Radiation Physics and Chemistry 124 (2016) 212–215

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Radiation-initiated conversion of paraffins to engine fuel: Direct and indirect initiation

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HIGHLIGHTS

- Three radiolytic ways to produce engine fuel from paraffins.
- Synthesis from methane results in small yield of high-octane gasoline.
- Cracking of heavy wax yields mainly solar oil along with heavy waste.
- Combined gas/wax beaming provides waste-free formation mainly of gasoline.

ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form
25 January 2016
Accepted 2 February 2016
Available online 16 February 2016

Keywords:
Paraffins
Methane
Wax of Fischer–Tropsch synthesis
Radiolysis
Cracking
Gas-to-liquid conversion
Gasoline
Diesel fuel

ABSTRACT

Formation of gasoline and diesel fuel has been investigated using three various radiation-induced ways: (1) cracking of wax, (2) synthesis from methane, (3) high-temperature conversion of wax dilute solution in methane. The wax, synthesized by Fischer–Tropsch method, initially contained a mixture of C_{17}–C_{120} linear paraffins. The yield of wax conversion to liquid mixture (C_4–C_{27} alkenes and 61.5% alkanes) via mode (1) was 0.83 ± 0.09 μmole/J, whereas yield of gas conversion to liquid mixture (C_5–C_{13} alkanes) via mode (2) was 0.95 ± 0.02 μmole/J. In the dilute solution wax underwent indirect action of radiation. In comparison with (1) the mode (3) produces similar amount of lighter fuel containing 80% of alkanes (C_5–C_{15}). At the same time degree of methane fixation is almost three times higher.

1. Introduction

The radiation chemistry has originated several high-yield methods to transform paraffins. The radiation-induced cracking (RTC) and isomerization are the most known (Cserep et al., 1981; Woods and Pikaev, 1994). Cracking of heavy paraffins includes chain formation of the alkyl macroradicals susceptible to a thermal fragmentation. Smaller alkanes and alkenes are final products. Radiation-induced isomerization provides various structural changes in hydrocarbons. The chain conversion mechanism results in high productivity of these both methods.

Other approach envisioning radiolysis of recirculating gaseous alkanes can serve as perspective basis to synthesize gasoline without a waste (Ponomarev, 2009). This GTL-conversion includes various radical reactions, such as an exchange, a combination, addition to alkenes, etc. Liquid isoalkanes mixture of high knock value is final product. However radiation-controlled GTL-conversion is low-productive owing to absence of chain reactions.

Comparing RTC and GTL methods as well as their combination was a subject of the present study. The scientific task consisted in search for ways to raise a yield of the gas fixation and to select innovative control principles for radiation conversion in alkane mixtures. Three modes of alkanes processing were compared: RDC (radiation-distillation cracking)-a high-temperature wax irradiation, combined with distilling-off a fragmentation products; GTL (gas-to-liquid conversion)-a circulating gas radiolysis, combined with condensing a synthesis products; TPC (two-phase conversion)-a high-temperature wax irradiation in gas circulating through separator evacuating a fragmentation and synthesis products.

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http://dx.doi.org/10.1016/j.radphyschem.2016.02.002
0969-806X/

2. Experimental

Methane (99.99% CH_4) was used as feedstock for GTL-conversion. Mixture of C_{17}–C_{120} solid linear paraffins (wax), synthesized via Fischer–Tropsch process (Gazohim Techno, LLC, Russia), served as feedstock to cracking. Final boiling point of wax was ≈ 700 °C (Fig. 1b). Initially the content of C atoms per an average molecule of wax was $n_a = 26.1$. The total content of extraneous impurities was less than 0.11 wt%. The paraffins distribution in wax is partially shown on Fig. 1a (minor components C_{81}–C_{120} are not presented on the Fig.). Hydrocarbons of gasoline and diesel fractions (≤ 350 °C boiling range) were a target product. Respectively, the components belonging to these fractions have been distilled off from initial wax in advance. As consequence, n_a value increased to 28.6.

LINS-02-500 linear accelerator (energy, 2 MeV; average beam current, ≤ 500 μA; steady direction of electron beam) and UEVK-10-10T linear accelerator (energy, 8 MeV; average beam current, ≤ 500 μA; beam scanning; scan frequency, 1 Hz) were used as irradiation sources. The intermittent irradiation was applied in the latter case-the scan width was 20 times more than width of sample processed. Phenazine dye-doped copolymer film standard reference material SO PD(F)R-5/50 [GSO (Certified Reference Material) no. 7875-2000] was used as dosimeter. Dose rate was varying from 0.1 to 1.0 kGy s^{-1}.

The one-fill glass vessel (40 mm diameter, 250 mm height) served as reactor for RDC by 8 MeV electron beam. The steel horizontal reactor (diameter of 300 mm, length of 700 mm), associated to linear accelerator LINS-02-500, has been used for GTL and TPC modes. Schematic diagram of the laboratory converter is shown on Fig. 2. Units *2*–*5* and 7–9 have been used for non-circular RDC mode whereas the circulation loop for GTL mode included units *2* and *4*–*9*.

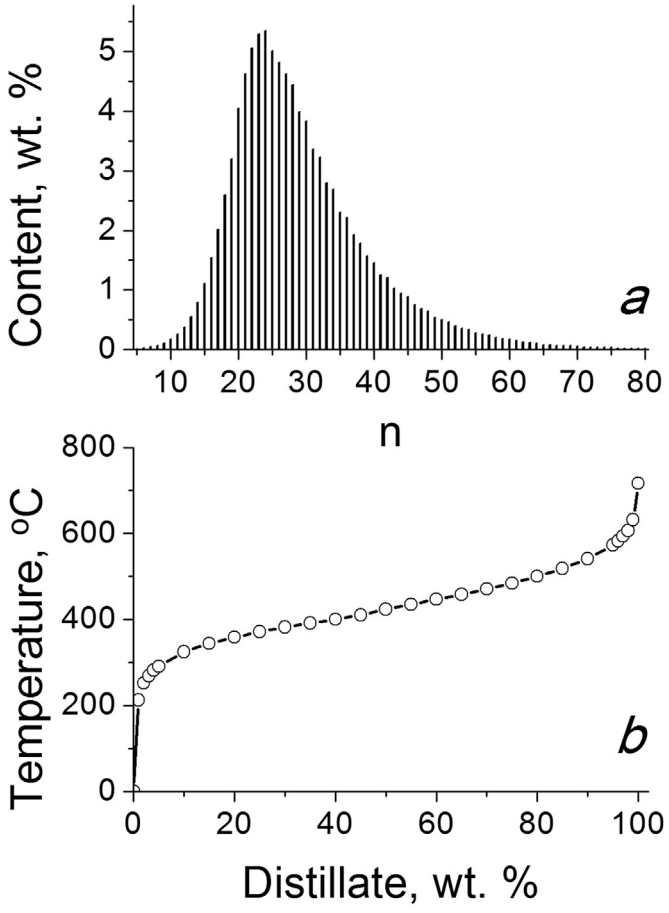

Fig. 1. Component composition (a) and atmospheric distillation curve (b) of initial wax (n-number of C atoms per a molecule).

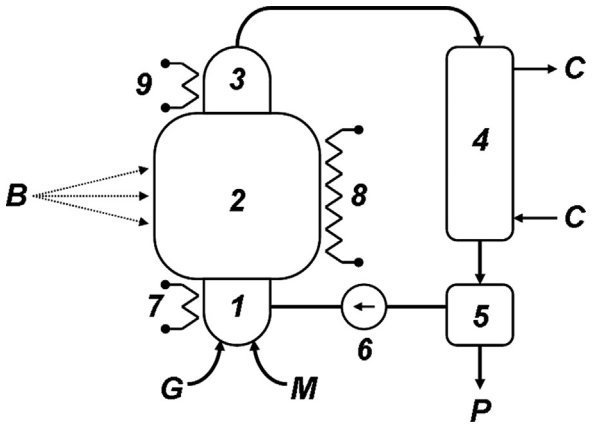

Fig. 2. The schematic diagram of the laboratory converter: *1*-injector pump, *2*-reactor, *3*-dephlegmator, *4*-condenser, *5*-separator, *6*-circulating pump, *7*-*9*-electroheaters; *B* – electron beam, *C* – cooling agent, *G*-gas, *M* – wax melt, *P* – final product.

In TPC mode the wax melt (*M*) fed into reactor (*2*) by a jet type pump (Perry and Green, 2007) (*1*) using heated gas (*G*) as an actuation medium. From a reactor the irradiated mixture of gaseous and liquid alkanes (sol and molecular solution) were moving into a dephlegmator (*3*), whence heavier components were returning into a reactor (*2*), and lighter fragmentation products together with gas were passing to the condenser (*4*). The gas liberated in a separator (*5*) was reverted into a reactor (*2*) by a circulating pump (*6*). Electric heaters (*7*–*9*) together with air-coolers were applied to adjust temperature in an injector (350–400 °C), a reactor (350–400 °C) and a dephlegmator (180–300 °C). Additional heating of a dephlegmator was used to prevent congelation of heavy components. All equipment, except for *2* and *8*, was placed outside the radiation area. The wax content in the mixed flow was adjusted in a range of 3–5 wt%. In this case electron beam energy was absorbed mainly by gas whereas wax underwent indirect action of radiation (Woods and Pikaev, 1994), so that the main transformations of wax were initiated under the influence of gas radiolysis products.

Gas chromatograph and mass spectrometer (Agilent 5977EMSD/7820AGC; helium as carrier gas; 60 m × 0.320 mm glass capillary column (19091S-916) of 0.25 μm inner diameter; NIST library of mass spectrums) was used for analysis of conversion products.

3. Results and discussion

3.1. RDC mode

Main radiation-thermal transformations in RDC mode took place in the bulk of wax melt, as high-energy electrons (8 MeV) provided low energy absorption in low-density vapor phase. During irradiation at ≈ 385 °C the transparent uncolored condensate was arriving to a separator (***5*** on Fig. 2). This liquid contained 38.5 wt% of linear alkenes C_4–C_{22} (Fig. 3) whose $n_a \approx 11$. Unirradiated wax did not contain any alkenes hence all detected alkenes fraction in condensate represented products of alkyl macroradicals thermal fragmentation (Woods and Pikaev, 1994).

The condensate consisted mainly of alkanes – 61.5 wt% (Fig. 3). The content of C_6–C_{27} linear alkanes was 57.8 wt% whose $n_a \approx 14.7$. Isoalkanes (C_{14}–C_{21}) were also present among alkanes. Their content in condensate was 3.7 wt% and $n_a \approx 17.8$.