The separation of evaporation from the catalytic reforming process is crucial for fuel processing. Unfavourable mixtures lead to degradation by local hot spots in the sensitive catalysts and formation of unwanted by-products. Cool flames offer a complete and residue-free evaporation of liquid hydrocarbon mixtures. The conditions determining whether cool flames can be stabilised or not are related to the heat management of the vaporizer. To determine this, examinations were conducted in a flow reactor to investigate stable cool flame operation under reformer conditions. A validation of the vaporizer is examined in combination with different reforming technologies.

INTRODUCTION

The mixture generation constitutes a key factor in terms of the quality of a reforming reaction. Inhomogeneities increase the tendency for soot to be formed and favour hot spots in the sensitive catalysts. Thus efforts are made to establish a homogenous educt mixture prior to the reforming zone. Therefore, liquid fuels such as diesel first need to be atomised and vaporised into microscopically sized droplets. Temperatures of 400°C, however, are required for the evaporation because the upper boiling point of diesel and industrial gas oil (IGO) lies at around 380°C. With direct vaporisation into a preheated airstream, the vaporisation can be provided by saturation. Already with temperatures about 150° to 200°C, a complete evaporation can be achieved (1). However, in technical applications the validity of this theoretical calculated temperature is restricted by non-ideal heat and mass transfer as well as a limited time scale.

Commonly the evaporation takes place in temperature areas and under residence times where auto-ignition can occur. One model to describe the ignition process is the thermal ignition-model where an auto-ignition arises from the self-heating produced by exothermic low-temperature reactions. The question of whether it comes to an explosion or not is related to the heat release compared with the heat losses of the system. Generally the heat release $\dot{R}$ rises exponentially with the temperature governed by the Arrhenius equation [1], whereas the heat losses $\dot{L}$ can be described by linear temperature behaviour due to the Newton law of cooling equation [2]. The impellent temperature difference is given by the mixture temperature $T$ and the wall temperature $T_w$. 

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In a certain temperature range a divergence from the Arrhenius behaviour can be observed for several fuels, including diesel or IGO. This temperature region is characterised by a decrease in the heat release with an increase in temperature. It is also referred to as the negative temperature coefficient (NTC). The key to this characteristic lies in the lack of stability of the links formed within the chain reactions as a result of oxygen being absorbed (2).

Figure 1 shows the relationship between heat release and heat loss in a closed vessel at different fixed surface temperatures for a mixture with NTC-characteristic. If the temperature of the mixture is below the initialisation temperature, $T_{\text{init}}$, heat losses dominate heat production. No relevant pre-reactions can be observed in the mixture. If the temperature exceeds the value of $T_{\text{init}}$, which has been identified for IGO in a range of 300°C, the heat production tops the heat losses, and a temperature increase up to $\Delta T = 180\,\text{K}$ is noticeable. As long as there is an intersection between $\dot{R}$ and $\dot{L}$, stable conditions could be established. The system will remain at a stationary state with constant temperature $T_s$. If the temperature is changed somewhat the system will return back to the stable point. This form of low-temperature reaction is called cool flame. Within this paper the cool flames have been investigated to realise a complete and residue-free evaporation of liquid hydrocarbon mixtures. The target is to determine the limits of cool flame stability in respect to three different fuel processor boundary conditions.

Equations:

\[ \dot{R} = \frac{\dot{Q_e}}{V} = \Delta U \cdot A \cdot e^{-\left(\frac{T}{k_f}\right)} \cdot c_f \]  
\[ \dot{L} = \frac{\dot{Q_l}}{V} = \alpha \cdot \frac{A}{V} \cdot (T - T_w) \]
Cool Flame Evaporation

The cool flame experiments are conducted in stainless steel tubes with diameters between 50 and 100 mm. The total length of the cool flame reactor is 200 mm in principle. The tube is contained in an insulation tube equipped with electrical radiation heating. The air is controlled by a mass flow controller and preheated with a heating cartridge up to 650°C. The fuel (industrial gas oil) is supplied to an injector with ambient temperature and injected via water-cooled commercially available simplex pressure atomizer (0.4 gal/h, 60°S). The power output is determined gravimetrically. The initialisation of the cool flame reactions takes place when the hydrocarbons are atomised in the preheated evaporator. For a technical evaporator the heat needed to actuate the pre-reaction can be produced with a startup burner. Once the cool flame has been initialised, air pre-heating is not mandatory when the hot product gas of the cool flame is recirculated into the reaction zone by aerodynamic methods (3).

All heat fluxes and flows of enthalpies have been measured to draw an energy balance of the evaporator tube (Figure 2). For simplification the assumption was considered that the outlet product gas consists only of air and oil vapour. The heat release of the cool flame reaction \( \dot{Q}_f \) is calculated by the balance heat supply of the evaporator tube \( \dot{Q} \) and the differences of the enthalpy flows of air \( \Delta H_{air} \) and fuel \( \Delta H_f \).

\[
\dot{Q} + \dot{Q}_r = \Delta H_{air} + \Delta H_f \quad [3]
\]

The balance heat supply \( \dot{Q} \) means the negative value of the heat loss in equation[2]. In further discussion the balance heat supply is referred to as the volume of the evaporator \( V \).

\[
B = \frac{\dot{Q}}{V} = -L \quad [4]
\]

![Figure 2. Simplified energy balance of cool flame vaporizer.](image)

Diesel Reformer

The diesel reformer is designed to produce fuel-cell suitable gases under atmospheric pressure by partial oxidation or autothermal reforming. Generally, the reforming
efficiency increases with decreasing air ratios while sufficient water takes place in the reforming reaction. The kind of reforming process, e.g., catalytic or thermal, is directly related to the sulphur content of the liquid fuel. If marketable IGO is the fuel, the fuel processor must work at high temperatures without catalysts so that sulphur components in the fuel do not lead to a degradation of the system. If diesel fuels with sulphur contents below 50 ppm are involved, catalytic fuel processing is the choice.

The reformer consists of two process stages, the evaporator and the catalytic reforming zone. In case of thermal partial oxidation, a ceramic porous matrix is used to stabilize the reaction zone (Figure 3). The homogeneous mixture of the liquid fuel and air is produced in the first reaction chamber using exothermic cool flame pre-reactions. With a temperature of 400°C to 480°C, the mixture is transferred into the second stage of the fuel processor to be converted by catalytic partial oxidation or by autothermal reforming if water vapour is supplied. A flashback protection is implemented to decouple both reaction chambers thermally as well as to prevent flashbacks.

RESULTS OF COOL FLAME EVAPORATION

According to Figure 1, the reaction mechanism of cool flames is nearly temperature-limited. A shift in the value of heat loss leads to a marginal change in the stabilisation temperature $T_s$. For this reason a reduction in the preheating of the air has only a small effect on the final temperature of the cool flame. In Figure 4 the educt conversion and product yields for CO, CO$_2$, and HC are given with respect to air inlet temperature for $n$-heptane. The cool flame reaction starts at temperatures of 330°C. The hydrocarbon and oxygen conversion decreases significantly with an increase in air preheating. Due to oxidation and decay reactions, it is mainly long hydrocarbon chains that react to form short molecules during this process. Also a noticeable conversion into carbon monoxide and carbon dioxide can be verified in the cool flame product.

The influence of air ratio and air inertisation on the cool flame temperature is given in Figure 5. In technical reformers, inertisation can result from off-gas or water vapour to control the partial oxidation temperature. Under the chosen boundaries, the inertisation
results from substitution of the air by combustion products. The ratio of the mass flows of inertisation gas $\dot{m}_{\text{inert}}$ to air $\dot{m}_{\text{air}}$ is defined as the recirculation ratio $r$:

$$ r = \frac{\dot{m}_{\text{inert}}}{\dot{m}_{\text{air}}} $$


Figure 4. Conversion of oxygen and $n$-heptane and yields of CO, CO$_2$, and HC with respect to air inlet temperatures; $p = 1.3$ bar, $\lambda = 1.2$, $t = 0.8$ s (5).

Figure 5. Influence of air ratio $\lambda$ and inertisation on cool flame temperature; $d = 100$ mm, isothermal conditions, IGO (1).
The inlet temperature is independent from the recirculation rate constant at 400°C. The wall temperatures are adjusted in the same magnitude. Without admixture of combustion products the cool flame temperature increases proportional with decreasing air ratio λ. Under the chosen boundary air ratios below λ = 0.68 led to auto-ignition of the mixture. By increasing inertisation the cool flame temperature reduces significantly, so that auto-ignition can be inhibited. The linear relationship between the cool flame temperature and the air ratio lasts in spite of the inertisation.

At air ratios below λ = 0.2, the linear coherence between the cool flame temperature and air ratio is not remarkable anymore (Figure 6). Instead of that at λ = 0.15 the cool flame temperature reaches a maximum which is followed by a temperature decrease with lower air ratios. In this case the lack of oxygen limits the cool flame reaction conversion.

![Figure 6. Influence of air ratio λ and inertisation on cool flame temperature; d = 100 mm (1).](image)

Although the temperatures of cool flame and partial oxidation approach at low air ratios a general difference can be deduced from the temperature courses. With the exception of air ratios below λ = 0.2 the cool flame decreases with rising air ratio whereas the adiabatic temperature increases. This is caused by the fact that higher air ratios mean a higher heat capacity which has to be heated up by the cool flame reaction. However, the conversion is limited both by the oxygen fraction and the partial pressure of hydrocarbons.

In Figure 7, the measured heat release $k$ of the cool flame reaction for $P = 5$ kW calculated by [1], [3] and [4] is drawn. The adjustable ranges of cool flames are limited by thermal ignition (high-temperature oxidation) and quenching where no reaction can be observed. The ranges of high temperature oxidation as well as the shift with higher heat supply $B$ to increasing air ratios. Lower air ratios prevent reaction quenching. Crucial is the lower heat capacity to heat up which causes higher reaction temperatures of the cool flame. The same effects are responsible for auto-ignition at higher heat supplies. If so the heat release tops the heat loss which is transferred by the reactor wall and the enthalpy.
Figure 7. Heat release $\dot{R}$ of the cool flame reaction with respect to heat supply/loss $\dot{Q}$ and air ratio $\lambda$, $d = 70$ mm, $P = 5$ kW (1).

flow of the product gas. It can be recognised that the evaporator runs autothermal up to air ratios $\lambda = 0.30$. So no heat transfer from the high temperature zone of the reformer is needed for the cool flame operation. Under these conditions the volume based heat release $\dot{R}$ lies in the magnitude of 600 kW/m³. Generally the heat release increases proportionally with the air ratio because the gas temperature only changes a little, but the heat capacity flow rises with higher values of $\lambda$. Increasing heat loss causes rising heat release because the cool flame temperature remains almost at the same level. Independent of heat supply/loss, the slope of the curves is nearly the same. Compared to the fuel input up to 10% of the caloric value can be converted into heat by cool flame reactions.

RESULTS OF DIESEL REFORMING

Compared with thermal fuel processing, the motivation to involve catalysts for reforming is to lower the process temperature at least by 200K to 300K as well as reactor volume. Already space velocities more than $SV = 40,000$ h⁻¹ are sufficient for main hydrocarbon conversion (1). To avoid catalyst poisoning, the use of sulphur-reduced fuels is mandatory. In this work an alkane-rich diesel fuel with sulphur content below 10 ppm was used. For quantitative comparison, the reforming efficiency $\eta_{ref}$ was introduced. This value gives information about the energy content of the product gas after fuel processing. It is defined as the ratio of the heating value of product gas to fuel (Eq. 6). The data for the fuel $H_{uf}$ and hydrogen $H_{m}\text{H}_{2}$ are based on the lower heating value (LHV).

$$\eta_{ref} = \frac{(\dot{n}_{H_{2}} + \dot{n}_{CO}) \cdot H_{m}\text{H}_{2}}{m_f \cdot H_u}$$

If the air preheating temperature is below the initialisation temperature of the cool flame, about 300°C, an evaporation operation without cool flames can be realised. Figure 8 compares both operation modes. Without cool flames an evaporation temperature of
about 180°C results with an air preheating temperature of 250°C. With cool flames the evaporation temperature reaches 410°C. As a result of the advanced mixture preparation by cool flames the inlet temperature of the CPO catalyst decreases by 50K.

Another imaginable reason for the decrease of the inlet CPO temperature can be attributed to the hydrocarbon conversion by cool flames. Among other reactions the conversion of alkanes to olefins and water in the cool flame reaction can be significant. Measurements of cool flame products for n-heptane verify olefin yields of about 10% (5). The dominant cooling effect is that endothermic steam reforming reactions already occur simultaneously in the catalyst entry. This is facilitated by the existence of water formed by cool flames. Furthermore the reforming efficiency increases by the advanced evaporation by cool flames from $\eta_{\text{ref}} = 0.67$ to $\eta_{\text{ref}} = 0.74$.

The measured inlet temperatures of the CPO catalyst between 950° and 1000°C exceed the operation temperature of the reforming catalyst, which is limited to 900°C. Degradation of the catalyst cannot be avoided. However, formation of soot can be predicted by thermochemical calculations at air ratios below $\lambda = 0.35$. Thus a narrow operation sector remains for CPO operation. Under real conditions the CPO temperature exceeds the adiabatic temperature because the kinetics of the reforming reaction are slower than oxidation reactions. Extending the operation sector for CPO is achievable by:

- optimisation of the catalyst performance by lifting the operation temperature
- off-gas recirculation
- water modulation.

The latter point means a shift from catalytic partial oxidation to autothermal reforming (ATR). Reforming temperatures can be controlled more easily by supply of water vapour. First, water vapour substitutes for the amount of oxygen and allows lower air ratios than CPO. Second, water vapour provides endothermic reforming reactions. Within the tests water vapour is produced externally and mixed with combustion air before the air nozzle.

![Figure 8. Gas concentrations, reforming temperature, and reforming efficiency for CPO with respect to air ratio $\lambda$ for catalytic partial oxidation of sulphur-reduced diesel, $\lambda = 0.36$, $P = 5.8$ kW, $T_{\text{air}} = 250$ °C, $SV = 21,000$ h$^{-1}$ (1).](image-url)
The measured temperatures for ATR operation with respect to the steam to carbon ratio SCR are given in Figure 9. The temperatures in the cool flame evaporator and in the ATR decrease with increasing SCR. Even at SCR = 0.5 the maximum operation temperature is reached in these measurements. Depending on water input, the cool flame reactions cause a temperature lift of up to 200K. In Figure 10 the measured gas concentrations of ATR are given with respect to thermochemical equilibrium. The yields of hydrogen and carbon monoxide agree with equilibrium values. Moreover, the type of catalyst material, both the expensive noble metal and nickel, seem to have no effect on hydrocarbon conversion. In both cases, the measured hydrocarbon concentration is strictly below 0.5% independent of the value of SCR, and degradation cannot be observed even after 500 hours.

Figure 9. Measured temperatures in ATR reformer with respect to SCR, sulphur reduced diesel, $\lambda = 0.30$, $P = 5.8$ kW, $SV = 30,000$ h$^{-1}$ (1).

Figure 10. Gas concentrations for different catalyst materials versus thermochemical equilibrium for ATR, sulphur reduced diesel, $\lambda = 0.35 +/- 0.01$, $P = 5.8$ kW, $SV = 12,000 - 40,000$ h$^{-1}$, operation time = 400 to 500 hours.
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NOMENCLATURE

| Symbol | Description          |
|--------|----------------------|
| $A$    | pre-exponential factor |
| $A_s$  | surface              |
| $\dot{B}$ | volume based balance heat supply |
| $c$    | concentration        |
| $d$    | diameter             |
| $E$    | activation energy    |
| $\dot{H}$ | enthalpy flow      |
| $\dot{H}_m$ | molar enthalpy flow |
| $H_u$  | calorific value      |
| $\dot{L}$ | volume based heat loss |
| $\dot{m}$ | mass flow           |
| $\dot{n}$ | mole flow           |
| $p$    | pressure             |
| $P$    | power output         |
| $R_n$  | universal gas constant |
| $\dot{Q}$ | heat flow           |
| $\dot{Q}_r$ | heat release flow    |
| $\dot{Q}_l$ | heat loss flow      |
| $\dot{R}$ | volume based heat release |
| $r$    | recirculation ratio  |
| $SV$   | space velocity       |
| $T$    | temperature          |
| $U$    | internal energy      |
| $V$    | volume               |
| $\alpha$ | heat transfer coefficient |
| $\lambda$ | air ratio         |
| $\beta$ | temperature          |
| $\tau$ | time                 |