98% conversion 36.46% selectivity) for the same feed conditions. The Rh based catalysts are reported to have very high activity for reforming of hydrocarbons [20–23] and it is less likely to occur coke formation on Rh catalysts therefore lower steam to carbon ratios as in the case of present study are acceptable to Rh based catalysts. Because of the high activity of Rh, the steam reforming of the C₂ to C₄ products formed by thermolysis of iso-octane might have proceeded very efficiently on Rh-Ce catalysts.

4. Conclusions

The reforming of iso-octane was carried out on two different bimetallic catalysts viz Ni-Mn and Rh-Ce supported on alumina mesh. The catalyst activity and

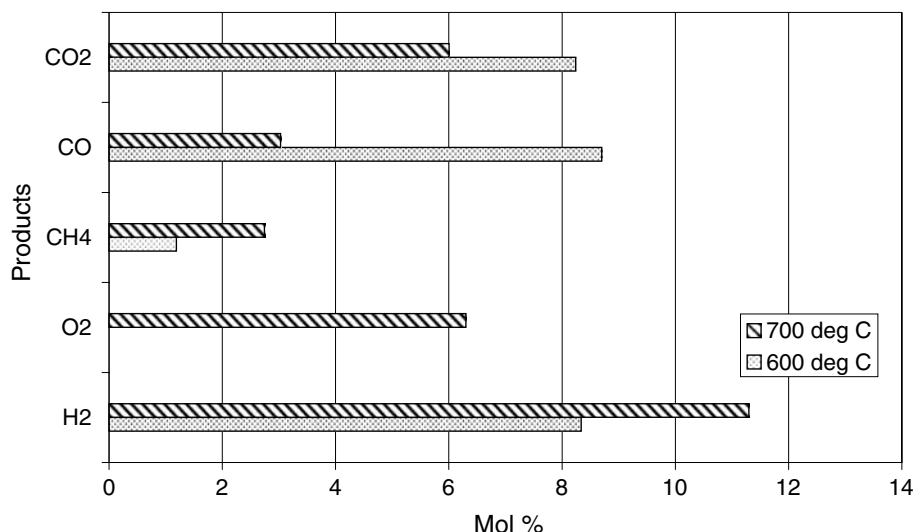


Figure 9. Product distribution over Rh-Ce at 600 °C and 700 °C at iso-octane feed rate of 0.553 m mol min⁻¹.

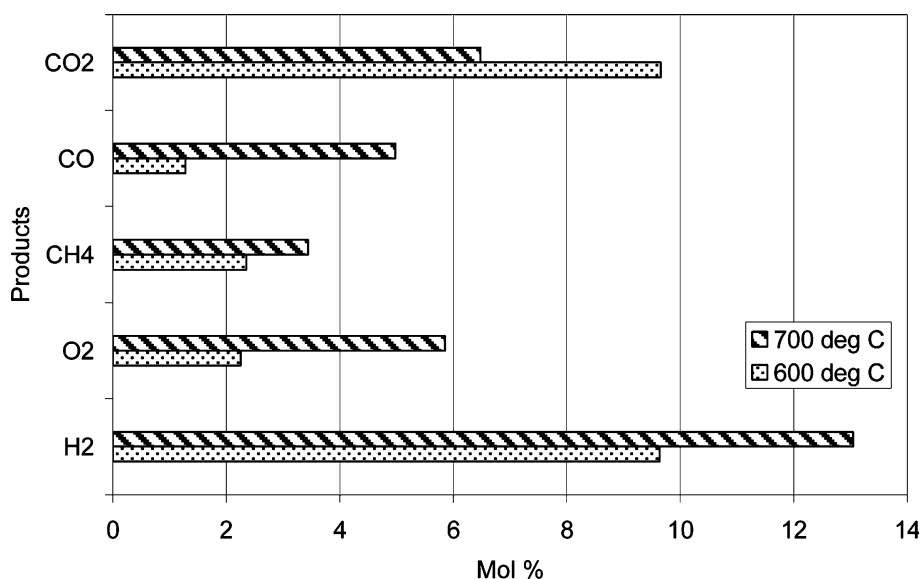


Figure 10. Product distribution over Rh-Ce at 600 °C and 700 °C at iso-octane feed rate of 1.107 m mol min⁻¹.

type of reactions possibly varied with variation in feed conditions with respect to pulse injection frequency and injection width. Similar to the dehydrogenation reaction of cyclohexane and decalin on Pt supported catalysts [15,16], it may be possible to deduce the optimizing the spray pulsed feed conditions for high rate of hydrogen production in the iso-octane reforming reaction. As in the case of present study the feed rate of 1.66 m mol min⁻¹ (0.552 m mol pulse, 20 s intervals) and the reaction temperature of 700 °C are the optimum conditions for reforming of iso-octane over Ni-Mn to produce hydrogen. The comparison of the catalyst activity under various pulse injection modes also suggests that the alternate wet and dry conditions created on catalyst is useful in enhancing the hydrogen production rate. A high H₂/CO ratio was obtained which is desirable for production of hydrogen from gasoline type hydrocarbons for the potential application to fuel cells.

Acknowledgments

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References

- [1] P.J. Berlowitz and P. Darnell, SAE Technical Paper 2000-01-0003.
- [2] A.A. Praharso, D.L. Adesina, S. Trimm and N.W. Cant, Chem. Eng. J. 99 (2004) 131.
- [3] K. Murata, L. Wang, M. Saito, M. Inaba, I. Takahara and N. Mimura, Energy Fuels 18 (2004) 122.
- [4] M.G. Sobacchi, A.V. Saveliev, A.A. Fridman, L.A. Kennedy, S. Ahmed and T. Krause, Int. J. Hydrogen Energy 27 (2002) 635.
- [5] S. Springmann, G. Friedrich, M. Himmen, M. Sommer and G. Eigenberger, Appl. Catal. A 235 (2002) 101.
- [6] G.A. Deluga, J.R. Salge, L.D. Schmidt and X.E. Verykios, Science 303 (2004) 993.
- [7] M. Pacheco, J. Sira and J. Kopasz, Appl. Catal. A: Gen. 250 (2003) 161.
- [8] A. Ersoz, H. Olgun, S. Ozdogan, C. Gungor, F. Akgun and M. Tiris, J. Power Sources 118 (2003) 384.
- [9] T. Inui, K. Saigo, Y. Fujii and K. Fujioka, Catal. Today 26 (1995) 295.
- [10] V.R. Choudhary, B.S. Uphade and A.S. Mamman, Microporous and Mesoporous Materials 23 (1998) 61.
- [11] C. Palm, P. Crener, R. Peters and D. Stolten, J. Power Sources 106 (2002) 231.
- [12] S. Ahmed and M. Krumpelt, Int. J. Hydrogen Energy 26 (2001) 291.
- [13] J.R. Rostrup-Nielsen, in: *Catalysis Science and Technology*, J.R. Anderson and M. Boudart (eds), Vol. 5 (Springer-Verlag, Berlin, 1984) Ch. 1.
- [14] A.K. Avci, Z.I. Onsan and D.L. Trimm, Appl. Catal. A: Gen. 216 (2001) 243.
- [15] N. Kariya, A. Fukuoka and M. Ichikawa, Appl. Catal. A 233 (2002) 91.
- [16] N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto and M. Ichikawa, Appl. Catal. A: Gen. 247 (2003) 1.
- [17] P.E. Savage, J. Anal. Appl. Pyrol. 54 (2000) 109.
- [18] J.P. Kopasz, R. Wilkenhoener, S. Ahmed, J.D. Carter and M. Krumpelt, Chemical Technology Division, Argonne National Laboratory, Argonne, IL, USA. Preprints of Symposia – American Chemical Society, Division of Fuel Chemistry 44(4) (1999) 899.
- [19] J.R. Rostrup-Nielsen and I. Alstrup, Catal. Today 53 (1999) 311.
- [20] J.R. Rostrup-Nielsen, J. Catal. 31 (1973) 173.
- [21] E. Kikuchi, K. Ito, Y. Ino and Y. Morita, J. Catal. 46 (1977) 382.
- [22] D.C. Grenoble, J. Catal. 51 (1978) 203.
- [23] J.R. Rostrup-Nielsen and J.H. BakHansen, J. Catal. 144 (1993) 38.