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Pyrolysis of furan and its derivatives at 1100 °C: PAH products and DFT study

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ABSTRACT

In this work, the pyrolysis of furans (furan, 2-methylfuran, furfuryl alcohol, and furfural) have been checked by Py-GC–MS at 1100 °C to detect the decomposition of furans and the formation of benzene derivatives and PAH. From the Py-GC–MS results, different side chain functional groups on furan-ring lead to different kinds of products and product distributions, such as hydroxyl group leading to dimers, and aldehyde group leading to pyrans, but the mechanism for furan-ring opening and decomposition is universal for furans pyrolyzed in this study. In order to explain the experimental results and the formation of benzene derivatives and PAH, the formation of benzene from furan has also been calculated by B3LYP/6-31G++(d,p). Two possible benzene formation mechanisms, Diels-Alder and acetylene reaction mechanism, have been proposed and calculated. By comparison, it has been regarded that Diels-Alder reaction was more possible for PAH formation as this mechanism has a lower activation energy for initiation step, but acetylene reaction mechanism was more possible for benzene formation as this mechanism has a lower global activation energy.

1. Introduction

Nowadays, the attempt of using furan and its derivatives in internal combustion engine is on the increase, especially the alkylated furans (2-methylfuran and 2,5-dimethylfuran) [1–5]. The performances and physical properties of these alkylated furans in internal combustion engine are closely similar to gasoline [6].

Zhong et al. firstly tested the combustion and emission of 2,5-dimethylfuran in a direct-injection spark-ignition engine, reporting that both the combustion performance and regulated emissions are comparable to commercial gasoline [2]. Then the combustion performance 2.5-dimethylfuran blends using dual-injection was compared to direct-injection in a SI engine by Daniel et al. [7], a speciation on hydrocarbon and carbonyl emissions has also been reported by them [8]. Continually, the combustion characteristics and emissions of 2-methylfuran has been tested by Wang et al. [5], Wei et al. [1], Thewes et al. [4], and others, validating the possibility of its application in internal combustion engine. However, though there are many reports about the combustion kinetics of furans, their usage in internal combustion engine are really limited.

Considering to the heated research of their possible usage in internal combustion engine, the combustion chemistry and kinetics of furan and its derivatives have been tested and revealed by different analytical methods, such as MBMS [9–12], shock tube [13–17], microreactor [18], and so on. In addition, quantum calculation has also been used for the decomposition of furan derivatives. Sendt et al. used CASPT2 and G2(MP2) method to calculate the pyrolysis of furan, giving the unimolecular decomposition pathways of furan to CO, C_3H_4, ketene, and acetylene [19]. Vasiliou et al. combined experimental results and quantum calculations to explain the generation of propargyl radicals [20]. Simmie et al. calculated the decomposition of 2,5-dimethylfuran, suggesting that the demethylation to yield highly unsaturated species such as allenylketenes appears to be a feature of 2,5-dimethylfuran decomposition chemistry [21]. A recent review on the production and combustion kinetics of furan derivatives has been published by Xu et al. [22].

Though there are many reports about the application of furan derivatives in internal combustion engines and their combustion chemistry, there are few works about the formation of polycyclic aromatic hydrocarbons (PAH) from furan combustion. Only Tran et al. checked the influence of substituted furans on the formation of PAH in flames by electron-ionization molecular-beam mass spectrometry (EI-MBMS), revealing that PAH mole fractions in the 2,5-dimethylfuran are significantly lower than in a flame of pure

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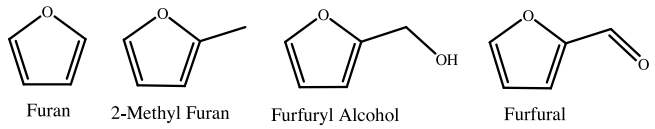

Fig. 1. The structure of furans used in this work.

toluene [12]. They also considered that C5H5 radial is an important intermediate for the formation of PAH from 2,5-dimethylfuran [12].

Considering to these, the pyrolysis of furans (furan, 2-methyl furan, furfuryl alcohol and furfural, seen in Fig. 1) and their formation of PAH have been analyzed by Pyrolysis–gas chromatography–mass spectrometry (Py-GC–MS) at 1100 °C in this work, the functional group on the side chain has been changed to see its effect on the PAH formation process and search for universal reaction mechanisms for PAH formation from furans. Then two possible formation mechanisms of benzene from furan have been calculated by Density Functional Theory (DFT) method.

2. Materials and methods

2.1. Materials

All the materials used in this work were bought form Aladdin Chemistry Co. Ltd at ACS standards. Some basic information about the furans used in this work is listed in Table 1.

2.2. Py-GC–MS

Normally, Py-GC–MS is suitable for solid sample pyrolysis and catalytic pyrolysis. Nevertheless, Laino et al. has successfully used Py-GC–MS for the pyrolysis of propylene glycol and triacetin at 527 °C, verifying the feasibility of Py-GC–MS for liquid pyrolysis [23]. The advantages of using Py-GC–MS for product distribution when compared with tradition methods, such as MBMS and shock tube, are as follows:

(1) Py-GC–MS could be handled with just one person.
(2) The operation time for Py-GC–MS is much shorter than MBMS and shock tube, normally, for one sample, it only takes less than one hour.
(3) The reproducibility of Py-GC–MS has been improved by its simple operation process.

But what we need to admit is that, when using Py-GC–MS for liquid pyrolysis, as parts of sample will mixed with the products and be brought into GC–MS by carrier gas, so the results of products distribution are qualitative, not quantitative.

In this study, Py-GC–MS was used to investigate the products distribution of furans under flash heating mode (heating rate from 10 to 20000 K/s). Fast pyrolysis analyzer (CDS5250) is coupled with the GC–MS instrument (Trace DSQ II) to indicate the distribution of products under the fixed temperature (1100 °C). Around 2 microliter liquid furans samples were loaded in the pyrolysis tube filled with quartz wool by microsyringe before the test. The experiment was carried out under the temperature of 1100 °C at the heating rate of 20 °C/ms with the residence time of 10 s. Due to the high heating rate of pyrolyzer, the actual pyrolysis temperature was lower than the set value, reported as 100 °C for the difference [24]. The evolved volatiles were analyzed by the coupled GC–MS, where the injector temperature was kept at 300 °C. The chromatographic separation was performed with a TR-35MS capillary column. The oven temperature was programmed from 40 °C (3 min) to 200 °C (1 min) with 4 °C/min heating rate, and then to 280 °C (1 min) with 20 °C/min heating rate. The mass spectra was operated in EI mode at 70 eV. The mass spectra was obtained from 35 to 650 (m/z). The chromatographic peaks were identified according to the NIST MS library v2.0. Limited to the running process of Py-GC–MS, internal calibration could not be used, so external calibration method was used in this study.

2.3. Density functional theory study

Density functional theory (DFT) was used to simulate the possible reaction pathways of the formation of benzene from furan, indicating the possible reaction mechanism of PAH generation from furans. Geometrics and frequencies of all the reactants, transition states, and products in this study were calculated by using B3LYP method with the 6-31G + +(d,p) basis set. Wang et al. has validated the accuracy of using B3LYP/6-31G + +(d,p) to calculate the formation of benzene from cyclopentadiene pyrolysis [25].

For the search of transition-states, both TS and QST2 methods have been used. Transition-state geometries were identified by the existence of only one imaginary frequency, and the movement of atoms in the imaginary frequency mode could be displayed to see if the atoms were moving in the right direction toward the reactant and product. IRC (intrinsic reaction coordinate) calculations were also carried out to guarantee that the transition states found indeed connected the right reactant and product of the reaction step. Zero-point energy corrections were also used in frequency calculations. All calculations were done by using Gaussian 09 package [26].

3. Results and discussions

3.1. The pyrolysis of furans by py-GC–MS at 1100 °C

According to the study of Esarte et al., soot formation was started above 1000 °C for ethanol and 2,5-dimethylfuran pyrolysis in a quartz reactor [27,28], and considering the possible thermal lag of Py-GC–MS [24], furans were pyrolyzed at 1100 °C in this study. Contributed to the problems stated above, only qualitative results could be given, so the product distribution among the detected products could be seen as Table 2. In Table 2, the products have been classified as linear hydrocarbons, ketones, alicyclic hydrocarbons, furans, pyrans, benzene derivatives, benzofurans, dimers and PAH. As a high pyrolysis temperature 1100 °C has been used in this study, most products have higher carbon numbers than samples (furan, 2-methylfuran, furfuryl alcohol, and furfural), typical compounds from decomposition process, only take up around 10% of the total product distribution. This suggests that 1100 °C is an appropriate temperature for PAH formation studies.

For linear hydrocarbons, there were no reports form furan and furfural pyrolysis, and only small amount of that reported form 2-methylfuran, but 3.64 wt% of 1-buten-3-yne detected for furfuryl

Table 1
Basic information of furans used in this work.

	Formula	CAS number	Boiling point (°C)	Density(g/ml at 25 °C)
Furan	C4H4O	110–00-9	31.4	0.942
2-Methyl Furan	C5H6O	534–22-5	63–66	0.910
Furfuryl Alcohol	C5H6O2	98–00-0	171	1.129
Furfural	C5H4O2	98–01-1	160–163	1.159