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Experimental and mechanistic investigation of benzene formation during atmospheric pressure flow reactor oxidation of n-hexane, n-nonane, and n-dodecane below 1200 K

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ABSTRACT

The reaction kinetics of three n-alkanes: hexane, nonane, and dodecane are investigated both experimentally and numerically through speciation data obtained in a high temperature flow reactor. The measurements are performed in the temperature range of 750–1200 K for three different equivalence ratios ($\Phi = 0.5$, 1.0, and 2.0) and major combustion products, intermediates such as olefins, oxygenates, and a soot precursor benzene have been measured.

Formation of benzene is emphasized in this work at intermediate flame temperatures (in this case below 1200 K). Even though this temperature regime has its importance to technical combustors (e.g. at aero engines), the regime is often not studied except a few flow reactor studies. From the three fuels studied, one can see that the benzene formation increases apparently with fuel stoichiometry as well as with increase in carbon number. Unlike at flame conditions, where propargyl recombination plays an important role in benzene formation, at lower flame temperatures (< 1200 K) the benzene formation is a result of reactions through small hydrocarbon species occurring from an even ($C_2 + C_4$) route. The benzene formation reactions present in the reaction model of current work are n-$C_4H_5 + C_2H_3 = C_6H_6 + H_2$, n-$C_4H_5 + C_2H_2 = C_6H_6 + H$, i-$C_4H_5 + C_2H_4 \rightarrow C_6H_6 + H + H_2$, i-$C_4H_5 + C_2H_2 = C_6H_6 + H$, and i-$C_4H_5 + C_2H = C_6H_6$. Analysis of the mechanism at conditions of present work shows that the benzene formation is dominated by the reactions of i-$C_4H_5 + C_2H_4 \rightarrow C_6H_6 + H + H_2$ and i-$C_4H_5 + C_2H_2 = C_6H_6 + H$, their relative importance being dependent on the temperatures at which C_2H_4 and C_2H_2 is formed. The predictions of the speciation data are also compared with prominent literature reaction models (JetSurF 2.0, POLIMI, and RWTH). It appears that absence of either or both of these two reactions in JetSurF 2.0 and RWTH models leads to noticeably lesser contribution to benzene formation giving maximum deviation observed with the measurements. For the DLR and POLIMI models where benzene predictions are close to the experiments, these two reactions are present.

As a consequence a detailed in-house reaction model, which was already extensively validated against global combustion characteristics, has been tested against the measured speciation data. The model succeeds in reproducing all the measured species and is in good agreement with the measurements. This study identifies the major paths during the oxidation of all three fuels studied and provides valuable database and insight into the product spectrum and prediction of soot precursors.

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1. Introduction

The future share of renewable energy supply depends on available conversion and storage technologies [1]. Energy from renewable sources e.g. from wind, solar energy is intermittent in nature and therefore the use of surplus power in energy storage is very important for a secure continuous supply. The power-to-fuel process has promising potential, where CO_2 and electricity is converted to liquid fuels [2,3]. Another carbon source, and in the context of this work, is use of energy from renewable sources (e.g. biomass) through chemical energy conversion technologies for producing high density liquid hydrocarbons [3,4].

The demand for synthetic liquid hydrocarbon fuels has increased rapidly, as they provide high energy density fuels and benefit from already existing infrastructures. Main applications include alternatives to fossil based fuels in aviation and road transportation or energy storage [5]. They are typically produced by the Fischer–Tropsch (FT) process from reaction of hydrogen with a

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carbon source obtained from the renewable feedstock or CO_2 capture techniques. The product spectrum of liquid hydrocarbons obtained from this technology is wide and provides a variety of hydrocarbons in different chemical classes. In this context, large alkanes are studied in this work [3].

The three selected alkanes, namely n-hexane, n-nonane, and n-dodecane, are considered as representative of a continuous distribution of n-alkanes as obtainable from FT-processes and is representative, when influences of the obtainable product distribution should be captured. In this study, we aim to understand the difference or similarities in the intermediate pool that arises from the chemical breakdown of the fuel. This is important for an understanding of the pollutant formation e.g. soot formation, which is dependent on the intermediate pool that determines the first benzene ring formation. The presented mechanism thereby allows for flexible representation of various FT product distributions, consisting of n-alkanes.

The aim of this study is to investigate larger hydrocarbons to identify the intermediate species pool, product spectrum, and benzene formation by considering variation in carbon number i.e. chain length and fuel stoichiometry. The objective is to study these effects at temperature from 750 to 1200 K, i.e. at the lower end of temperatures relevant for technical combustors.

We also aim to investigate, whether the benzene formation is influenced by the fuel structure (in this case chain length of alkanes) and whether its formation routes at intermediate temperatures of present study are different compared to flame temperatures. The influence of fuel structure is often studied at flame conditions [6–18], where temperatures are typically above 1400 K. The benzene chemistry at such temperatures is dominated by propargyl recombination chemistry. This has been successfully revealed in a variety of studies [7,13,14,19]. Previous works from different research groups on benzene formation reactions investigated in fuels of different chemical classes (summarized in Table 1s in the Supplemental material) concludes that at flame conditions the propargyl recombination is the most important and prominent route to benzene (with only few fuel dependence exceptions) [6–18]. Most technical combustors cover a very broad span of temperature and stoichiometry conditions due the complex interactions of the turbulent fluid dynamics and chemical kinetics. Time-resolved polycyclic aromatic hydrocarbon (PAH), soot (Laser induced incandescence – LII) [20] and temperature measurements [21] for an aero engine typical swirl burner showed the presence of a significant number of instantaneous cases with temperatures below 1000 K in regions of the combustor that are also identified as PAH and soot formation regions. Unfortunately, the measurements have not been performed simultaneously, so no strict coincidence between the individual events can be drawn. Numerical simulations [22] suggest PAH and benzene formation in these flames starting at temperatures below 1200 K for the selected test case. Reaction kinetics investigations on the reactions governing the benzene formation at lower temperature are surprisingly attended by only a few studies [23–27]. In this study we investigate the speciation data of three n-alkanes: n-hexane, n-nonane, and n-dodecane in a combustion environment. This study focuses on the importance of small species/radicals in the prediction of pollutants for large hydrocarbons at lower flame temperatures.

1.1. Current status on larger hydrocarbons kinetics

There is a considerable amount of literature available on the three hydrocarbons considered in this study. The present status on modeling and experimental studies on n-hexane, n-nonane and n-dodecane is summarized in Table 1. The ignition delay times of the above three hydrocarbons are well investigated and investigations are available for atmospheric to high pressures (20–60 atm) in the temperature range of 700–1600 K [28-37]. The characteristic burning velocities are studied mostly at atmospheric conditions [38–40] except for n-hexane (2, 5, and 10 atm) [41]. Surprisingly, at flame conditions, no speciation data is available in literature for any of the three hydrocarbons. Species profiles for the three alkanes are measured in Jet Stirred Reactors (JSR) up to 10 atm and 500–1200 K [30,31,42,43]. Although the above mentioned studies cover sufficient experimental conditions required for mechanism development, none of them have measured benzene.

On the theoretical side, reaction models available are: n-hexane by Dagaut and coworkers [45], Blanquart et al. [46], LLNL [47] and n-nonane by LLNL mechanism [47]. The JetSurF 2.0 mechanism [44] includes all the three alkanes. The reaction model of n-dodecane can be found in LLNL [47], POLIMI [50], and Dagaut and coworkers [43]. Only few of the above mechanisms also include pathways to benzene formation [44,50].

1.2. Current status on benzene formation kinetics

The PAH inception starts from the formation of the smallest aromatic compound: benzene. Though PAH formation is just a part of the entire soot formation process, benzene formation is the limiting step [51]. The reactions responsible for benzene formation vary from C_2 to C_6 species chemistry. The chemical structure of fuels has a major influence on the benzene formation, since depending on the fuel the different alkyl radicals formed are the determining factor on the intermediate pool, consequently leading to benzene [12,16,23,52]. The benzene formation is thus dependent on the fuel itself in addition to the temperature region where they are formed. Thus understanding the structural effect of the fuel on benzene formation plays an important role for fuel design strategies and for soot reduction strategies.

Several reaction pathways to benzene formation are extensively studied, both theoretically and experimentally, in the literature. Most of the direct measurements of benzene available in the literature are in flames and are focused on smaller hydrocarbons ($C < 4$) [7,9,10,13,18]. A few studies are involved in direct measurement of benzene in flames with fuels larger than $C > 4$ [10–12,17]. Although at flame temperatures (above ~1400 K) benzene formation is dominated by fuel dependent precursors, the propargyl recombination is the dominating path to benzene ring formation for most fuels [6–18]. In flames, lower temperatures prevail close to the burner surface, where benzene formation possesses high measurements uncertainty [53]. Thus understanding of low to intermediate temperature benzene formation is inadequate through flame studies. This is important because propargyl radicals may not be formed at lower flame temperatures and many other small radicals shall play an important role in the benzene formation. Most efficient studies in this case are flow reactor tests, which can measure fuel conversion at temperatures as low as 900 K [23–27].

The theoretical side, though extensively studied, reveals many uncertainties with respect to the benzene formation pathways e.g. [18]. Inaccuracy in the recombination reactions involving small species influences the benzene formation interpretation heavily. Despite tremendous progress in mechanism development, many reaction models are only capable reproducing the benzene formation over a limited temperature range. Even the well accepted propargyl self-recombination path in different literature mechanism varies where benzene is either directly produced from propargyl self-recombination or via intermediate phenyl or fulvene [7,9,10,13,54–58]. Among the limited reaction mechanisms of larger hydrocarbons available in the literature that incorporate benzene formation chemistry as well are JetSurF 2.0 [44] and POLIMI [50].

The above discussed studies have shown that formation of benzene is complex involving many different reaction routes owing to temperature and fuel structure. This study provides a discussion on

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