Polycyclic aromatic hydrocarbons in pyrolysis of gasoline surrogates (*n*-heptane/*iso*-octane/toluene)

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Abstract: Toluene primary reference fuels (TPRFs), i.e., a ternary mixture of toluene, *n*-heptane and *iso*-octane, better match the combustion properties of real gasoline fuels compared to simpler binary *n*-heptane/*iso*-octane mixtures. While there has been significant research on combustion of *n*-heptane/*iso*-octane mixtures, fundamental data characterizing polycyclic aromatic hydrocarbons (PAHs) formation in TPRFs combustion is lacking, especially under pyrolysis conditions. In this work, the pyrolysis of two TPRF mixtures (TPRF70 and TPRF97.5), representing low octane (research octane number 70) and high octane (research octane number 97.5) gasolines, respectively, was studied in a jet-stirred reactor coupled with gas chromatography (GC) analysis and a flow reactor coupled with synchrotron vacuum ultraviolet photoionization molecular beam mass spectrometry (SVUV-PI-MBMS). The experiments indicate that pyrolysis of TPRF70 produced slightly higher benzene and naphthalene than TPRF97.5. In contrast, TPRF97.5 pyrolysis produced slightly higher phenanthrene and pyrene than TPRF70. The mole fraction profiles of aromatics from benzene to pyrene were used to validate TPRF kinetic models from the literature. Specifically, the KAUST-Aramco PAH Mech 1-GS kinetic model was updated to match and elucidate the experimental observations. The kinetic analysis reveals that propargyl radical is a crucial intermediate forming the benzene and naphthalene, while benzyl radical, generated from the dehydrogenation of toluene, plays an important role for larger PAHs formation.

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1. Introduction

Soot particles and their precursors polycyclic aromatic hydrocarbons (PAHs) emitted from on-road vehicles contribute to anthropogenic aerosol emissions, thereby harming the environment and human health [1, 2]. Emission of these carcinogenic pollutants is expected to increase with the growing demand for light-duty vehicles powered by gas direct injection (GDI) engines. This type of engine is widely used in the transport sector because of its fuel efficiency; however, they are characterized by a higher tendency for soot formation [3].

Elucidating the formation mechanisms of soot and their precursors in combustion has been a research target for decades [4]. Fundamental data from well-defined reactors and kinetic modeling with detailed reaction pathways are promising tools to bridge the gap [4-8]. The combustion properties of molecules representative of those in gasoline, such as normal-alkanes, branched alkanes, and aromatics have been extensively investigated, providing data to develop detailed reaction mechanism for PAHs.

Gasoline surrogates comprising binary, ternary or multi-component mixtures are used to mimic gasoline combustion and guide the development of advanced combustion engine (ACE) technologies [4, 5, 9-11]. Among them, toluene primary reference fuel (TPRF) surrogates are ternary blends of toluene/*n*-heptane/*iso*-octane. The advantage of using a TPRF surrogate is to better match the composition and combustion properties (e.g., octane numbers [5]) of gasoline compared primary reference fuel (PRF, binary mixture of *n*-heptane/*iso*-octane). TPRFs emulate the aromatic, *n*-paraffinic and *iso*-paraffinic content in real gasolines, as these three classes represent more than 90% of the chemicals in commercial gasoline fuels [12]. The presence of aromatics in gasolines and their surrogates was observed to enhance PAHs formation [4, 13].

79 Literature experimental studies on PAHs formation for TPRF surrogates is scarce, as the focus
80 has been on binary mixtures. Choi et al. [14] studied PAHs and soot formation characteristics for
81 binary mixtures in counter-flow diffusion flames using laser-induced fluorescence (LIF) and laser-
82 induced incandescence (LII). Synergistic effect was observed in *n*-heptane/toluene and *iso*-
83 octane/toluene flames. Kashif et al. [15] studied sooting propensities of binary mixtures in laminar
84 flames. Tang et al. [16] studied the soot particles formation of *n*-heptane/toluene mixtures in laminar
85 premixed burner-stabilized stagnation flames, and found that the doping of toluene resulted in soot
86 inception at lower flame heights and reduced primary particle size of soot aggregates. Park et al. [13]
87 systematically investigated surrogate composition effects on PAHs and soot formation in flames (e.g.,
88 *n*-heptane/*iso*-octane, *n*-heptane/toluene, *iso*-octane/toluene, and *n*-heptane/*iso*-octane/toluene), and
89 developed a detailed PAH formation mechanism for TPRF mixtures (denoted “KAUST-Aramco
90 Mech 1-GS” or simply KAM-GS). However, quantitative analysis of PAHs was not performed
91 because of limitations of their LIF technique [17].

92 Several kinetic models for TPRFs exist in the literature. Blanquart et al. [10] developed a
93 mechanism for engine relevant fuels, highlighted the importance of acetylene, propyne, propene, and
94 1,3-butadiene in the formation of PAHs. Marchal et al. [18] developed a model of aromatics and soot
95 formation for large fuel molecules including reactions for benzene and PAHs up to four rings. Raj
96 et al. [19] and Park et al. [13] developed PAHs mechanisms for gasoline surrogate fuels to predict
97 the synergistic effect of PAHs formation. An et al. [20] and Wang et al. [21] presented reduced
98 mechanism for TPRFs, and coupled them with numerical simulations to predict PAHs and soot
99 formation in engines. However, due to the lack of fundamental data for PAHs in TPRF combustion,
100 these kinetic models have been typically validated using pure *n*-heptane, *iso*-octane, and toluene
101 experimental results or un-quantified data with a focus of predicting trends in PAHs formation [13,
102 19].

Motivated by these gaps in experiments and kinetic models, this work provides speciation data of PAHs during the pyrolysis of two representative TPRF mixtures, i.e., TPRF97.5 and TPRF70 [12], which were formulated to match the octane number and octane sensitivity of high octane and low octane (i.e., naphthas) gasolines, respectively. In studying these TPRF mixtures, the effect of surrogate composition on PAHs formation is elucidated. The aforementioned TPRF kinetic models were validated by comparing mole fraction profiles of benzene and PAHs up to four rings. As an ongoing work to develop the KAUST PAHs kinetic model, the latest version by Park et al. [13] was improved to better match the experimental data in this work and explain the PAHs formation behavior for the two TPRF mixtures.

2. Experimental and simulation methods

Pyrolysis of TPRF 97.5 and TPRF 70 at 1 atm was performed in a jet stirred reactor (JSR) at KAUST and in a flow reactor at NSRL in USTC, China. Intermediates from fuel decomposition and aromatics from benzene to PAHs with four rings were measured by GC and SVUV-PI-MBMS. The formulation of the two TPRF mixtures followed the methodology described in Ref. [12] to match the research octane number (RON) and octane sensitivity (S) of a typical high-octane gasoline with RON=97.5 and S=10.9 and a low-octane gasoline (naphtha) RON=70, S=4. The molar composition of toluene/*iso*-octane/*n*-heptane is 0.285/0.365/0.35 for TPRF70 and 0.775/0.08/0.145 for TPRF97.5.

The JSR with volume of 76 cm³ and the sampling systems are similar to those of Dagaut et al. [22]. Details of the KAUST JSR is described in [23]. The experiments were conducted at a fuel concentration of 0.25% and residence time 1s. The JSR is located in an oven and the temperature of the reactor is measured by a K-type thermocouple. Good temperature homogeneity was observed by moving the thermocouple along the centerline of the reactor. The products are sampled by a sonic-throat gas sampling probe located at the outlet of the reactor and connected to a mechanical pump. The pressure-drop across the orifice is sufficient to prevent further reactions in the sample transfer line. The sample gas is analyzed online using Agilent Refinery Gas Analysis (RGA) and Agilent

128 7890B GC. The Agilent RGA system, following ASTM D1945, D1946, and UOP 539 method, with
129 by TCD and FID detectors was used to quantify H₂ and C₁-C₅ hydrocarbons during TPRF pyrolysis.
130 The Agilent 7890B system is equipped with an Agilent DB-1 column (15mm×0.320mm) and an FID
131 to separate and detect PAHs. The total time of the temperature program is 17.833 mins, oven
132 controlled as follows: 1. 45 °C for 6 mins; 2. Then 30°C /min to 100°C for 4 mins; 3. then 30°C /min
133 to 280°C for 0 min. Identification of PAHs was performed by injecting standard samples. PAHs
134 mole fractions were calculated by calibrating with toluene and applying corresponding effective
135 carbon numbers. The uncertainty is ±5% for reactant mole fraction, ±15% for C₁-C₅ pyrolysis
136 products , and ±30% for PAHs. The errors are a result of uncertainty in the mass flow controllers and
137 syringe pump, measurement reproducibility, and uncertainties in gas chromatograph measurements,
138 etc.

139 TPRF pyrolysis in a flow reactor with inner diameter of 7 mm was analyzed by SVUV-PI-
140 MBMS at NSRL in USTC [6, 24, 25]. The temperature profile of the flow reactor is measured by an
141 S-type thermocouple and denoted by its maximum temperature (T_{max}), which denotes the
142 experimental temperature. The temperature profiles used in simulations are provided in
143 Supplementary Material-1 (SM-1). The uncertainty of T_{max} is ±30 K. The total flow rate of the
144 mixture was kept at 1.0 standard liter per minute (SLM) at 298 K. The calculated residence times in
145 the studied temperature range are $1.2\text{--}2.0\times 10^{-1}$ s. A high fuel mole fraction of 0.0057 was used to
146 improve measurement of PAHs with three and four rings. Mole fractions of reactants and several
147 aromatics from benzene to PAHs with four rings were quantified. Photoionization cross sections
148 (PICSs) for the aromatics were obtained from literature [26-28] or estimated from species with
149 similar structure. The values at 10.5 and 9.5 eV are shown in Table S1 of SM-2. The measurement
150 uncertainty is ±10% for reactant species, ±25% for those with measured PICS (benzene,
151 ethylbenzene, styrene, indene, naphthalene), and a factor of 2 for those with estimated PICS
152 (bibenzyl, phenanthrene, and pyrene). Experiments with TPRF 70 and 97.5 were carried out using

the same experimental setup over the same period of time, the data evaluation procedure is the same for the two datasets, and the photoionization cross sections for the PAHs are from the same source. Although a factor of two in the uncertainty was estimated, the error for the same PAH obtained from the two TPRF mixtures cancels out. Therefore, the experimental observation for the mole fraction difference of the PAHs in the two TPRF mixtures is not affected by experimental uncertainty.

JSR simulations were performed in CHEMKIN-PRO [29] using the perfectly stirred reactor module (transient solver with an end time of 50 s). The flow reactor pyrolysis experiments were simulated as a plug flow reactor with the experimentally measured temperature profile as an input boundary condition (i.e., the gas-energy equation was not solved).

3. Results and discussion

It is interesting to note the significant difference in toluene composition of the two TPRF fuels; TPRF 70 (28.5%) has significantly less toluene than TPR97.5 (77.5%). Conventional knowledge would suggest that TPRF97.5 produces significantly more PAHs than TPRF70 due to the higher toluene content in the former. Experimental results and numerical analysis presented below shed further light on this conventional wisdom.

Mole fractions of reactants (*n*-heptane, *iso*-octane, and toluene), CH₄, C₂H₂, C₂H₄, C₃H₆, allene, propyne, benzene (A1), ethylbenzene, styrene, indene, and naphthalene (A2) were measured by GC analysis for both TPRFs. Apart from these intermediates, more PAHs were measured by the SVUV-PI-MBMS in the flow reactor pyrolysis experiments, such as bibenzyl (C₁₄H₁₄), phenanthrene (A3) and pyrene (A4). The structure of these cyclic intermediates including 1,3-cyclopentadiene and aromatics with one to four rings are shown in Table 1. The mole fractions of these C₁ to C₁₈ intermediates are valuable to examine fuel decomposition chemistry, as well as PAHs growth reactions. In the following discussion, we first evaluate the literature kinetic models for TPRFs by comparison to experimental data. Specifically, discrepancies between predictions of the KAM-GS model and experiments are analyzed. Several modifications of the model are presented to improve

predictions of fuel decomposition and formation of benzene and A4. Next, the model is used to discuss the pyrolysis chemistry of the two TPRFs, with focusing on PAH characteristics.

Table 1. Major aromatics detected in TPRF pyrolysis in this work.

Name	Structure	Name	Structure	Name	Structure	Name	Structure
C ₅ H ₆		C ₆ H ₆		C ₈ H ₆		C ₈ H ₈
C ₈ H ₁₀		C ₉ H ₈		C ₉ H ₁₀		C ₁₀ H ₈
C ₁₀ H ₁₀		C ₁₁ H ₁₀		C ₁₂ H ₈		C ₁₂ H ₁₀
C ₁₃ H ₁₀		C ₁₃ H ₁₂		C ₁₄ H ₁₀		C ₁₄ H ₁₂
C ₁₄ H ₁₄		C ₁₆ H ₁₀		C ₁₈ H ₁₂

3.1 Evaluation of literature kinetic models

In this section, four kinetic models for TPRFs, i.e., Blanquart [10], Wang [21], Marchal [18], and Park [13] were used to simulate the pyrolysis of TPRF70 in the JSR and flow reactor. The relative amounts of *n*-heptane, *iso*-octane, and toluene are similar in TPRF70, which facilitates investigating interactions among the three fuels. Fuel decomposition profiles, acetylene, allene, A1 and A2 in the JSR, as well as A3 and A4 in the flow reactor were selected as validation targets. Comparisons between the experimental measurements and kinetic modeling simulations from literature models are shown in Fig. 1. Blanquart [10] predicts *iso*-octane, toluene, acetylene and benzene well, but not the formation of larger PAHs. Narayanaswamy [30] updated Blanquart's mechanism, but the predictions of PAHs weren't improved. The simulated results from Wang [21] under-predict the consumption of the three fuels and the formation of A2 and A3. The accurate prediction of A1 and A4 is fortuitous given that fuel decomposition profiles are notably under-predicted. Marchal [18] well predicts the consumption of toluene, but the consumption of *n*-heptane and *iso*-octane is under-predicted. In addition, this model predicts higher mole fraction of benzene

196 and lower mole fractions of A2-A4. In contrast, Park [13] (KAM-GS) predicts well the consumption
197 of *n*-heptane and *iso*-octane, but over-predicts the consumption of toluene, and formation of benzene
198 and A4. The prediction of other species in JSR pyrolysis of TPRF70 by the literature models are
199 presented in Fig. S1 of SM-2.

200 In KAM-GS, the pyrolysis and oxidation of small hydrocarbons were updated with C₀-C₄ base
201 chemistry from AramcoMech 1.3 [31]. KAM-GS accurately captured the synergistic PAH formation
202 characteristics in *n*-heptane/toluene and *iso*-octane/toluene flames and the experimental trends in
203 formation of larger PAHs in TPRF mixtures. In this work, the Park et al. [13] model (KAM-GS) was
204 selected as the base model for improvement. To match the present set of experimental data, some
205 modifications to the PAH sub-mechanisms were made (details of model modification can be found in
206 Table S1 of SM-3). Model analysis shows that the rate of $C_6H_5CH_3 + H = A1 + CH_3$ is too fast in KAM-
207 GS, which leads to over-prediction of toluene consumption and benzene formation, as shown in Fig.
208 1. The rate constant was updated according to Vasu et al. [32]. Several pyrene (A4) formation
209 pathways are present in KAM-GS, but the reaction of two indenyl radicals addition
210 ($2C_9H_7 = A4 + C_2H_2 + H_2$) over-predicted A4 formation. In the toluene pyrolysis mechanism by Yuan et
211 al. [33], the self-combination of two indenyl radicals leads to chrysene, instead of pyrene. To
212 improve pyrene predictions, the original indenyl radicals addition reaction was replaced by reaction
213 $2C_9H_7 = CHRYSEN + 2H$ and the reaction rate of $C_6H_5CH_2 + C_9H_7 = A4 + 2H_2$ was updated according to
214 Sinha et al [34]. Furthermore, reactions of methyldene (C₉H₇CH₃), estimated from Yuan et al. [33],
215 were included in the model to better predict larger PAHs. Updating these reactions improved
216 prediction of PAHs formation from pyrolysis of both TPRFs. The following comparisons with
217 experimental measurements and analysis of the PAHs formation characteristics in the different TPRF
218 mixtures are based on the modified KAM-GS mechanism.

219

Figure 1. Comparison between experimental and simulated [10, 13, 18, 21, 30] mole fractions of TPRF components, acetylene, allene and one to four ring aromatics in TPRF 70 pyrolysis. The experimental data for A3 and A4 were taken from flow reactor pyrolysis while the rest were from JSR pyrolysis.

3.2 Pyrolysis chemistry of two TPRF mixtures

3.2.1 Fuel consumption

The mole fractions of toluene, *n*-heptane and *iso*-octane as a function of temperature in the JSR and flow reactor pyrolysis of TPRF70 and TPRF97.5 are shown in Fig. 2. Complete consumption of *iso*-octane and *n*-heptane in JSR pyrolysis is clearly seen at 1050 K and 1100 K, respectively. Although *n*-heptane is more reactive than *iso*-octane under oxidation conditions (i.e., higher rate of consumption), *iso*-octane has higher rate of consumption during pyrolysis due to the relatively weak tertiary-quaternary carbon bond [35]. This is also supported by the higher total unimolecular decomposition rate constants of *iso*-octane than those of *n*-heptane (Fig. S2 in SM-2). In TPRF97.5 pyrolysis, the consumption of toluene is much slower and a large amount of toluene is still present at high temperatures (i.e., 1205 K in JSR pyrolysis). Hypothetical simulations for pyrolysis of pure *n*-heptane, *iso*-octane, or toluene are shown in Fig. S3 of SM-2 to compare the pyrolysis of these fuel

237 components in TPRF mixtures. Toluene consumption is promoted in TPRF mixtures relative to when
 238 it is a pure fuel. The decomposition of toluene was strongly promoted when mixed with *iso*-octane
 239 and *n*-heptane, in contrast to the pure toluene decomposition in JSR pyrolysis at around 1130 K. This
 240 is attributed to toluene consumption by free radicals (i.e., H, CH₃, C₂H₃, C₃H₃, C₃H₂) produced
 241 during the pyrolysis of *iso*-octane and *n*-heptane. *iso*-Octane is shown to be the most reactive
 242 component (i.e., it is consumed completely at the lower temperatures) as a pure component as well as
 243 in the TPRF mixtures; its consumption is not greatly affected by blending with *n*-heptane and toluene.
 244 *n*-Heptane is consumed at slightly lower temperatures in TPRF97.5 pyrolysis. The rate of production
 245 analysis of fuel consumption (Fig. S1 in SM-3) in JSR at 1050 K indicates that the main pathways of
 246 fuel decomposition are similar in both TPRF70 and TPRF97.5 pyrolysis. Generally, the updated
 247 KAM-GS simulation shows good agreement with the experimental profiles. Nevertheless, the
 248 consumption of toluene was under-estimated for TPRF97.5 pyrolysis in both JSR and flow reactor at
 249 low temperature (e.g., before 1200 K). Also, the consumption of *iso*-octane in TPRF70 is slightly
 250 over-predicted in flow reactor pyrolysis.

251

252 **Figure 2.** Mole fraction profiles of three components of TPRF (toluene/ *iso*-octane/ *n*-heptane) in
 253 JSR and flow reactor (FR) pyrolysis and mole profiles of small molecules in JSR. Open symbols are
 254 experiment results while lines are simulation results. Blue triangles and dash dotted lines are
 255 TPRF70 while red circles and solid lines are for TPRF97.5.

256 The good prediction of *n*-heptane and *iso*-octane consumption for the two TPRF mixtures
257 pyrolysis in JSR is also reflected by the mole fractions of small molecule including CH₄, C₂H₂, C₂H₄,
258 C₃H₄, and C₃H₆ in Fig. 2. The overall agreement between the experimental data and the computed
259 data for these small intermediates is satisfactory. These species are produced from *iso*-octane's and
260 *n*-heptane's unimolecular decompositions and H-atom abstractions, as shown in Fig. S1 of SM-3.
261 The TPRF70 produced more small hydrocarbons than TPRF97.5, as the former contains more *iso*-
262 octane and *n*-heptane. The large production of C₂H₂, allene, and propyne in TPRF70 influences its
263 PAH formation characters, which will be discussed later.

264 3.2.2 Formation of first aromatic ring

265 The mole fraction profiles of benzene in JSR and flow reactor pyrolysis are shown in Fig. 3a
266 and 3b. The observed trend for benzene is similar in both JSR and flow reactor pyrolysis. The
267 formation of benzene starts at 900 K in JSR pyrolysis. In the range of 1050 K and 1200 K, the
268 concentration of benzene in TPRF70 pyrolysis is slightly higher than that in TPRF97.5 pyrolysis,
269 despite the higher toluene content in TPRF97.5. As mentioned by Park et al. [13], the main source
270 for benzene is the reaction of toluene with H atoms (C₆H₅CH₃+H=A1+CH₃) in TPRF mixtures.
271 Nonetheless, the self-combination of propargyl radicals (C₃H₃+C₃H₃=A1) and the reaction of
272 propargyl radical with allyl radical (C₃H₃+C₃H₅-A=A1+2H) also have large contribution to benzene
273 formation in TPRF70 pyrolysis. For example, according to ROP analysis at 1050 K in JSR (see
274 Figure S1 in SM-3), 28% of benzene formation is from C₃H₃+C₃H₅-A in TPRF70, but only 3% in
275 TPRF97.5. The higher concentration of allene and propyne in TPRF70 pyrolysis (Fig. 2j and 2k)
276 leads to higher mole fraction of propargyl radical via H-atom abstraction by H atom and CH₃ radical.
277 In addition, more allyl radical (C₃H₅-A) is produced in TPRF 70 pyrolysis than TPRF97.5 due to the
278 more formation of propene (Fig. 2l). Thus, the predominance of C₃H₃+C₃H₃ pathways in TPRF70
279 pyrolysis leads to comparable benzene mole fraction, even though TPRF97.5 contains a much higher
280 mole fraction of toluene. In addition, the formation of benzene in JSR pyrolysis of TPRF70 slows

down after 1200 K, while the benzene mole fraction continues increasing in TPRF97.5. The reaction of toluene with H atom is the dominant pathway for benzene after 1200 K in TPRF 97.5, while $C_3H_3 + C_3H_3$ reactions become less important.

Besides benzene, the formation of ethylbenzene ($C_6H_5C_2H_5$) in JSR pyrolysis also starts at 900 K in Fig. 3c and 3d. Model analysis shows that ethylbenzene is mainly produced from the reaction of benzyl radical with methyl radical ($C_6H_5CH_2 + CH_3 = C_6H_5C_2H_5$), while benzyl radical is formed from the H-atom abstraction of toluene. The higher concentration of benzyl radical in TPRF97.5 pyrolysis leads to higher mole fraction of ethylbenzene than that in TPRF70 pyrolysis. After 1050 K, ethylbenzene is mostly consumed by H-atom abstraction and two consecutive steps of dehydrogenation leading to styrene in Fig. 3e and 3f. The model predicts well the mole fraction profiles of ethylbenzene and styrene in both JSR and flow reactor pyrolysis.

Figure 3. The mole fraction profiles of aromatics with one ring (benzene, ethylbenzene, and styrene) in JSR and flow reactor (FR) pyrolysis of two TPRF mixtures. Blue triangles and dash dotted lines are TPRF70 while red circles and solid lines are TPRF 97.5.

3.2.3 Formation of large PAHs

Indene (C_9H_8) plays an important role in PAHs growth because indenyl radical (C_9H_7), produced by the dehydrogenation of indene, directly reacts with other radicals to produce A2, A3,

299 and A4 [7]. Experimental indene mole fractions of the two TPRFs shows opposite trends in the JSR
 300 and flow reactor pyrolysis (Fig. 4a and 4b). However, the simulation shows that TPRF97.5 produces
 301 more indene than TPRF70 in both reactors. The flux analysis in 1050 K indicates that the addition of
 302 acetylene (C_2H_2) to benzyl radical ($C_6H_5CH_2 + C_2H_2 = C_9H_8 + H$) contributes to 75% of indene
 303 formation in TPRF97.5 and 66% in TPRF70 in JSR. The low prediction of indene in TPRF70 may
 304 be due to the under-prediction of acetylene in Fig.2h. In addition, the reaction between phenyl (A1-)
 305 and allene, $A1- + C_3H_4 - A = C_9H_8 + H$, contributes 19% and 27% to indene formation in TPRF97.5 and
 306 TPRF70, respectively. Although additional reactions of methyindene were added to the model, the
 307 model still under-predicts indene profiles, which indicates that additional reactions may be missing.

308 The mole fractions of naphthalene are shown in Fig. 4c and 4d. Slightly higher mole fraction of
 309 naphthalene is produced in TPRF70 than TPRF97.5, in spite of the higher benzyl radical
 310 concentration in TPRF97.5. Further flux analysis shows that over 65% of naphthalene is produced by
 311 the dehydrogenation of 1,2-dihydronaphthalenyl radical ($C_{10}H_9$) at 1050 K, meanwhile over 90% at
 312 1234 K (Fig. S2 in SM-3). $C_{10}H_9$ is mainly produced from 1,2-dihydronaphthalene ($C_{10}H_{10}$). The
 313 main pathway for $C_{10}H_{10}$ formation is the addition of propargyl radical to benzyl
 314 ($C_6H_5CH_2 + C_3H_3 = C_{10}H_{10}$). Hence, the higher mole fraction of C_3H_3 radical in TPRF70 pyrolysis may
 315 be the reason for the slightly higher naphthalene formation than that in TPRF97.5 pyrolysis. The
 316 trend of A2 formation in the two TPRF pyrolysis is predicted by the model simulation in JSR
 317 pyrolysis. However, the simulation of flow reactor shows that the formation of A2 is close in two
 318 TPRF pyrolysis before 1350 K, while more A2 is produced during TPRF97.5 pyrolysis after 1350 K.

Figure 4. The mole fraction profiles of indene (C_9H_8) and naphthalene (A2) in JSR and flow reactor (FR) pyrolysis. Blue triangles and dash dotted lines are for TPRF70 while red circles and solid lines are for TPRF97.5.

PAHs with three and four rings were not observed in the JSR pyrolysis of both TPRF mixtures. The SVUV-PI-MBMS measured these intermediates in the flow reactor pyrolysis of both TPRF mixtures. In addition, bibenzyl was also measured in flow reactor pyrolysis. The mole fractions of bibenzyl, phenanthrene and pyrene obtained in flow reactor pyrolysis and model simulations are in good agreement, as shown in Fig. 5. The signal of bibenzyl in TPRF70 pyrolysis was weak, and its prediction by the model was also low (not shown in Fig. 5). In TPRF97.5 pyrolysis, slightly higher phenanthrene and pyrene concentrations are generated because benzyl radical produced from toluene dehydrogenation plays a significant role in PAHs growth. For example, self-combination of benzyl radicals leads to bibenzyl, which undergoes consecutive dehydrogenation reactions to form phenanthrene ($C_{14}H_{14}=C_{14}H_{12}+H_2$ and $C_{14}H_{12}=A_3+H_2$). Experimentally, bibenzyl consumption begins around 1200 K and initiates the production of phenanthrene. The traditional HACA (hydrogen abstraction- C_2H_2 addition) mechanism [36] also leads to phenanthrene, and eventually forming pyrene in TPRF70. However, the HACA pathway is much slower compared to the bibenzyl pathway. Instead, the reaction of benzyl radical with indenyl radical ($C_6H_5CH_2+C_9H_7=A_4+2H_2$) is the main source for pyrene in pyrolysis of both TPRF70 and TPRF97.5. The reaction rate of $C_6H_5CH_2+C_9H_7=A_4+2H_2$ in present model is calculated by Sinha et al.[34], which has a lower reaction rate comparing to Slavinskaya's [37] work. However, it still over-predicts A4 in TPRF97.5 pyrolysis.

Figure 5. The mole fraction profiles of bibenzyl ($C_{14}H_{14}$), phenanthrene (A3) and pyrene (A4) in flow reactor pyrolysis. Blue triangles and dash dotted lines are for TPRF70 while red circles and solid lines are for TPRF97.5.

4. Conclusions

PAHs formation characteristics in pyrolysis of two gasoline surrogates, TPRF97.5 representing a high octane number and high octane sensitivity gasoline and TPRF70 representing a low octane number gasoline (naphtha), were studied in a jet-stirred reactor and flow reactor. The mole fraction profiles of the reactants, C_2H_2 , C_3H_4 , C_3H_6 , and aromatics including benzene and PAHs up to four rings were measured. Evaluation of literature kinetic models for TPRFs and PAHs formation revealed discrepancies in predicting the formation of PAHs. The KAUST PAH kinetic model was updated to better predict the experimental observations and to analyze fuel decomposition and PAHs profiles. Despite having significantly less toluene, the low octane gasoline surrogate TPRF70 produces slightly higher benzene and naphthalene compared to the high octane gasoline surrogate TPRF97.5. On the other hand, the pyrolysis of TPRF97.5 leads to slightly higher production of phenanthrene and pyrene. Both propargyl radical and benzyl radical play critical role in the formation of benzene and naphthalene in TPRF mixtures. In PAHs growth, benzyl radical is a key intermediate in the production of larger PAHs like phenanthrene and pyrene. The latter reaction sequence leads to more large PAHs in the pyrolysis of TPRF surrogates having a high toluene concentration. Further development of the PAHs kinetic model for gasoline surrogates is needed. The experimental data presented in this work are suitable targets for validation of PAH reaction mechanisms.

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Figure Captions

(Color figures in electronic version only)

Figure 1. Comparison between experimental and simulated [10, 13, 18, 21] mole fractions of TPRF components, acetylene, allene and one to four ring aromatics in TPRF 70 pyrolysis. The experimental data for A3 and A4 were taken from flow reactor pyrolysis while the rest were from JSR pyrolysis.

Figure 2. Mole fraction profiles of three components of TPRF (toluene/ *iso*-octane/ *n*-heptane) in JSR and flow reactor (FR) pyrolysis and mole profiles of small molecules in JSR. Open symbols are experiment results while lines are simulation results. Blue triangles and dash dotted lines are TPRF70 while red circles and solid lines are for TPRF97.5.

Figure 3. The mole fraction profiles of aromatics with one ring (benzene, ethylbenzene, and styrene) in JSR and flow reactor (FR) pyrolysis of two TPRF mixtures. Blue triangles and dash dotted lines are TPRF70 while red circles and solid lines are TPRF 97.5.

Figure 4. The mole fraction profiles of indene (C_9H_8) and naphthalene (A2) in JSR and flow reactor (FR) pyrolysis. Blue triangles and dash dotted lines are for TPRF70 while red circles and solid lines are for TPRF97.5.

Figure 5. The mole fraction profiles of bibenzyl ($C_{14}H_{14}$), phenanthrene (A3) and pyrene (A4) in flow reactor pyrolysis. Blue triangles and dash dotted lines are for TPRF70 while red circles and solid lines are for TPRF97.5.

Table Caption

Table 1. Major aromatics detected in TPRF pyrolysis in this work.

Supplement Material

SM-1: The temperature profiles of flow reactor; **SM-2:** The PICSS of species in Table S1, the evaluation of literature models by other species in JSR pyrolysis of TPRF70 in Fig. S1, the reaction rates of unimolecular decomposition of *iso*-octane and *n*-heptane in Figure S2, and the comparison of fuel consumption in pure fuel and TPRF in Figure S3; **SM-3:** The description of kinetic model modification and ROP analysis; **SM-4:** The detailed kinetic model; **SM-5:** The experimental data.