Autothermal Reforming of Gasoline Using a Cool Flame Vaporizer

J. Matos da Silva and I. Hermann
Global Alternative Propulsion Center, Adam Opel AG, 65423 Ruesselsheim, Germany

C. Mengel, K. Lucka, and H. Köhne
Dept. of Heat and Mass Transfer, Technical University of Aachen, 52056 Aachen, Germany

DOI 10.1002/aic.10100

The phenomenon of cool flames can be used for mixing, evaporation, and overheating of a mixture of fuel, air, and steam. This method is used to provide a homogeneous mixture preparation. This study investigates the existence of cool flames running a stationary cool flame reactor under autothermal reforming conditions. It particularly characterizes the thermal limits of the cool flame reaction at high steam-to-carbon ratios. The experiments show that a cool flame vaporizer can be combined with an autothermal reformer leading to a homogeneous temperature profile in the front of the catalyst bed. This results in a good conversion of the fuel in the reforming process. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1042–1050, 2004
Keywords: autothermal reforming, cool flames, premixing, fuel cell

Introduction

The quality of the mixture preparation of hydrocarbons and an oxidizer represents an essential issue for the use of liquid fuels. Inhomogeneities that unavoidably lead to a deterioration of the fuel conversion in following processes have to be avoided. In the fuel cell application of catalytic reformer techniques, the mixture preparation can have a strong effect on the system performance (Pereira et al., 2000). In particular, the problem of soot formation has to be avoided by good mixture (Zizelmann et al., 2002). The catalytic reformer process requires a uniform fuel admission of the catalyst to avoid temperature peaks that can lead to a material damage. A sufficient conversion can be achieved only in the case of an ideal homogeneous mixture, given that only the set parameters are globally valid at the catalyst, so that locally unfavorable ratios can be prevented.

A premixing technology with downstream reforming has to guarantee that in any case flashback and autoignition before the oxidation step are avoided. To prevent flashback, the mixing zone has to be thermally decoupled, and sufficient flow velocity between mixing zone and reformer is needed. The problem of autoignition before the catalyst can be handled by selecting the appropriate mixing technique. This article presents and discusses a suitable premixing technology using cool flames for the evaporation, coupled with an autothermal reformer for gasoline. The fuel processor is aimed at a technological rather than a laboratory scale system (for example, Moon et al., 2001). For mixing of fuel and oxidants, the exothermic reactions of cool flames are used for the evaporation. Those restricted oxidations have been extensively studied both in experimental setups (Dagaut et al., 1994; Lignola et al. 1988) and in modeling surveys (Curran et al., 1998, 2002; Ranzi et al. 1995, 1997), with special focus on the ignition process in internal combustion engines (for example, Lemaire et al., 2001). This study presents the stationary cool flame reaction as a mixture preparation unit in a technical apparatus and its impact on reforming performance.

Mixture Preparation Technology

Basically three methods exist to execute a premixing in a lined-up process for liquid fuels, as shown in Figure 1. One

---

Correspondence concerning this article should be addressed to C. Mengel at cme@owi-aachen.de.

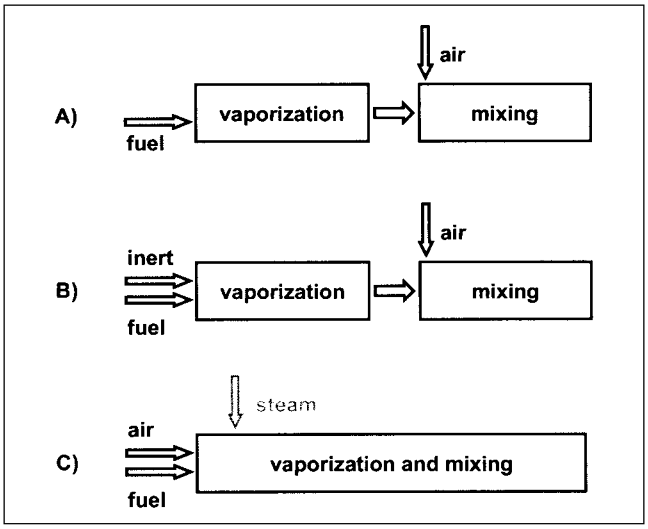


Figure 1. Premixing technologies (Lucka et al., 2000).

possibility is the direct evaporation of the liquid fuel before the actual mixing process with the air (case A), which is a standard engineering technique. This enables evaporation of the liquid without igniting conditions being achieved because there is no oxygen present. The energy, necessary for the evaporation, has to be provided to the process from outside (endothermic process) so that the modulation capability of such systems is restricted. On the other hand, the prevention of deposit formation on hot components is mandatory. For the production of a homogeneous mixture of fuel vapor and air, the mixing process is still necessary. The phenomena occurring in this case are dependent on the mixing temperature and correspond to the points discussed for case C.

A second method is the evaporation in an inert medium (case B). Steam is a gas available in a technology near fuel cell application. The use of nitrogen or fuel gas is also principally conceivable. According to this principle, a technical apparatus is a saturator, where the solubility of the fuel in an inert gas stream depends on the temperature and system pressure. However, in this case, the same boundary conditions turn out for the application in premixing technologies, as in the case of the direct evaporation of a liquid fuel (case A). The modulation capacity is restricted because the process is endothermic. Also in this case, the mixing with air has to be achieved in a following step after the evaporation when the phenomena described below occur.

The third possibility is to make the evaporation of the fuel take place in an air flux (case C). Considering the technical expenditure, this process is always preferable. A technically suitable system for mixing reaction air and fuel represents the injection of hydrocarbons into a preheated air stream. In this case, conventional component technology can be used. Because of the noncontact evaporation in an air flow, the formation of deposits can be avoided. In this case, different phenomena of low temperature oxidation occur.

These effects appear when long-chain hydrocarbons are mixed with air in a distinct range of pressure and temperature within the ignition boundaries of the *p*–*T*-ignition diagram (Pilling, 1997). The low-temperature oxidation of cool flames is basically independent of the state of the hydrocarbon: it can be fed into the mixing region liquidly or it may be derived from a preconnected evaporation and therefore be added in gaseous form.

For industrial gas oil, the different ranges of reaction phenomena depending on the present temperature become clear from Figure 2 (Lucka et al., 1999). Here, the temperatures of a gas flow are shown before and after fuel addition into a hot air stream. If the air temperature before fuel injection lies in the range below 310°C, no appreciable reaction occurs; the hydrocarbons are volatilized in the air stream. In this temperature range, the phenomenon of slow combustion can be observed (Gaffuri et al., 1997).

In a temperature range between 310 and 500°C, cool flame reactions occur. These are combined with a partial consumption of oxygen and a fuel conversion, which is regained in a temperature increase. This partial oxidation and the ongoing chemical branching reactions lead to a molecular chain shortening and the formation of numerous oxidation products (Dagaut et al., 1995). Because of the kinetic limitation of the cool flame reaction, a temperature increase—without resulting in an ignition of the fuel air mixture—can be observed. The limiting of the chemical reactions that occur is based on complex fuel-specific mechanisms. Warnatz describes a model that explains this limiting for a specific temperature level (Warnatz, 1993). In the case of the low-temperature oxidation of cool flames, the balance reaction of hydrocarbon radicals with oxygen, which produces peroxi-radicals, is significant. In the following equation, the reaction of the peroxi-radicals' production is given for *n*-heptane. In this case, $R^{\bullet}$ stands for C_7H_{15}

$$R^{\bullet} + O_2 \Leftrightarrow RO_2^{\bullet}$$

The key to the production of cool flames lies in the lack of stability of the oxygen link formed within the reaction. At higher temperatures, the chemical equilibrium shifts back to the side of the hydrocarbon radicals.

The heat released within the partial fuel conversion can be used for a complete evaporation of the liquid. The resulting mixture is ignitable. For the representative fuel *n*-heptane, cool

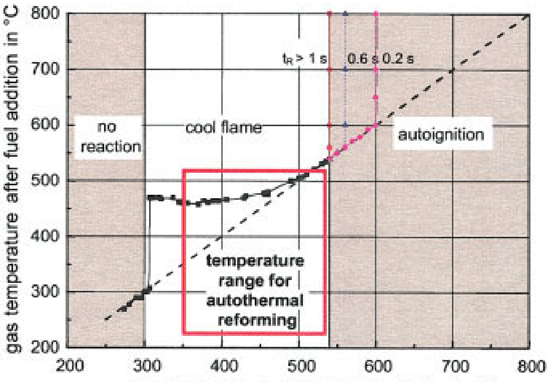


Figure 2. Areas of reactions atomizing fuel into a hot stream of air (IGO, 1 atm, air-ratio = 1) (Lucka et al., 1999); temperature range according to Figure 9 for high efficiency of autothermal reforming.

flame reactions are observed under atmospheric conditions (Ranzi et al., 1995), whereas for iso-octane, cool flames are not expected below a system pressure of 300 kPa gauge (Ranzi et al., 1997).

The temperature range above about 500°C is characterized by exothermic reactions, which end in an ignition of the mixture depending on the thermal boundary conditions. Above about 550°C, a mixing of fuel and air is possible only within the ignition delay time. After that time, the mixture always ignites.

In the application of the catalytic reforming of hydrocarbons, the required system inlet temperatures are higher than 350°C to reach sufficient reformer efficiencies (compare Figure 9). Therefore, the premixing technologies of cool flames and those using the ignition delay time are conceivable to use. Referring to this technology, the addition of steam has to occur. On the one hand, an addition of steam fed directly into the evaporation chamber is possible. On the other hand, a mixing of reaction air and steam before the fuel evaporation is also possible. In any case, the production of a homogeneous air, steam, and fuel composition, both fluids being necessary for autothermal reforming, is carried out in one process step.

The technologies that work within the igniting delay show a considerable sensitivity onto the system temperature and the ignition delay time connected with that. Variation of the power input causes considerable changes of the residence time, which is restricted through the ignition delay time on the one hand, and the time needed for complete evaporation on the other hand. Therefore, the modulation capability of such systems is limited. In a technical apparatus, an autoignition of the mixture attributed to exceeding the igniting delay time has to be securely excluded because the occurring pressure peaks can lead to damage of components with ignition.

Because of the limited reaction kinetics of cool flames, the modulation capability of systems in this temperature range is not restricted. An autoignition of the mixture can surely be avoided. The complete evaporation and mixing of the liquid fuel is guaranteed. The produced composition at the outlet of the evaporation zone is available on an almost constant temperature level, which hardly changes with capacity variation. Because the reaction temperature is independent of the preheating temperature to the greatest possible extent, technical degrees of freedom are opened that enable a secure control of the evaporation process.

Cool flame vaporizer

There are extensive investigations using the cool flame reaction for the evaporation of liquid fuels under atmospheric conditions (Hartmann et al., 2000; Mengel et al., 2000). On this basis, an evaporator was designed for a working pressure of a maximum of 300 kPa(g) (Figure 3). The studies presented here were carried out using a gasoline representative fuel, fed into the evaporation chamber with mixed air and steam.

The reaction air was added using a mass flow controller and preheated by means of an electrical heating. The air-ratio was operated in the range between 0.2 and 0.5. The steam was produced by an electrical steam generator and superheated before mixing with the reaction air. The experiments were carried out with steam-to-carbon (S/C) ratios of up to 2.0.

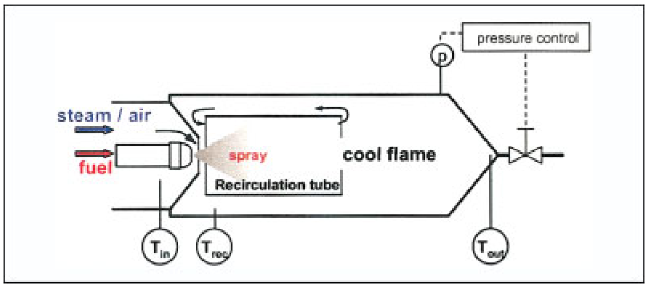


Figure 3. Cool flame reactor.

The fuel injection was carried out using components that were taken from classical burner technology. Two coupled geared pumps, connected in series, produced the necessary fuel pressure for a simplex pressure atomizer. This allowed a modulation ratio of 1 to 4. The capacity determination was executed through gravimetry. The cool flame reaction is not subjected to a limitation with regard to the modulation capability, so that an adequate injection system could fulfill the modulation of up to 1 to 30 required in the mobile fuel cell application.

The mixing of reaction air and vapor with the fuel spray occurs in the reaction room in a conical nozzle, in which the fuel nozzle is attached centrally. The tube reactor is equipped with an external electrical heating for the startup sequence. A recirculation tube is used for transporting reaction products to the reaction root at the spray. Several temperature-measuring points in the interior of the reactor enable the control of the reaction. A pressure control system regulates the system pressure in the reactor through an electropneumatic regulation valve. For the autonomous experimental operation, the cool flame products were completely burned in an afterburner with a natural gas–supported flame.

Existence of the cool flames

Within the cool flame reaction, a characteristic temperature exists, defined by the limited reaction kinetics where the reaction stabilizes under defined thermal boundary conditions. For industrial gas oil, this characteristic temperature is given at 480°C (Lucka et al., 1999). The actual temperature of the reaction depends on the thermal boundary conditions and the flow field within the mixing zone. For example, lower temperatures can be achieved with the application of a recirculation tube stretching the reaction zone, or through increased heat loss through the reaction chamber walls. Furthermore, the rate of inert gas (such as the steam content) and also the system pressure are of great importance for the reaction temperatures.

If the characteristic temperature of the reaction system is exceeded by changing one of the mentioned boundary conditions, this results in a suspension of the limitation of the reaction kinetics, so that further reactions occur, which may end in a complete ignition of the fuel air mixture. Such a state is combined with additional oxygen consumption and considerable pressure and temperature variations and should always be avoided in a technical system. These reactions will be called *succeeding reactions* in this article. Eventually adequate steps have to be undertaken to avoid these conditions. Unlike an ignition attributed to exceeding the igniting delay time, the occurring pressure variations are less component critical because they were detected in a range of about 50 kPa(g). At the same time controlling techniques are available to stabilize the

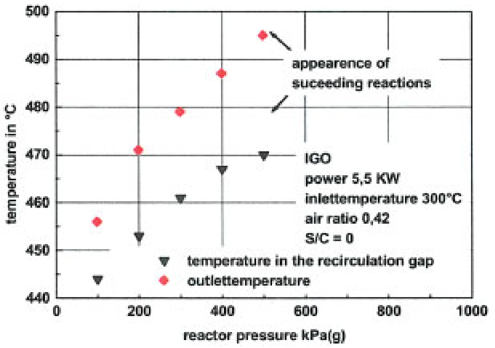


Figure 4. Dependency of reaction temperature vs. pressure (Mengel et al., 2000).

reaction and return to a constant evaporation operation by means of changing the boundary conditions.

Simultaneously an *extinguishing limit* exists at which the cool flames stop because of low temperatures of the reaction and unfavorable conditions to the reaction kinetics. In this state, no appreciable reactions occur.

A change of the system pressure has an essential influence on the cool flames that are dominated by the reaction kinetic. An increase of the reactor pressure leads to a temperature increase in the reaction. The result of increasing the pressure by 10 kPa is a temperature increase of 8 to 12 K. This correlation is depicted in Figure 4 for industrial gas oil (Mengel et al., 2000). If the limiting temperature of the reaction is exceeded, the above described succeeding reactions occur. A pressure decrease causes a concomitant cooling of the system, so that temperatures of the reaction can be reached that cause an extinction of the cool flames.

For an operating level that is defined by the thermal boundary conditions, the air-ratio, and the steam-to-carbon ratio, a distinct pressure range exists between the appearance of succeeding reactions and extinction of the cool flames in which the reaction can be stabilized in the evaporation reactor (see Figure 5).

The air-ratio influences the reaction temperatures through the fuel partial pressure. Decreasing the air-ratio has the effect that the partial pressure of the hydrocarbons is increased, whereas that of the oxygen is slightly decreased. The decrease of the air-ratio therefore results in an increase of the temperatures (Hartmann et al., 2000). Correspondingly, the range of the cool flames moves to higher pressures for higher air-ratios (compare Figure 5).

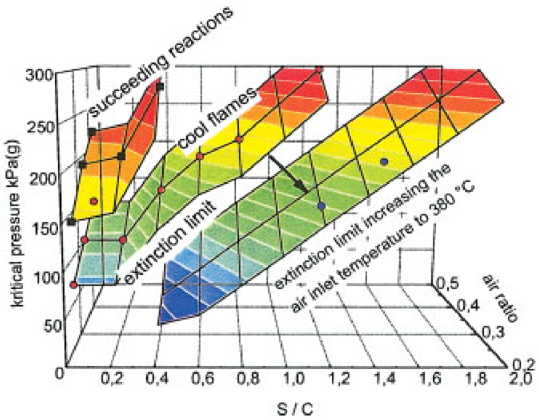


Figure 5. Appearance of cool flame reaction depending on the steam-to-carbon ratio and the air-ratio, critical pressure, when succeeding reactions occur and when reaction is extinguished.

Thermal power $P = 6$ kW, inlet temperature 300°C, gasoline representative fuel.

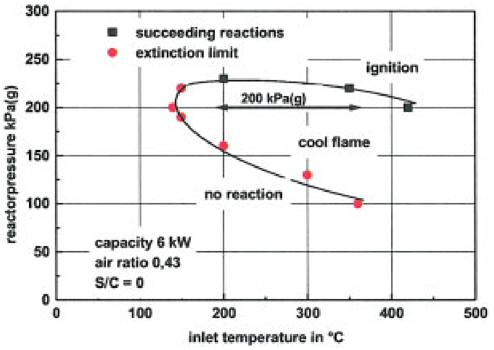


Figure 6. Existence of cool flame reaction depending on the thermal boundary conditions.

Likewise, the addition of steam into the air stream to the reactor causes a decrease of the reaction temperatures because the fuel partial pressure is reduced. As obvious from Figure 5, the limits of the reaction move to higher pressures according to the conditions when increasing the air-ratio. Therefore, a distinct operating range of the cool flames exists for constant thermal boundary conditions, depending on the air-ratio and the steam-to-carbon ratio.

The cool flame reaction at higher steam content can be stabilized through a change of the thermal inlet conditions. Higher preheating temperatures of the air and steam mixture move the extinguishing limit to lower pressures. If changing the thermal conditions is not sufficient to add enough steam into the process, there is still the possibility of splitting the steam addition at the beginning of the reaction and at the end of the cool flame reaction zone. In each case, the steam needed for the reformer process can be added and mixed within one preliminary step.

Influence of the thermal boundary conditions

A detailed consideration of the influence of air preheating proves the possibility of a displacement of the reaction limits through the change of the air inlet temperature. In particular, there is an influence on the extinguishing limit.

In addition to the operating range of cool flames depending on the air-ratio and the steam-to-carbon ratio described above, a further operating panel exists, which mounts itself dependent on the air inlet temperature (see Figure 6). For an air-ratio of 0.43 the extinction limit can be accordingly lowered from about 200 to 100 kPa(g), changing the inlet temperature from 150 to 350°C. Below an air inlet temperature of 150°C, no cool flame reaction occurs in the setup used. Simultaneously, the limit to succeeding reactions moves slightly from 230 to 200 kPa(g). Above a pressure of 230 kPa(g), no stable cool flames can be found with the chosen boundary conditions.

If the system runs in a secure operating state, for example, at a constant pressure of 200 kPa(g), the operation of the cool

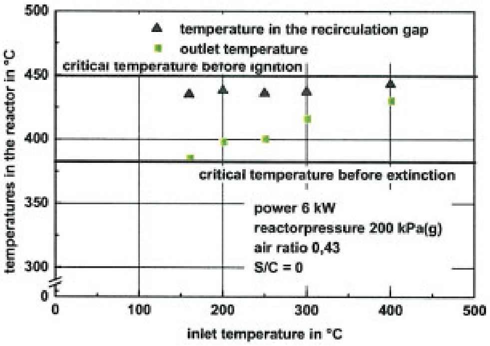


Figure 7. Reaction temperatures depending on inlet temperature, pressure 200 kPa(g).

flames is basically independent of the air preheating temperature within the given limits. This results in a high degree of regulation freedom, for example, in case of fast capacity modulation.

The temperatures in the reactor for the operating pressure of 200 kPa(g) appear dependently on the air preheating in Figure 7. It becomes clear that when changing the inlet conditions, the temperature in the recirculation gap remains almost constant because of the high residence time of the backflow. The reaction is dominated here by the air-ratio and the system pressure. The outlet temperature at the end of the reactor changes by only 80 K when the inlet temperature is varied by 250 K.

The critical temperature above which succeeding reactions occur was determined as being 450°C for the used gasoline-representative fuel. A complete extinction of the reaction is united with a temperature decrease below 380°C at the reactor outlet. Then, the recirculated gas is no more sufficiently active, so that the reaction collapses in the recirculation gap and therefore in the entire reactor.

A complete evaporation of the fuel can always be guaranteed within the operating limits. With high excess temperatures $\Delta\vartheta_{\text{excess}}$ (that is, the temperature difference between outlet and inlet temperature), high conversion rates U_{CFR} in the cool flame have to be expected. This correlation can be verified by a simplified energy balance, after which—in first approximation with otherwise identical boundary conditions—the following is valid

$$\Delta\vartheta_{\text{excess}} \sim U_{\text{CFR}} \tag{1}$$

Experiments with high steam-to-carbon ratios

High steam-to-carbon ratios influence the cool flame reaction; therefore, the thermal inlet conditions have to be changed so as not to fall below the extinction limits (compare Figure 5). The extinction limit can be moved by increasing the inlet temperature. This approach is followed for determination of the appropriate thermal inlet conditions (Table 1). The pressure was kept constant because of the downstream catalytic reformer.

Fuel Conversion through the Cool Flame Reaction. A simplified heat balance for the cool flame reactor provides results about the fuel conversion. The heat is divided mainly into three heat fluxes:

(1) Overheating of air and steam from inlet to outlet temperature:

$$\dot{Q}_1 = (\dot{m}_{\text{air}}c_{p,\text{air}} + \dot{m}_{\text{steam}}c_{p,\text{steam}})(T_{\text{outlet CFR}} - T_{\text{inlet mixture}}) \tag{2}$$

(2) Estimation of heat loss to periphery considering the outlet temperature without reaction

$$\dot{Q}_2 = (\dot{m}_{\text{air}}c_{p,\text{air}} + \dot{m}_{\text{steam}}c_{p,\text{steam}})(T_{\text{inlet mixture}} - T_{\text{outlet wo reaction}}) \tag{3}$$

It is assumed that the heat losses at temperatures without reaction are close to the thermal losses at cool flame temperatures.

(3) Vaporization and heating of the fuel from boiling to outlet temperature

$$\dot{Q}_3 = \dot{m}_{\text{fuel}}[c_{p,\text{fuel,liq}}(T_{\text{boiling}} - T_{\text{inlet fuel}}) + r_0 + c_{p,\text{fuel,vapor}} \cdot (T_{\text{CFR,out}} - T_{\text{boiling}}) \tag{4}$$

Dividing the sum of the three heat fluxes by the thermal power of the fuel

$$\dot{Q}_{\text{Fuel,in}} = \dot{n}_{\text{Fuel,in}}\text{LHV}_{\text{Fuel}}$$

gives the conversion rate in the cool flame reaction, expressed in percent

$$U_{\text{CFR}} = \frac{\dot{Q}_1 + \dot{Q}_2 + \dot{Q}_3}{\dot{Q}_{\text{Fuel,in}}} \times 100\% \tag{5}$$

The heat streams $\dot{Q}_1$ and $\dot{Q}_3$ are quantities that relate to the cool flame reaction, independent of the device where the cool flame reaction takes place. These also depend on the inlet conditions and the thermodynamical properties of air, steam, and fuel. The heat stream $\dot{Q}_2$ represents the heat losses to the periphery and is therefore dependent on the reactor characteristics (such as thermal insulation and geometry). Hence, $\dot{Q}_2$ is not directly measurable in the used apparatus. However, they influence the fuel conversion through the cool flame. Keeping the inlet temperature, the rate of inert gas, and the pressure constant, $\dot{Q}_2$ represents the only quantity that describes the effect of changing thermal boundary conditions to the cool flame reaction. When analyzing the fuel conversion through the cool flame, the specific heat losses to the periphery, given by Eq. 3, have to be considered

$$\%\text{losses} = \frac{\dot{Q}_2}{\dot{Q}_1 + \dot{Q}_2 + \dot{Q}_3} \tag{6}$$

Table 1. Thermal Inlet Conditions for Experiments

Fuel Power (kW)	*T* Inlet, Mixture (°C)	Pressure [kPa(g)]
7	380–385	180
11	380–395	180

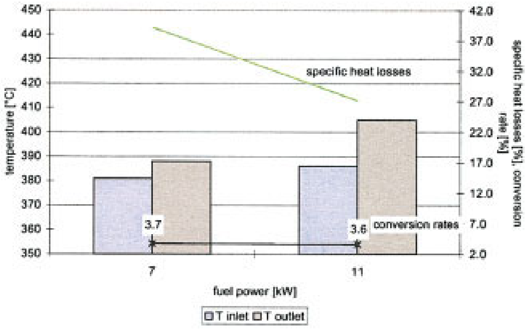


Figure 8. Correlation between specific heat loss and excess temperature at constant fuel conversion.

$P_{\text{reactor}} = 180$ kPa(g), air-ratio $= 0.34$, steam to carbon $= 2.0$.

The conversion rate U_{CFR} relates to excess temperature between outlet and inlet (compare comments in Conclusions). If heat losses are minimized at higher loads at short residence times, the excess temperature increases while the fuel conversion is kept constant. This is demonstrated in Figure 8. The variation of ±4 K in the inlet temperature occurs as a result of restriction of the controls of the apparatus.

It can be concluded that the cool flame reaction converts a defined portion of the fuel, when the reaction takes place within the temperature limits of the cool flame (compare Figure 7). The remaining fuel is converted through the cool flame reaction to hydrocarbons with lower molecular weight than that of the crude fuel. If the specific heat losses are too high, respectively too low, the extinction of the succeeding limits of the cool flames may be violated. In such a case, the defined conditions of the cool flames no longer exist. Therefore, it is important to balance the thermal losses with the overall thermal boundary conditions, which alone leads to stable cool flames, and which is one important restricting factor that must be accounted for in system architecture. Using the cool flame reactor as integrated mixing, vaporization, and overheating unit of an autothermal reforming process requires the control of the thermal boundary conditions: inlet temperature and specific heat losses.

Integration of a cool flame reactor with a primary reactor for autothermal reforming of liquid fuels

In an autothermal reforming process, fuel, air, and steam react to a synthesis gas with the main components hydrogen, carbon monoxide, carbon dioxide, and water. In an ideal reformer, two reactions take place—partial oxidation (POx) and steam reforming (SR)—and the heat balance of the process is neutral. Steam reforming requires heat that is provided through the partial combustion of the fuel in the reformer. The reactions are represented by

$$C_nH_m + \frac{n}{2}O_2 \leftrightarrow nCO + \frac{m}{2}H_2 \quad \text{(POx)}$$

$$C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \quad \text{(SR)}$$

Autothermal reforming of liquid fuels has a growing importance in the production of synthesis gas. An important characteristic of this process is the thermal efficiency given by

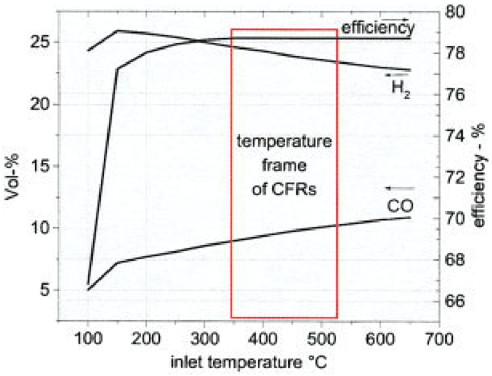


Figure 9. Simulated thermal efficiency, hydrogen and carbon monoxide concentrations related to the inlet temperature of the mixture for an ideal reformer at a steam-to-carbon ratio of 2.0, and an air-ratio of 0.34 at constant pressure.

Temperature frame of cool flames according to Figure 2.

$$\eta_{\text{th}} = \frac{\dot{n}_{H_2}\text{LHV}_{H_2} + \dot{n}_{CO}\text{LHV}_{CO}}{\dot{n}_{\text{Fuel}}\text{LHV}_{\text{Fuel}}} \tag{7}$$

$$\text{LHV}_{H_2} = 242 \text{ kJ/mol} \quad \text{LHV}_{CO} = 283 \text{ kJ/mol}$$

The efficiency of the process depends on, among other factors, the inlet temperature of the inlet mixture. Simulations provide the range of parameters (such as inlet temperature, steam-to-carbon ratio, and air-ratio), where autothermal reforming reaches high efficiency. Figure 9 shows the correlation between the inlet temperature, efficiency, and the concentrations of hydrogen and carbon monoxide for a steam-to-carbon ratio of 2.0 and an air-ratio of 0.34.

The simulation of an ideal reformer could be simplified using an adiabatic Gibbs reactor module: the reaction takes place in a way that the free energy or Gibbs energy is minimized. In this case, the products and the outlet temperature of

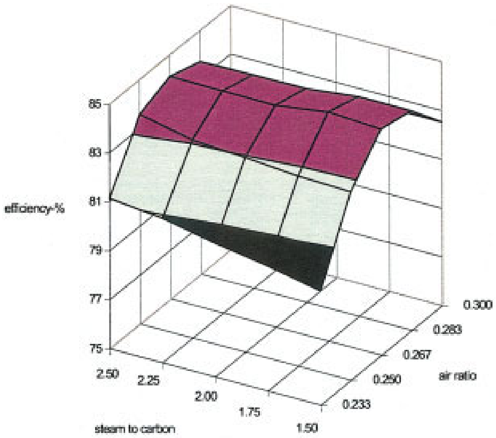


Figure 10. Simulated thermal efficiency by varying steam-to-carbon and air-ratio for an inlet temperature of 400°C in an adiabatic Gibbs reactor.

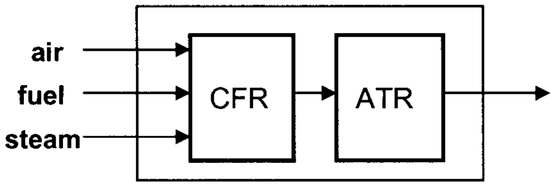


Figure 11. Integration of the cool flame reactor as vaporization and superheating unit with the autothermal reformer.

the reaction are generated in dependency on the inlet conditions. In the case of the inlet temperature being lower than 150°C, less hydrogen and carbon monoxide is formed and consequently the efficiency is low. High temperatures favor the formation of carbon monoxide and affect the formation of hydrogen. This effect is caused by the limitation of reaction, which is defined by the chemical equilibrium of the reaction: Above an inlet temperature of 350°C, the efficiency curve becomes asymptotic. At higher temperatures, no substantial improvement of the efficiency is reached.

At an inlet temperature of 400°C, the steam-to-carbon ratio and air-ratio were changed (Figure 10). The simulation shows that an efficiency of 80 to 85% can be achieved by varying the steam-to-carbon ratio and the air-ratio at a constant inlet temperature of 400°C.

An inlet temperature of the cool flame reaction in the range of 380 to 390°C was chosen for the experiments with high steam-to-carbon ratio (see Figure 8). Because autothermal reforming reaches satisfactory efficiency in this temperature range, cool flame reactor and primary reactor were linked together as one unit (Figure 11).

Temperature profile

The primary reactor requires uniform temperature and concentration profiles at the entry of the catalyst bed. A good mixing and a homogeneous, volumetric conversion are the results. Hence, hot spots, damage of the catalyst, and soot formation are avoided. Representative for the homogeneous conversion, the temperatures are measured between the cool flame and the primary reactor. Figure 12 schematically shows a cross section, where the positions of the thermocouples are visualized.

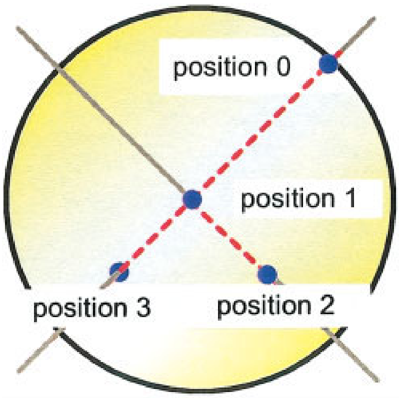


Figure 12. Position of the thermocouples in the cross section of the primary reactor.

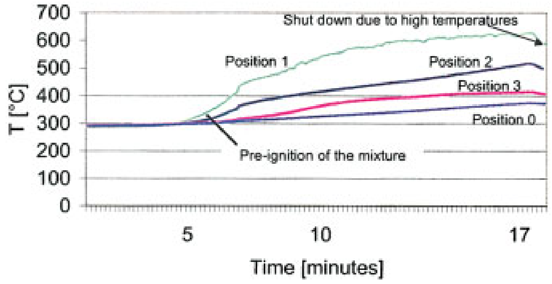


Figure 13. Temperature profile before the mixture comes to the catalyst bed using conventional mixing technologies: P_{Fuel} = 11 kW, $p_{reactor}$ = 180 kPa(g), air ratio = 0.34, steam-to-carbon ratio = 1.5.

Figure 13 shows the radial temperature profile before the catalyst when running the primary reactor with conventional mixing technologies (compare case A in Figure 1). The mixture has a preheating temperature of about 300°C. Because of a nonuniform mixing at the inlet, the mixture ignited before reaching the catalyst bed. This effect caused very high temperatures, which resulted in catalyst deterioration.

Figure 14 impressively shows the use of the cool flame reactor as vaporization and mixing unit of the primary reactor. At the time of fuel injection into the preheated cool flame reactor, a temperature increase occurs that is caused by the exothermic prereactions of cool flames. The excess temperature further increases the evaporation process. The reaction is stabilized at temperatures below 420°C. There was no preignition and the temperature profile was more uniform than it is depicted in Figure 13, which indicates a homogeneous approaching flow that equally distributes the reactant mixture on the catalyst. In this case, a deterioration of the reforming catalyst could be avoided and high reforming efficiency was observed.

Composition of the reformate gas

The autothermal primary reactor was run using a cool flame reactor as vaporization and mixing unit. Table 2 summarizes

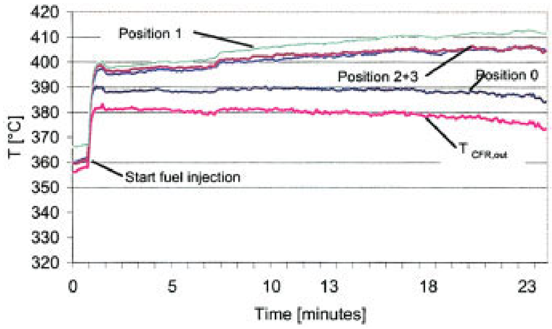


Figure 14. Radial temperature profile in the front of the catalyst bed using the cool flame reactor: P_{Fuel} = 11 kW, $p_{reactor}$ = 180 kPa(g), air-ratio = 0.34, steam-to-carbon ratio = 1.5.

Table 2. Conditions and Efficiency for Autothermal Reforming Using a Cool Flame Reactor for Vaporization and Mixing at Constant Pressure

	Air Ratio	Steam to Carbon Ratio	*T* Inlet (°C)	*T* Outlet (°C)	Efficiency (%)
Meausred conditions of the primary reactor	0.34	1,6	405	712	72
Simulation conditions of an adiabatic Gibbs reactor	0.34	1,6	405	928	78

the conditions of the experiment and the conditions of the simulation. The efficiency was calculated using Eq. 4.

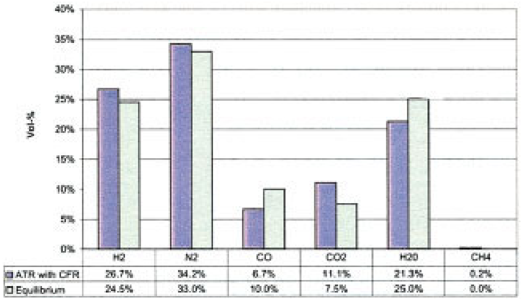
The difference between the outlet temperature of the experiment and the simulation results can be explained partly by the nonadiabatic conditions of the autothermal reformer. Additional explanations for the discrepancies can be found when comparing the concentration of the measured and simulated reformat gas (Figure 15).

The experimental results differentiate strongly from the simulation results for the concentrations of carbon monoxide, carbon dioxide, and water. These three components are part of the water gas shift reaction, which is an additional reaction occurring during the autothermal process. The water gas shift reaction (WGS) is the conversion of carbon oxide with steam to hydrogen and carbon dioxide, given by

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \text{(WGS)}$$

This reaction is exothermal, so it is favored at low temperatures. Figure 16 shows the concentrations of the four components involved in the water gas shift related to the outlet temperature of the adiabatic reactor.

Supposing that the water gas shift reaction would take place in the experiment, lower temperatures could be expected. The experimental conditions show exactly this effect: lower temperatures were found within the experiment than expected because of the adiabatic simulation. Also, the hydrogen concentration of the experiment reinforces the assumption that the water gas shift reaction took place in the nonadiabatic primary reactor.



	H2	N2	CO	CO2	H20	CH4
▨ ATR with CFR	26.7%	34.2%	6.7%	11.1%	21.3%	0.2%
☐ Equilibrium	24.5%	33.0%	10.0%	7.5%	25.0%	0.0%

Figure 15. Composition of the reformat gas.

Oxygen was not detected.

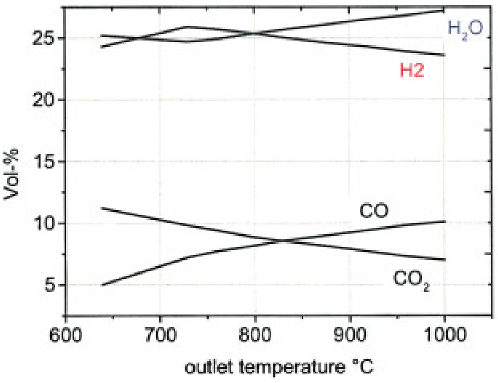


Figure 16. Simulated concentration of carbon monoxide, carbon dioxide, water, and hydrogen related to the outlet temperature.

Conclusions

The experiments conducted demonstrated the function of the cool flame reactor under autothermal reforming conditions. As a result of the investigation, the existence of cool flames, dependent on the parameters air-ratio, steam-to-carbon ratio, reactor pressure, and preheating conditions, are demonstrated for a gasoline-representative fuel. The cool flame reaction takes place within the conditions of autothermal reforming: air-ratio range of 0.2 to 0.5, steam-to-carbon ratio up to 2.0, and a pressure range of 150 to 250 kPa(g). The inlet temperature of the mixture is the essential parameter that can be varied to avoid violating the limit of succeeding reactions and the extinction limit of the cool flame. These characteristics are demonstrated during the stand-alone experiments with the cool flame reactor.

In the subsequent experiments, the cool flame reactor was linked to the autothermal reformer as a unit to vaporize and mix the fuel homogeneously with air and steam. An analysis of the experiments shows that the cool flame reaction is sensitive to the thermal boundary conditions—temperature of the inlet mixture and heat losses to the periphery—when running under constant pressure. As a result of heat losses to the periphery, the inlet temperature of the linked autothermal reformer, which is the outlet temperature of the cool flame reactor, is negatively influenced. Nevertheless, the cool flame reaction converts a defined portion of fuel independent of the heat losses. A combined unit, cool flame reactor and autothermal reformer, requires the control of the thermal boundary conditions: inlet temperature and specific heat losses.

The quality of the mixing produced through the cool flame reactor, as shown in our experiment, is characterized through a more homogeneous radial temperature profile between the cool flame reactor and the autothermal reformer compared with that of conventional mixing technology. This profile is stable over time, indicating good control of autothermal reforming inlet conditions using cool flames. A good mixing leads to good conversion at the catalyst bed. An analysis of the reformat gas shows that the combined unit produces a gas of composition close to the expected simulation results. Deviation occurs because of the model assumption of perfectly adiabatic reactor behavior and excluding of water gas shift reactions under autothermal reforming conditions.

These findings open up the way to promising investigations in the field of combining cool flame and autothermal reforming for liquid fuels. The characterization of the products of the cool flame under autothermal conditions, the development of a compact combined unit, and of control strategies to lead system requirements are the most important fields of further investigations.

Notation

η = efficiency
$\Delta\vartheta_{\text{excess}}$ = excess temperatures
c_p = specific heat capacity
D = diameter
$\dot{m}$ = mass flow
$\dot{n}$ = mole stream
p = pressure
P = thermal power
$\dot{Q}$ = heat flux
T = temperature
U = conversion rate
ATR = autothermal reforming
CFR = cool flame reaction
LHV = low heat value
S/C = steam-to-carbon ratio
WGS = water gas shift

Literature Cited

Curran, H. J., P. Gaffuri, W. J. Pitz, and C. K. Westbrook, "A Comprehensive Modeling Study of *n*-Heptane Oxidation," *Combust. Flame*, **114**, 149 (1998).

Curran, H. J., P. Gaffuri, W. J. Pitz, and C. K. Westbrook, "A Comprehensive Modeling Study of iso-Octane Oxidation," *Combust. Flame*, **129**, 253 (2002).

Dagaut, P., M. Reuillon, and M. Cathonnet, "High Pressure Oxidation of Liquid Fuels from Low to High Temperature. 1. *n*-Heptane and iso-Octane," *Combust. Sci. Technol.*, **95**, 233 (1994).

Dagaut, P., M. Reuillion, and M. Cathonnet, "Experimental Study of the Oxidation of *n*-Heptane in a Jet Stirred Reactor from Low to High Temperature and Pressures up to 40 Atm," *Combust. Flame*, **101**, 132 (1995).

Gaffuri, P., T. Faravelli, E. Ranzi, N. Cernansky, D. Miller, A. d'Anna, and A. Ciajolo, "Comprehensive Kinetic Model for the Low-Temperature Oxidation of Hydrocarbons," *AIChE J.*, **43**(5), 1278 (1997).

Hartmann, L., K. Lucka, C. Mengel, and H. Köhne, "Two-Stage Fuel Processor for Oil-based Fuel Cell Applications," *Proceedings of HYFORUM 2000* (Vol. II), The International Hydrogen Energy Forum 2000, Munich, Germany, (Sept. 2000).

Herman, I., J. Matos da Silva, C. Mengel, K. Lucka, and H. Köhne, "Interner Abschlussbericht," *Entwicklung eines Verdampfers für die mobile Brennstoffzellenanwendung unter Ausnutzung der Kalten Flammen*, Mainz-Kastel, Aachen, Germany, 25 (Feb. 2001).

Lemaire, O., M. Riboucour, M. Carlier, and R. Minetti, "The Production of Benzene in the Low-Temperature Oxidation of Cyclohexane, Cyclohexene and Cyclohexa-1,3-diene," *Combust. Flame*, **127**, 1971 (2001).

Lignola, P. G., F. P. Di Maio, A. Marzocchella, and R. Mercogliano, "JSFR Combustion Processes of *n*-Heptane and Isooctane," *21st International Symposium on Combustion*, The Combustion Institute, Pittsburgh, PA, 1625 (1988).

Lucka, K., and H. Köhne, "Usage of Cold Flames for the Evaporation of Liquid Fuels," *Fifth Conference on Technologies and Combustion for a Clean Environment*, Lisbon, Portugal, 207 (July 1999).

Lucka, K., and H. Köhne, "Moderne Gemischaufbereitung für flüssige Brennstoffe," *Third Aachener Kolloquium "Heizwärme aus Ölverbrennung"*, Aachen, Germany, 35 (Sept. 2000).

Mengel, C., L. Hartmann, K. Lucka, and H. Köhne, "Synthesegas für die Brennstoffzelle aus Heizöl EL," *Third Aachener Kolloquium "Heizwärme aus Ölverbrennung,"* Aachen, Germany, 113 (Sept. 2000).

Moon, D. J., K. Sreekumar, S. D. Lee, B. G. Lee, and H. S. Kim, "Studies on Gasoline Fuel Processor System for Fuel-Cell Powered Vehicles Applications, " *Appl. Catal. A, General* **215**, 1 (2001).

Pereira, C., J.-M. Bae, S. Ahmed, and M. Krumpelt, "Liquid Fuel Reformer Development: Autothermal Reforming of Diesel Fuel," *Hydrogen Program Technical Review*, U.S. Department of Energy, San Ramon, CA (May 2000).

Pilling, M. J. *Low-Temperature Combustion and Autoignition*, Vol. 35, Elsevier Applied Science, London (1997).

Ranzi, E., T. Faravelli, P. Gaffuri, A. Sogaro, A. D'Anna, and A. Ciajolo, "A Wilde-Range Modeling Study of Iso-Octane Oxidation," *Combust. Flame*, **108**, 24 (1997).

Ranzi, E., P. Gaffuri, T. Faravelli, and P. Dageaut, "A Wilde-Range Modeling Study of *n*-Heptane Oxidation," *Combust. Flame*, **103**, 91 (1995).

Warnatz, J., and U. Maas, *Technische Verbrennung*, Springer-Verlag, Berlin (1993).

Zizelmann, J., C. DeMinco, S. Mukerjee, J. Tachtler, J. Kammerer, and P. Lamp, "Auxiliary Power Units with Solid Oxide Fuel Cell Technology for Independent Electric Power Supply in Passenger Cars," *The Fuel Cell World Proceedings*, Lucerne, Switzerland (2002).

Manuscript received Jan. 16, 2003, and revision received Aug. 25, 2003.