

Syngas formation by selective catalytic oxidation of liquid hydrocarbons in a short contact time adiabatic reactor

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Abstract

The research of pilot plant scale explores syngas formation from such liquid fuels like isooctane and gasoline by selective catalytic oxidation at short contact times in nearly adiabatic reactor operating with the representative throughputs. The original monolithic catalysts with different (microchannel ceramics and metallic honeycomb structure) supports have been used in the experiments. The results demonstrated that over the range of the operational parameter $O_2/C=0.50-0.53$ required for syngas generation, equilibrium synthesis gas was produced over the catalysts employed, thus proving some evidence of their high activity and selectivity. Pre-reforming of fuel with releasing of some chemical energy before the catalytic monolith can occur in reactor. Both feed composition and superficial velocity affect the pre-reforming process. The phenomenon may be favored in syngas production because of a milder catalyst temperature mode is created. In general, axial temperature profile depends on catalytic composition in the frontal part of monolith, while the back-face catalyst temperature controls equilibrium product gas. Minimal both longitudinal and transversal temperature gradients were observed in the metallic catalytic monolith in comparison to the microchannel ceramic one. This helps to decrease deformations and thermal stresses in monolithic catalysts at the process performance.

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1. Introduction

At present, hydrogen is believed to be the fuel of choice for the future automotive applications. There is a large current interest of discovering new ways to convert current transportation liquid fuels, such as gasoline or diesel to high-content hydrogen and combustion products by on-board processing [1,2]. One of the ways to generate hydrogen-rich gases is a hydrocarbon reforming to produce synthesis gas or syngas ($H_2 + CO$). Gasoline and diesel fuels are very complex mixtures, which both contain compounds such as aromatics that are hard to reform [3], therefore, in practice liquid fuels are converted to predominantly CH_4 in a pre-reformer unit [4]. Selective oxidation of hydrocarbons in monolithic catalysts at very short contact times has a great promise for on-board processing because it is capable of producing even highly non-equilibrium products with no carbon formation using reactors that are much smaller and simpler than with

conventional technology. Two leading liquid fuel reforming techniques are considered to be the candidates for transportation application [5]: direct partial oxidation, intensively studied by Schmidt and co-workers in Minneapolis [6–8], and so-called indirect partial oxidation, i.e. combination of partial oxidation and steam reforming in stand-alone catalytic system, viewed as autothermal reforming, represented by Argonne National Laboratory [2,9,10]. Both of the oxidation reforming processes in monolithic catalysts at short contact times are autothermal and nearly adiabatic because the rate of heat generation is large. After light-off, the reactions usually run to completion of the limiting reactant. No reactor preheat was necessary other than that required to vaporize the fuel. Depending on the catalyst used the reforming reactions may require temperatures of 700–1200 °C [2,11].

For transportation application monolithic catalyst should exhibit a high activity, thermal and mechanical stability. The structure of the catalyst is important for reducing mass and heat transfer resistances and thus maintains a high overall throughput. Moreover, gas-phase reactions can be suppressed

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by minimization the void volume between catalytic surfaces. Ceramic monoliths, foam or extruded one, are commonly used as supports for the structured catalysts.

The research explores syngas formation from liquid fuels such as isooctane and reformulated gasoline, in a nearly adiabatic reactor at short contact times with representative throughputs in a pilot plant scale. The Institute of Catalysis proprietary monolithic catalysts with microchannel ceramics and metallic honeycomb support structure [12,13] have been used in the process performance.

2. Experimental

2.1. Catalysts

The monolithic catalysts were prepared according to procedures described in details in [12,13]. To synthesize composite ceramometal microchannel monoliths, a powder of aluminum (a commercial PA-4 grade) as well as CeO_2 (40 wt.%, prepared by decomposition of nitrate) were used as raw materials. To form the transport microchannels along the monolith length, easily burned organic fibers were inserted into the cermet matrix before the hydrothermal treatment (HTT) stage by a proprietary procedure [11]. The channels running along the monolith length (diameters ~ 0.5 mm, channel density ~ 300 cpsi, porosity ~ 0.3) are intersected by narrow (~ 0.1 mm) channels winded into spirals and separated by distances ~ 0.05 mm. The mixture of aluminium and CeO_2 loaded into a special die was subjected to HTT at 200°C followed by calcination in air at 900 – 1200°C . Platinum and LaNiO_3 as basic active components were introduced by the incipient wetness impregnation with corresponding solutions

followed by drying and calcination in air at 900°C . The inlet and outlet parts of a monolith were separately promoted by Rh or Ru + La by two additional impregnations with corresponding solutions followed by drying and calcination.

For catalysts based upon thermal conducting metallic substrates ($4700\text{ m}^2/\text{m}^3$, porosity ~ 0.8), the first preparation stage includes supporting of a thin (~ 5 – $10\ \mu\text{m}$) protective corundum sublayer on a feralloy foil (50 – $100\ \mu\text{m}$ thickness) by blast dusting technique [12]. Monolithic substrates are obtained via stacking a flat and corrugated foils and winding them into an Arkhimed spiral. Secondary Ce–Zr–La–O mixed oxide support is coated via a standard washcoating procedure using an alumina hydroxide as a binder. LaNiPt (1 wt.%) and LaRu (1 wt.%) active components were successively supported via wet impregnation followed by drying and calcination at 900°C .

2.2. Experimental apparatus and materials

2.2.1. Flow scheme

The experimental results reported in this work were obtained using high purity isooctane and commercial desulfurized reformulated gasoline as fuels and the oxygen of air as an oxidant. Flow rates and compositions of inlet reactants (including distilled water addition) were altered in the experiments. Gasoline composition is illustrated by chromatogram shown in Fig. 1. The tested gasoline contained 191 types of hydrocarbons. Amount of aromatics was about 40 wt.%. According to analysis data, the averaged composition of gasoline required for estimation of a stoichiometric air/fuel ratio in the feed corresponds to $\text{C}_{7.2}\text{H}_{13.36}$. To control the inlet feed flow rates and composition, air entering from a high-pressure host system was adjusted using a mass-flow

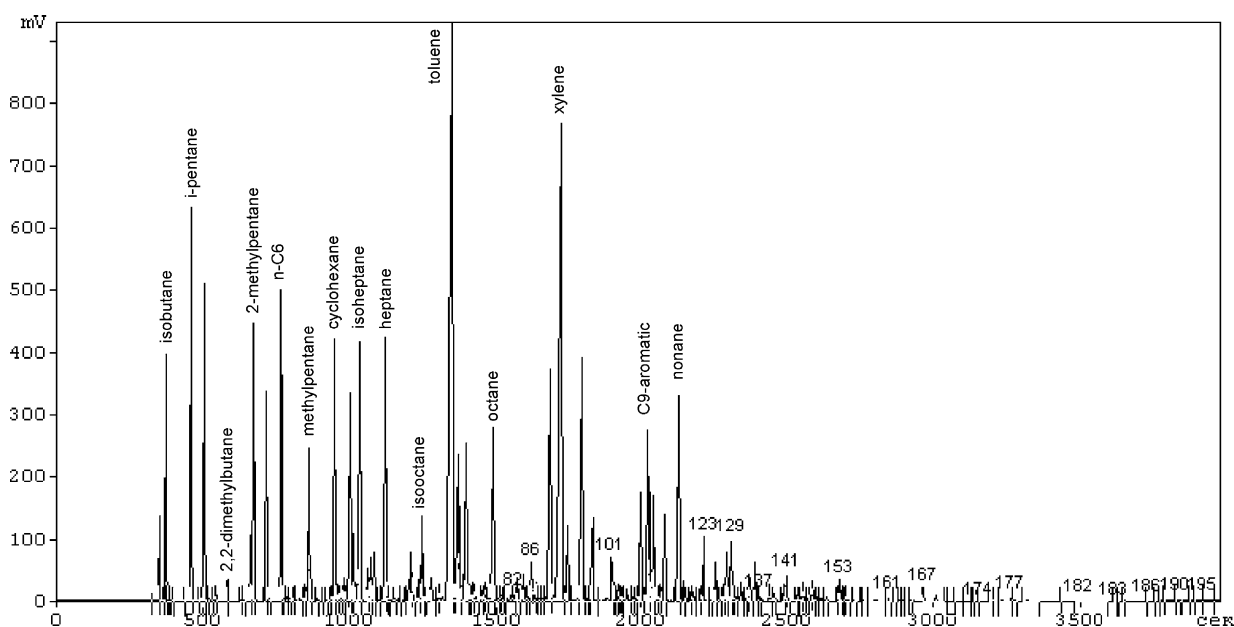


Fig. 1. Chromatogram of reformulated gasoline. Operation conditions: DB-1 column 60 m, programming 20 – 300°C , $4^\circ\text{C}/\text{min}$.

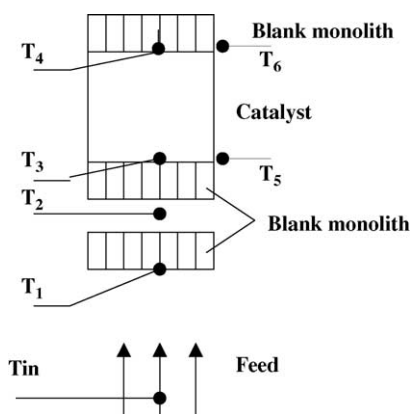


Fig. 2. Schematic of the monoliths assembling in the quartz tube. T_{in} , T_1 – T_6 , thermocouples.

controller (Brooks), while the liquid fuels and distilled water were metered with plunger pumps. Heating, vaporization and mixing fuel with air occurred simultaneously inside a stainless steel tube (length of 3 m, i.d. 30 mm) filled with Rashig rings ($d = 7$ mm), positioned into fluidized bed heater to keep an uniform temperature along the tube. The tube wall was heated up to 350°C , depending on the inlet temperature required in the reactor for a given feed and catalyst. A vertical reforming reactor (for details see below) was fixed on the top of the fluidized bed heater. Exit gas samples were taken periodically directly after the blank monolith served as a heat shield downstream from the catalyst. The reactor product gases were incinerated in a fume hood and vented.

2.2.2. Reactor

All experiments have been carried out with a reactor specially designed to operate with a maximum of 90% adiabaticity. Catalytic monoliths of different diameters and length were utilized. A catalytic monolith and three blank 80 ppi uncoated honeycomb cordierite monoliths (10 mm thickness) served as heat shields were housed into a quartz tube of required diameter according to the scheme shown in Fig. 2. Chromel–alumel thermocouples were used to control the temperature at selected points of this package. The distance between two blank monoliths placed upstream the catalytic one was about 10 mm. Bypassing of gases along the inner quartz wall was prevented by wrapping the monoliths with thin alumina–silica fibers. An electrical resistance wire was coiled over the quartz tube to light-off the catalyst. The quartz

tube was placed into stainless steel 85 mm diameter reactor. Empty space between the metal and quartz tube walls was thoroughly closed up with clay and alumina–silica fibers.

2.3. Methods

Gas composition was analyzed by GC method at using “Zvet –500” chromatograph equipped with Porapac Q, activated carbon and zeolite NaX columns in a series/bypass arrangement. Inert nitrogen was a standard in the procedure of balance calculations. Carbon balance was typically closed within 6%.

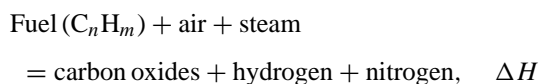
In general, an experimental procedure was performed as follows. Air blown through the fluidized bed heater was admitted first to heat the reactor. If the catalyst temperature was not sufficient to light-off the catalyst, the electrical coil wound around the quartz tube was switched-on to ignite the reaction. The reaction was shut down by stopping first the air supply, then the fuel and water. Inert gas was used occasionally to lower the temperature in the catalyst bed.

Ranges of experimental conditions applied are shown in Table 1.

3. Results

3.1. Thermodynamic considerations

In general, reforming process considered for the production of syngas from the fuels can be expressed as follows:



The process is carried out in the presence of a catalyst, which controls the product composition. A desirable future of the catalyst is a close approach to the thermodynamic equilibrium. Fuel/air/steam ratio determines both hydrogen yield in the product gas (reformate) and the energy released or absorbed by the reaction and hence, the adiabatic reaction temperature.

The operation conditions and process intensity, yield of the products desired and power consuming, as well as the ways for intensification of the process performance can be clarified on the basis of thermodynamic laws. The work employs a series of multi-component equilibrium

Table 1
Ranges of experimental conditions applied in adiabatic reactor catalytic experiments

Parameters	Microchannel monolith $\text{CeO}_2 + \text{Al}_2\text{O}_3$	Metal honeycomb (FeCrAl) monolith
Catalyst	LaNiPt: 7.8 wt.%, LaRu: 0.87 wt.%, front-face Rh: 0.02 wt.%	LaNiPt: 1 wt.%, LaRu: 1 wt.%
Catalytic monolith size and volume	Diameter: 46 mm, length: 23 mm, $38.2 \times 10^3 \text{ mm}^3$	Diameter: 55 mm, length: 45 mm, $107\text{--}214 \times 10^3 \text{ mm}^3$
Light-off temperature ($^\circ\text{C}$)	275–245	280–420
Inlet feed temperature ($^\circ\text{C}$)	200–270	200–320
Flow rates of reagents	Isooctane: 0.350 kg/h, air: 1.2–1.38 m^3 (n)/h	Isooctane: 0.757 kg/h, air: 3 m^3 (n)/h; gasoline: 0.757–1.86 kg/h, air: 3.58–6.90 m^3 (n)/h, water: 0–2.3 kg/h

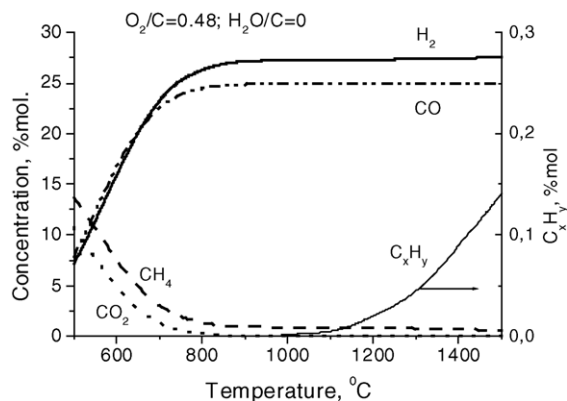


Fig. 3. Thermodynamic predictions of equilibrium gas composition produced in the isothermal partial oxidation of isooctane with air as a function of temperature ($O_2/C=0.48$).

calculations. Reforming isooctane, as a standard reference fuel for gasoline was used in the thermodynamic analysis. Thermodynamic equilibrium in both isothermal and adiabatic reactors was calculated by varying the tunable parameters of the process, such as fuel/air (expressed as O_2/C molar ratio) and water/fuel (H_2O/C molar ratio), with a purpose of determining operating temperature, maximum hydrogen yield, and adiabatic temperature rise available. Equilibrium calculations were performed for each experiment as well. Specified reaction stoichiometry was used for carrying out the computations. The condition that the Gibbs free energy of the reacting system including such components as H_2 , CO , CO_2 , H_2O , CH_4 , C_2H_4 , C_2H_6 was at a minimum at equilibrium was used to calculate the resultant mixture composition. Computations were executed with HYSYS simulator software (HyproTech HYSYS Process v2.2 AEA Technology).

3.1.1. Effect of the fuel/air ratio

The thermodynamic limits for the case of isooctane selective oxidation in the isothermal reactor are shown in Fig. 3. In the range of 800–1200 °C, which is a practical temperature range of the process, concentrations of syngas key components—hydrogen and carbon monoxide change only weakly. At high temperatures, a small increase in the hydrogen content is accompanied by appearance of secondary hydrocarbons in the equilibrium mixture. In the real experiments, the content of by-products depends not only on the temperature and fuel/air ratio, but also on the catalytic activity and a monolith structure [6]. Increasing O_2/C molar ratio up to stoichiometric value of 0.5 affects the hydrogen concentration rather than CO, as shown in Fig. 4. The maximum concentration of hydrogen of 27.54% is observed at $O_2/C=0.5$. The concentration of carbon monoxide holds near 23.7% over the range of $O_2/C=0.42$ –0.5 at the given inlet temperature. The operational temperature in the adiabatic reactor is defined by the adiabatic temperature rise at given inlet conditions. In the range of O_2/C ratio considered, the adiabatic temperature rise is nearly constant with the average value being close to 650 °C (Fig. 4). It means, that at the inlet feed temperature

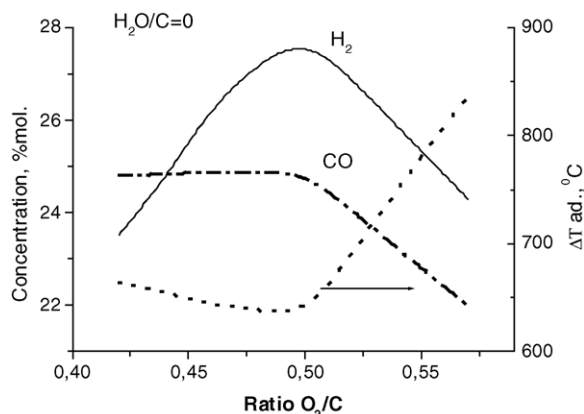


Fig. 4. Plot of thermodynamic equilibrium concentration of hydrogen and CO in the product gas and corresponding adiabatic temperature rise vs. O_2/C molar ratio in the feed ($T_{in}=270$ °C).

(T_{in}) of 200 °C for example, equilibrium product gas in adiabatic reactor would have the temperature of 850 °C over the wide range of O_2/C ratio up to the value of 0.5. With further dilution of the feed with air both the concentration hydrogen and carbon monoxide strongly decline because excess of oxygen in the feed oxidizes H_2 and CO to H_2O and carbon dioxide resulting in increasing the adiabatic temperature rise, hence operational temperature in the adiabatic reactor.

3.1.2. Effect of the water/fuel ratio

The presence of steam in the feed mixture changes the thermodynamic behavior of the reforming process considerably (Fig. 5). Autothermal reforming occurs at relatively low operational temperatures. The maximum concentration of hydrogen is observed at 700–750 °C. Thermodynamic limitations reveal a low tendency to the by-product hydrocarbons formation. Hydrogen concentration increases due to converting carbon monoxide to carbon dioxide with releasing thus one molecular of hydrogen from a molecule of water. Fig. 6

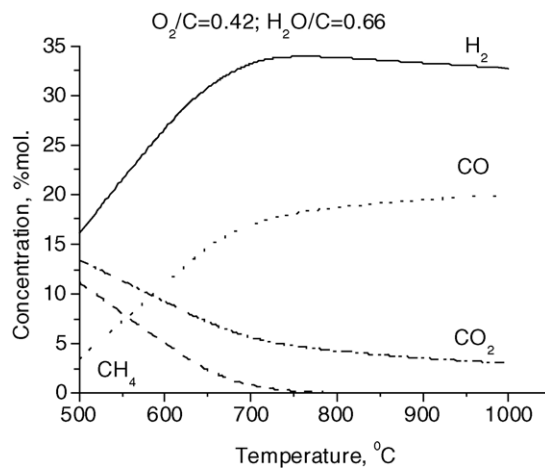


Fig. 5. Thermodynamic predictions of equilibrium gas composition produced in autothermal reforming of isooctane versus temperature with O_2/C ratio=0.48, H_2O/C ratio=0.66.

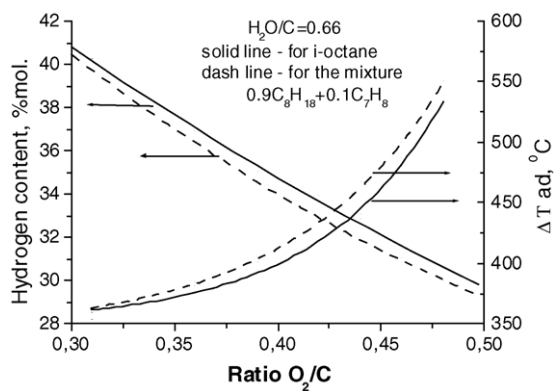


Fig. 6. Concentration of hydrogen (on a dry basis) in the product gas and adiabatic temperature rise for autothermal reforming of *i*-octane or its mixture with toluene vs. the O_2/C ratio in the feed according thermodynamic predictions ($T_{in} = 270^\circ C$).

depicts an influence of the O_2/C molar ratio in the feed containing *i*-octane or its mixture with toluene as fuels, on both the maximum achievable percentage of hydrogen in the product gas and adiabatic temperature rise for the chosen molar ratio of $H_2O/C = 0.66$. Theoretically, the highest percentage of H_2 is observed under steam reforming conditions. At air addition, the concentration of hydrogen in the product gas diminishes because of the dilution effect, and also because more hydrogen is converted to H_2O . As it can be seen in the same figure, an adiabatic temperature rise depends exponentially on the air/fuel ratio. The higher dilution, the higher adiabatic temperatures rise is and, hence, the operational temperatures in the adiabatic reactor.

Due to a lower adiabatic temperature rise in comparison with the partial oxidation, a higher preheat temperature is required in an autothermal reforming performance. To achieve the autothermal operation temperature desired, e.g. $750^\circ C$, the feed mixture consisting of fuel, water and air must be heated up to a higher temperature, a lower respective adiabatic temperature rise is (Fig. 6). The maximum reformer efficiency around 80% is achieved at the preheat temperature for the fuel–water–air mixture around $300^\circ C$, as it was found in [14].

Toluene is typically the largest aromatic component in gasoline. Fig. 6 illustrates the effect of aromatics in the fuel on its reforming to synthesis gas. At the same O_2/C ratio, toluene addition decreases the hydrogen yield, but operational temperature increases due to a higher adiabatic temperature rise. Similar results were obtained by O'Connor et al. [6] at feeding toluene–isooctane–air mixture into the experimental short contact time reactor.

The catalyst affects the relative contribution of endothermic and exothermic reactions in an autothermal fuel processing. However, at given characteristics of the feed (inlet temperature and O_2/C ratio), there is an equilibrium limit for the relative content of hydrogen in syngas, even in the case of a highly active catalyst (Fig. 7). Steam addition increases the hydrogen percentage in the product stream

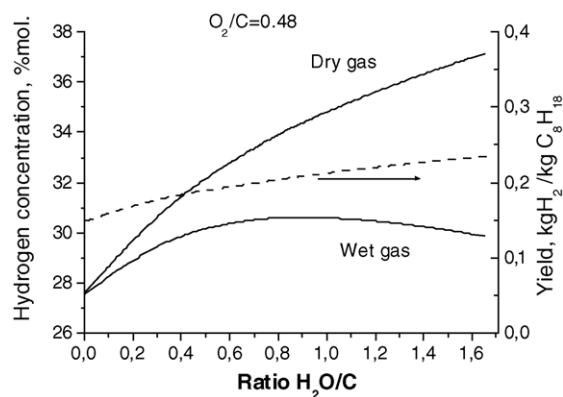


Fig. 7. Thermodynamic predictions of influence of H_2O/C ratio in the feed ($T_{in} = 270^\circ C$) on both concentration (left-axis) and hydrogen yield.

at increasing the value of H_2O/C up to ~ 1 . This value corresponds to the maximum reformer efficiency, because further increasing in the hydrogen yield requires an additional energy input to dry the reformate gas. The maximum reformer efficiency at the ratio $H_2O/C = 0.7$ was found by Docter and Lamm [14] in the thermodynamic calculations of equilibrium in adiabatic reactor for a mixture of 35% hexane, 25% hexane and 40% xylol with a general formula C_7H_{12} .

3.2. Experimental results

3.2.1. Microchannel monolith (Table 1)

Selective oxidation of isooctane with air has been investigated over the microchannel catalytic monolith (see Table 1). In the related experiments, the flow rate of isooctane was fixed at 0.350 kg/h, flow rates of air were varied from 1.2 to 1.38 m^3/h . These flow rates correspond to the operational parameter $O_2/C = 0.458–0.527$. The appropriate catalyst contact time slightly varied within 0.094–0.108 s, while the superficial velocity (at STP) was of 0.20–0.24 m/c at the total feed flow rates. The light-off temperature for the pristine (fresh) catalyst utilized in isooctane reforming was about $275^\circ C$, while in further runs the temperature of $246^\circ C$ was detected.

Fig. 8 shows both the front- and back-face catalyst temperatures in the steady-state modes of isooctane selective oxidation at various O_2/C ratios. As O_2/C ratio increases, the front-face temperature increases too due to the high exothermicity of the local oxidation reactions occurring in the inlet part of the monolith. The back-face temperature responds badly to altering the inlet conditions. The difference of $200–250^\circ C$ between the front and back faces is characteristic of both reforming chemistry and the catalytic monolith structure.

Comparing an experimental adiabatic temperature rise with the theoretical one showed poor adiabaticity for the low throughput experiments. At the ratio $O_2/C = 0.5$ the difference between the feed stream temperature (T_{in}) and the back-face temperature (T_4) of $560^\circ C$ was registered. Theoretical adiabatic temperature rise for reforming of the

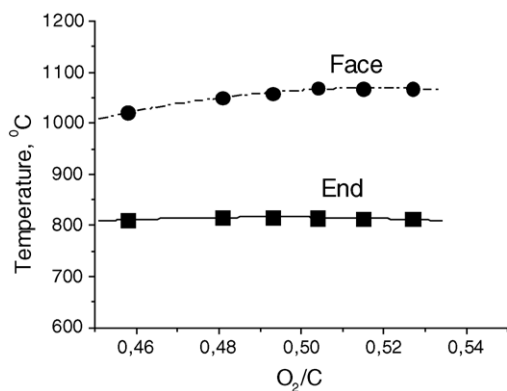


Fig. 8. Steady-state front-face (face) and back-face (end) catalyst temperatures measured by T_3 and T_4 thermocouples (Fig. 2) vs. O_2/C parameter.

isooctane–air mixture was about 643°C (see Fig. 4). The difference of 83°C , or 13% is characteristic of the heat loss at given both flow rates and reactor design. Indeed, the effect of these losses becomes apparent from the fact that the temperatures measured at the quartz tube wall (see T_5 and T_6 in Fig. 2) were of 90°C (9–11%) less than corresponding axial temperatures. It was the lowest throughput experiment with the poorest adiabaticity observed. At higher flow rates the rate of heat generation increases causing the reactor to operate closer to adiabatic one.

At the feed flow rate, which resulted in superficial velocity of 0.2 m (STP)/s the temperature measured by the thermocouple T_2 mounted between two blank monoliths placed upstream of the catalyst gradually went up with the run time. The steady-state mode with T_2 temperature of about 600°C (Fig. 9, set 1) was settled down in 30 min after light-off. This temperature was high enough to initiate pre-reforming reactions upstream of the catalyst. We have revealed the same phenomenon at the superficial velocity of 0.27 m (STP)/s on isooctane reforming over identical catalytic foam (20 ppi) monolith with only one heat shield placed upstream (not shown in this paper for brevity). The gradual increasing of the heat shield temperature up to about 350°C was followed by the abrupt rise of the temperature up to 800°C , while

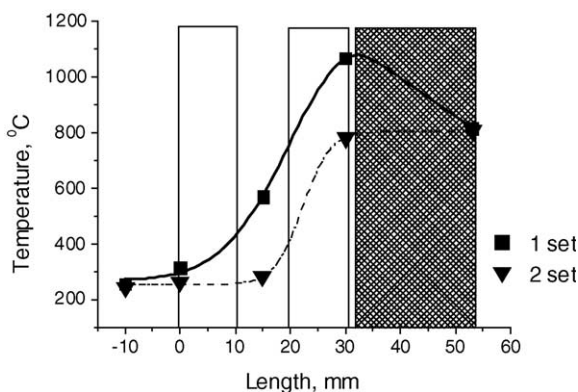


Fig. 9. Axial temperatures measured along the reactor with the pristine (set 1) catalyst and after sintering procedure (set 2) ($O_2/C = 0.504$).

descending the front-face catalyst temperature was observed. In steady-state mode, nearly uniform axial temperatures in the range of $850\text{--}900^\circ\text{C}$ were achieved over both the front heat shield and catalyst. This could be a result of nonselective thermalolysis and pre-reforming reactions occurred in front of the catalyst. Indeed, homogeneous reactions are known to play a prominent role in the reactions of hydrocarbon selective oxidation. Thus, for the reaction of butane partial oxidation studied in the presence of Pt–Rh gauze and in an empty tubular reactor under identical conditions, Marengo et al. [15] observed a fast transition from heterogeneous to homogeneous reaction mechanism at the temperature around 380°C . These results show that a reaction front can be stabilized in the inlet section of the reactor, where butane is converted to partial oxidation products: ($C_1\text{--}C_4$)—olefins and oxygenates. A mechanism involving free radicals is also known to control the oxidation of butane and higher alkanes in the region of cool flames, near the borderline of the explosion region [16].

In our experiments described above, the gas samples taken in 10 min after light-off and at the steady-state mode with the high temperature upstream the catalytic monolith were found to differ only slightly in the syngas key components. Namely, 25.5% H_2 , 21.6% CO , 2.2% CO_2 after light-off, and 28.6% H_2 , 24.6% CO , 0.34% CO_2 in the steady-state mode were detected. This suggests that syngas yield is slightly affected by speculated pre-reforming reactions occurring in the front shield. Nevertheless, they could favor a lower temperature gradient along the catalyst bed.

A close approach to the thermodynamic equilibrium is a desirable feature of the catalyst. Equilibrium calculations were performed for each experiment basing on the exit temperatures for the given feed composition. It is seen (Fig. 10), that over the range of the operational parameters $O_2/C = 0.50\text{--}0.53$ required for syngas production, a close approach mentioned above is achieved. Accordingly, an equilibrium synthesis gas is indeed produced over the catalyst. For the rich feed ($O_2/C < 0.5$), reactions kinetics seems to affect the reforming process thus departing it from equilibrium.

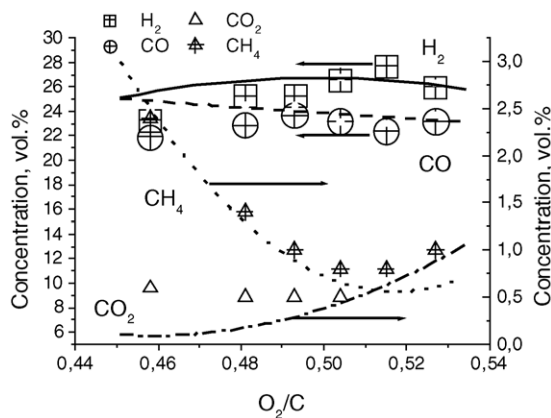


Fig. 10. Experimentally measured (symbols) and thermodynamic predictions (curves) of concentration of components in the product gas vs. O_2/C ratio in the feed stream.

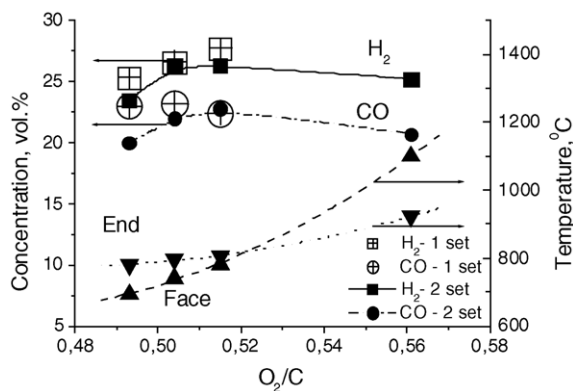


Fig. 11. Closed symbols exhibit experimental data of concentrations of H₂ and CO in the product gas, the front- and back-face temperatures for the partly sintered catalyst (0.350 kg/h isooctane). Comparable experimental data for the pristine catalyst are exhibited by the open symbols. Data at O₂/C = 0.56 corresponds to 0.525 kg/h isooctane flow rate.

The idea of the next set of experiments was to show that changing the catalytic composition in the frontal part of the catalytic monolith affects a temperature profile in the catalytic monolith due to changing reforming chemistry. The microchannel catalyst was partly sintered during the short-term (3 min) temperature excursion up to 1250 °C caused by decreasing the fuel flow rate. After renewing flow rates, the front-face temperature went down by 250–300 °C, while the catalyst back-face temperature was kept unchanged at around 800 °C (see Fig. 9, set 2). Overheating appears to cause evaporation of Rh (0.02% wt) supported within inlet (~2 mm) part of the catalyst. This seems to coincide with a drop in their catalytic activity in exothermic reactions. With reference to Fig. 11, this resulted in a milder thermal mode of the catalyst operation with a low axial temperature gradient. However, the product gas composition was determined by equilibrium at the exit temperature. Only at high isooctane flow rates the front-face temperature exceeded the back-face temperature in the sintered catalyst due to a higher heat generation (see Fig. 11).

In all experiments with the microchannel monolith, C₂–C₃ components were not detected in product gas.

3.2.2. Metal honeycomb (FeCrAl) monolith (Table 1)

For this catalyst, both partial oxidation and autothermal reforming processes using isooctane as well as gasoline have been experimentally investigated. In the first experiment with the pristine catalyst, the light-off temperature was ~420 °C. The ignition temperatures of ~280–320 °C for isooctane and ~350 °C for gasoline were detected for used (activated) catalyst in further experiments.

3.2.2.1. Load of one monolith. In the experiments described below liquid volumetric flows of both fuels were equal, while mass flow rates of isooctane and gasoline amounted to 0.757 and 0.893 kg/h, respectively due to the different densities (0.682 g/ml for isooctane and 0.775 g/ml for gasoline). The

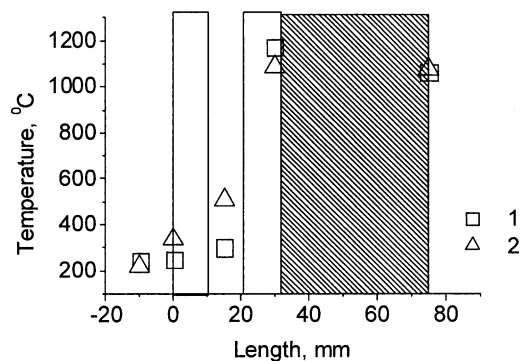


Fig. 12. Gasoline partial oxidation with air. Axial temperatures along the reactor with one metallic honeycomb monolith: (1) shortly after light-off; (2) 1 h later.

inlet temperature, air and water supply were varied in the experiments. Representative results of the experiments are listed in Table 2. Of particular note in Table 2 is the increase of about 100 °C in the catalyst temperature observed for gasoline compared with that for isooctane reforming at the same molar O₂/C ratio.

The same phenomenon of elevation of the temperature upstream catalytic monolith was observed in the gasoline partial oxidation experiments at superficial velocity of 0.45 m (STP)/s (Table 2, mode 3 and Fig. 12). Increasing the T₂ temperature from 220 to 520 °C coupled with decreasing the front-face catalyst temperature from 1185 to 1085 °C was monitored. Thermocouple T₂ measured a gas phase temperature of the feed directly in the face of a heat shield adjacent to the catalyst. It means that the temperature in the heat shield of itself was higher than the bulk gas phase temperature measured upstream. The observations are consistent with the assumption that pre-reforming reactions accompanied with releasing of some chemical energy occur, thus evolving a reaction front upstream the catalyst. At isooctane reforming this effect was detected at superficial velocities lower than 0.3 m (STP)/s. It looks like a fuel composition is most likely to affect the velocity limit.

Therefore, superficial velocity is one of the critical operational parameter at the process performance.

As follows from Table 2, a product gas is a function of both the feed composition and the fuel reformed. In partial oxidation of gasoline–air mixture with the ratio O₂/C = 0.53 the molar ratio of hydrogen and carbon monoxide in syngas ~0.84 correlates with corresponding H₂/C ratio ≈ 0.93 in gasoline (C_{7,2}H_{13,36}). Reforming of isooctane (C₈H₁₈ with H₂/C ≈ 1.13) gives synthesis gas with H₂/CO molar ratio ≈ 1.1. These results show a high activity and selectivity of the metallic monolith tested.

3.2.2.2. Load of two monoliths. The idea that motivated the experiments was to clarify an effect of altering throughput in the metallic monolith operation. The representative results are shown in Table 3 and Fig. 13. It is of a prime importance to arrange co-feeding the reactants in the right proportion

Table 2
Experimental data of fuel reforming over one metallic honeycomb monolith

Parameter	Experimental mode			
	1	2	3	4
Flow rates	Isooctane: 0.757 kg/h, air: 3.00 m ³ (n)/h, $Q = 3.15 \text{ m}^3/\text{h}$, $\text{O}_2/\text{C} = 0.53$, $T_{\text{in}} = 205 \text{ }^\circ\text{C}$	Isooctane: 0.757 kg/h, air: 3.00 m ³ (n)/h, water: 0.735 kg/h, $Q = 4.1 \text{ m}^3$ (n)/h, $\text{O}_2/\text{C} = 0.53$, $\text{H}_2\text{O}/\text{C} = 0.8$, $T_{\text{in}} = 265 \text{ }^\circ\text{C}$	Gasoline: 0.893 kg/h, air: 3.58 m ³ (n)/h, $Q = 3.75 \text{ m}^3$ (n)/h, $\text{O}_2/\text{C} = 0.53$, $T_{\text{in}} = 220 \text{ }^\circ\text{C}$	Gasoline: 0.893 kg/h, air: 3.58 m ³ (n)/h, water: 1.14 kg/h, $Q = 5.17 \text{ m}^3$ (n)/h, $\text{O}_2/\text{C} = 0.53$, $\text{H}_2\text{O}/\text{C} = 1.0$, $T_{\text{in}} = 280 \text{ }^\circ\text{C}$
Contact time (s)	0.105	0.081	0.092	0.064
Superficial velocity (m (STP)/s)	0.38	0.5	0.45	0.63
Front-face catalyst temperature (°C)	1033–1067	985–957	1185–1085 ^a	1063–1058
Back-face catalyst temperature (°C)	903–951	913–892	1087–1076 ^a	1001–1003
Synthesis gas (dry) composition (mol%)				
H ₂	26–27.3	31–31.6	22.8–22.2 ^a	27.5
CO	22.2–24.8	19.2–17.7	27.1–26.3 ^a	17.4
CO ₂	0.4–2.7	4.5–6.0	Trace–0.3 ^a	7.1
N ₂	49–53.0	44.5–49.1	50.4–51.4 ^a	49.4
CH ₄	Trace–0.2	0.1–0.3	0.4–0.4 ^a	Trace
C ₂ –C ₃	0	0	0	0

^a Data with T₂ thermocouple temperature of 520 °C.

over entire range of throughputs. The fuel–oxygen ratio is the most important tunable parameter that can affect the reforming performance. Only two percent altering in the air flow rate at the same amount of gasoline causes pronounced variation in both the catalyst temperature and reformat composition. Fig. 13 illustrates the influence of an air/fuel ratio on both synthesis gas composition and the temperature in selective catalytic oxidation of gasoline with air over the metallic monolith. Both hydrogen and CO concentrations decline, as the feed becomes leaner. Contrary to observations in reforming process over microchannel ceramic monolith, where the temperature gradient along the monolith length grows in similar conditions, the increase of the air/fuel ratio

causes the back-face metallic monolith temperature to increase while the front-face temperature changes only slightly. It stems due to the high thermal conductivity for the metallic monolith. Hence, thermal axial (longitudinal) gradient is minimized in the metallic monoliths. A similar trend was observed for the radial (transversal) catalyst temperature. Maximum difference of 60° was detected between the axial and wall temperatures in the reactor with the metallic monolith against the difference of 90 °C for microchannel ceramic catalyst.

In the experiments concentration of CO₂ was less than 0.5 mol%, while CH₄ and C₂₋₃ by-products were not detected at all.

Table 3
Experimental data of fuel reforming over two metallic honeycomb monoliths

Parameters	Experimental mode			
	1	2	3	4
Flow rates	Gasoline: 0.893 kg/h, air: 3.31 m ³ (n)/h, $Q = 3.51 \text{ m}^3$ (n)/h, $\text{O}_2/\text{C} = 0.48$, $T_{\text{in}} = 220 \text{ }^\circ\text{C}$	Gasoline: 1.86 kg/h, air: 6.90 m ³ (n)/h, $Q = 7.32 \text{ m}^3$ (n)/h, $\text{O}_2/\text{C} = 0.48$, $T_{\text{in}} = 206 \text{ }^\circ\text{C}$	Gasoline: 0.893 kg/h, air: 3.38 m ³ (n)/h, water: 1.14 kg/h, $Q = 5 \text{ m}^3$ (n)/h, $\text{O}_2/\text{C} = 0.49$, $\text{H}_2\text{O}/\text{C} = 0.9$, $T_{\text{in}} = 290 \text{ }^\circ\text{C}$	Gasoline: 1.86 kg/h, air: 6.98 m ³ (n)/h, water: 2.3 kg/h, $Q = 10.18 \text{ m}^3$ (n)/h, $\text{O}_2/\text{C} = 0.48$, $\text{H}_2\text{O}/\text{C} = 0.86$, $T_{\text{in}} = 250 \text{ }^\circ\text{C}$
Contact time (s)	0.19	0.09	0.13	0.065
Superficial velocity (m (STP)/s)	0.42	0.9	0.6	1.23
Front-face catalyst temperature (°C)	1081	1117	992	958
Back-face catalyst temperature (°C)	963	1000	971	898
Synthesis gas (dry) composition (mol%)				
H ₂	23.9	24.8–24.7	29.5	30.6–30.3
CO	28.6	27.7–28.7	18.6	18.0–18.8
CO ₂	Trace	Trace–0.4	7.2	7.3–7.0
N ₂	50.3	51.6–51.7	47.0	46.3–50.5
CH ₄	0.4	trace–0.1	Trace	Trace
C ₂ –C ₃	0	0	0	0

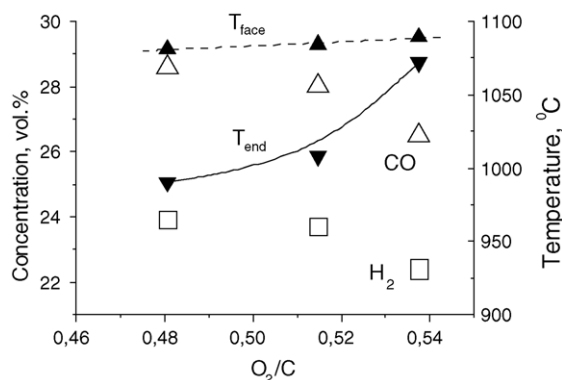


Fig. 13. The influence of the O₂/C ratio on H₂ and CO concentrations in the product gas produced in gasoline partial oxidation (open symbols), front- and back-face temperatures over two metallic monoliths bed (closed symbols) for 0.893 kg/h gasoline flow rate.

The influence of altering throughput (0.893 and 1.86 kg/h gasoline flow rate) on the metallic monolith operation in the partial oxidation and autothermal reforming processes is demonstrated by the results listed in Table 3. A ratio slightly lower than syngas stoichiometry was used for the experimental reactor tests. In the experiments being differed in throughputs, nearly identical feed compositions were applied. It can be seen that in both tests, namely partial oxidation (modes 1 and 2 in Table 3) and autothermal reforming (modes 3 and 4 in Table 3), the products are basically the same. A small difference in the catalyst temperatures was observed in spite of the different heat generation in the reforming process. Molar ratio of hydrogen to carbon monoxide (H₂/CO) in syngas produced in gasoline partial oxidation is ≈ 0.84 –0.9 at the theoretical value 0.93.

4. Summary

The research of pilot plant scale explores syngas formation from such liquid fuels as isooctane and gasoline by selective catalytic oxidation in nearly adiabatic short contact time reactor at representative throughputs. Original monolithic catalysts on different supports, viz. microchannel ceramics and metallic honeycomb structure have been employed in the experiments. Both the feed composition and throughputs have been varied.

These experiments demonstrated that over a range of tunable parameter O₂/C = 0.50–0.53 required for syngas generation, equilibrium synthesis gas was produced over the catalysts employed, thus proving some evidence of their high activity and selectivity. Composition of the active component in the frontal part of monolith affects an axial temperature profile, while the product composition was ruled by equilibrium at the back-face temperature. Pre-reforming accompanied with releasing of some chemical energy before the catalytic monolith can occur. Both a feed composition and superficial velocity affect the pre-reforming process. This

phenomenon can be favorable for syngas production because a milder catalyst temperature mode is created. Minimal both longitudinal and transversal temperature gradients were observed in the metallic catalytic monoliths in comparison to the microchannel ceramic monoliths. This feature is particularly important for the selective oxidation short contact time process, because lower thermal stresses and deformations in the metallic monolith based catalysts can occur.

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