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The study of 1-ethylnaphthalene pyrolysis in a flow reactor

Jun Yang [a], Mingming Lu [b,*], Ming Chai [b]

[a] Trinity Consultants, 12770 Merit Drive, Suite 900, Dallas, TX 75251, United States
[b] Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221, United States

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ABSTRACT

Ethylnaphthalenes (ENs) and other alkylated naphthalenes exist in a variety of fuels such as coal and petroleum, and their decomposition is closely related to soot and polycyclic aromatic hydrocarbons (PAHs) formation in fuel combustion. In this paper, 1-EN pyrolysis was studied experimentally in a quartz tube reactor in the temperature range of 600–850 °C. The products quantified include 1-vinylnaphthalene (VN), 1-methylnaphthane (MN), acenaphthalene (AceN), naphthalene, 2-MN, 2-VN, and acenaphthene, with 1-VN as the most abundant. Ethane, ethylene and methane have also been identified as gaseous products. The results suggested that the reactivity of 1-EN is higher than that of the MNs. Possible product formation pathways are discussed, which gives rise to hypothesized reaction mechanisms. There are three decomposition routes for 1-EN: hydrogen abstraction from the ethyl group forming naphthylethyl radicals (both primary and benzylic) and then forming 1-VN, homolytic cleavage of the bond between the α- and β-carbons forming 1-MN, and hydrogen displacement of the ethyl group forming naphthalene.

1. Introduction

Naphthalene and its several alkylated homologues are the most abundant polycyclic aromatic constituents in coal tars and the higher distillation fractions of crude oil, such as diesel fuel, aviation fuel and heating oil [1,2]. These compounds usually form soot more easily in combustion than aliphatic hydrocarbons due to the formation of resonance stabilized radicals. Soot and PAHs are of health and environmental concerns due to their respirable sizes and the carcinogenicity of some PAHs. Sooting is also undesirable due to the loss of fuel efficiency.

Compared with the number of studies on naphthalene [3–7] and methylnaphthalene (MN) [7–11] pyrolysis, the study on the pyrolysis of ethylnaphthalenes (ENs) has been inadequate. Studies on MNs have indicated that in addition to the formation of naphthylmethyl radical, hydrogen displacement of the methyl side chain can also contribute to PAH and soot formation [11]. The methyl displacement of the side chain can even be favored at higher temperatures over that of benzylic radical formation. In order to better understand the reactivity of the side chain, it is necessary to study ENs, which have a longer side chain than MNs and may potentially lead to more complex product formation mechanisms.

Beltrame et al. [12,13] studied the hydrodealkylation of 1 and 2-EN from 550–710 °C at elevated pressures (2.9–44.6 atm). The main products of 2-EN hydrodealkylation were naphthalene, 2-MN and 2-VN, whose total yields accounted for more than 96% of naphthalene ring input (the author's terminology to account for product yields) [12]. The rapidly decreasing yield of 2-VN at pressures higher than 20 atm served as an indication that it is the product of dehydrogenation. The identified gaseous products were methane, ethane, and ethylene in the order of abundance. In the subsequent study of 1-EN hydrodealkylation, naphthalene, 1-MN, acenaphthene and AceN were identified as main products accounting for more than 97% of naphthalene ring input. The pathways of 1-EN forming 1-MN, naphthalene and AceN were proposed in the kinetic study, and kinetic parameters were obtained from experimental data [13]. The reactivity of the ethyl side chain has been observed in this study, however, the high concentrations of hydrogen and high pressure are not always typical in most combustion applications. The study of 1-EN pyrolysis at atmospheric pressure is still essential in understanding its reactivity in practical combustion conditions. This study will also help with the understanding of byproduct formation from 2-ENs, based on the prior studies of 1- and 2-MNs [11].

The experimental study of 1-EN pyrolysis is presented in this paper. Only one EN isomer is studied as our earlier work on 1 and 2-MNs indicated that the governing thermal decomposition mechanisms of the two MNs are similar [11]. Pyrolytic products have been identified and their possible formation mechanisms are discussed.

Abbreviations: AceN, acenaphthalene; DMN, dimethylnaphthalene; EN, ethylnaphthalene; FTIR, Fourier transform infrared; GC-FID, gas chromatography-flame ionization detector; GC-MS, gas chromatography-mass spectrometry; MN, methylnaphthane; PAHs, polycyclic aromatic hydrocarbons; VN, vinylnaphthalene.

* Corresponding author at: Department of Civil and Environmental Engineering, PO Box 210071, University of Cincinnati, Cincinnati, OH 45221, United States. Tel.: +1 513 5560996; fax: +1 513 5562599.
E-mail address: mingming.lu@uc.edu (M. Lu).

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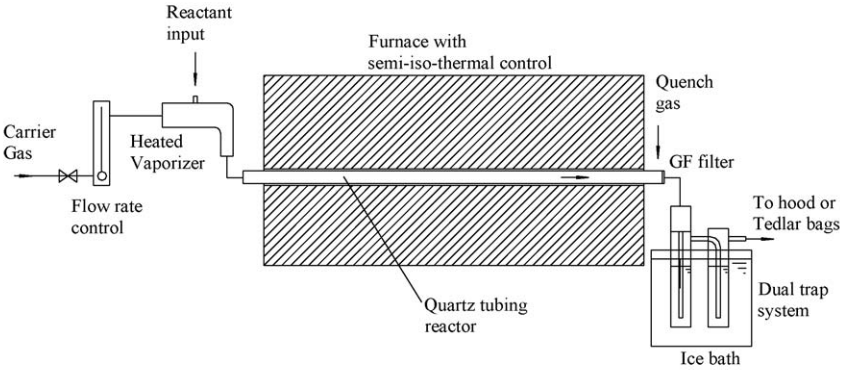

Fig. 1. Schematic diagram of the experimental setup.

2. Experimental methods

The experimental setup and analytical methods have been described elsewhere and the necessary details are briefly provided here for clarity purposes [11,14]. Experiments for 1-EN pyrolysis were conducted in an isothermal reactor at atmospheric pressure which has been used in MN pyrolysis [11]. The setup is illustrated in Fig. 1, which consists of a vaporizer, a quartz tube reactor (17 mm inner diameter and effective length of 24 inches or 0.61 m) and a sample collection assembly. During an experiment, 30 μl of 1-EN (Aldrich) was continuously injected into the preheated glass vaporizer by a syringe pump and the reactant input lasted for 4 min. The vaporizer was heated to around 200 °C to ensure gradual vaporization of the reactant without decomposition. The vapor was carried by prepurified helium (99.995%, Wright Brothers Inc.) into the reactor. Compressed room temperature air was applied outside the quartz tube at the exit end to cool the tube quickly and quenched further reactions. The products were collected by a dual trap impinger filled with dichloromethane (DCM) and put in ice bath. A small piece of glass fiber (GF) filter was also used before the impinger to collect soot, and light gaseous products were collected by Tedlar (by SKC) sample bags.

The experiment temperatures ranged from 600 to 850 °C with 50 °C increments. The axial temperature distributions of the reactor were measured with a K-type thermocouple probe (Omega molded quick connect probe KQSUP-14G-12) from 700 to 900 °C at nonreacting conditions and shown in Fig. 2. The temperatures in the reaction zone, i.e. the middle 61 cm (24 in.) of the reactor, are consistently within ±5 °C of the set point, and the temperature in the isothermal zone is referred to as the reaction temperature throughout the paper.

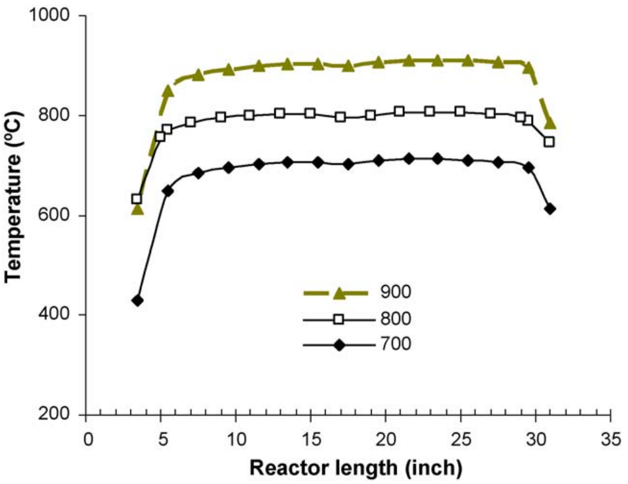

Fig. 2. Temperature profiles in the quartz tubular reactor: atmospheric pressure and helium as carrier gas.

The residence time in the reactor was fixed at approximately 1.0 s for all temperatures. The input reactant concentrations and gas flow rates are listed in Table 1. Each run lasts approximately 5 min, with 4-min reaction and 1 min purging. For the purpose of quantity assurance, multiple runs were performed for each experimental condition. Products were quantified by a Varian (Saturn 2200) gas chromatography-mass spectrometry (GC-MS) with a capillary column (CP-Sil 8 CB Low Bleed/MS, 30 m × 0.25 mm × 0.25 μm). Product yields are reported as percent of input on carbon basis. The purity of the reactant has been quantified as 98% 1-EN, with 1.94% 2-EN and 0.06% 1-(2-propyenyl)-naphthalene. The separation of the EN isomers was achieved by using a DB-FFAP column as indicated in literature [15].

3. Results and discussion

3.1. Experiment results

Byproducts were identified from the total ion chromatograph (TIC) with the aid of individual chemical standards. Fig. 3 provides an example of the TIC of product distribution from 1-EN pyrolysis

Table 1
Experimental conditions.

Parameters	Temperature (°C)					
	600	650	700	750	800	850
Helium flow rate (nlpm[a])	2.8	2.65	2.52	2.4	2.28	2.18
Reactant input concentration (ppm)	416	439	462	485	510	534

[a] nlpm: normal liters per minute at 20 °C, 1 atm.

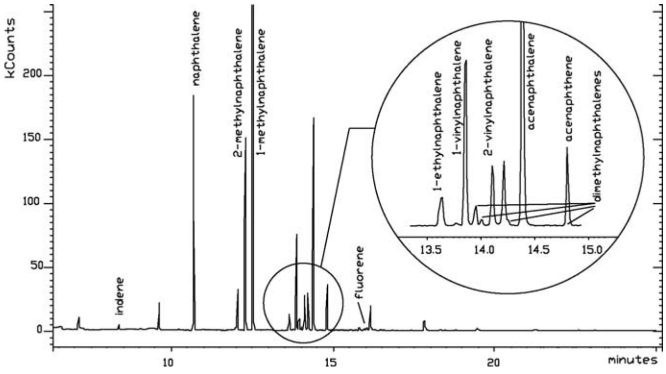

Fig. 3. Total ion chromatogram of 1-EN pyrolysis at 850 °C.