Fuel 161 (2015) 295–303

Contents lists available at ScienceDirect

Fuel

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

Palmitoyl hyperbranched polyglycerol as a nanoscale initiator for endothermic hydrocarbon fuels

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HIGHLIGHTS

- PHPG is applied as a novel nanoscale initiator for hydrocarbon fuels.
- Decomposition of PHPG starts above 200 °C.
- The cracking conversion and the heat sink of fuels are promoted in the presence of PHPG.

ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form 17 July 2015
Accepted 25 August 2015
Available online 4 September 2015

Keywords:
Hyperbranched polymers
Macroinitiator
Hydrocarbon fuels
Cracking
Heat sink

ABSTRACT

One of hyperbranched polymers is developed as a novel nanoscale initiator to enhance the heat sink of endothermic hydrocarbon fuels to meet the great cooling requirement of hypersonic aircrafts. In this work, the hyperbranched polyglycerol (HPG) is treated with palmitoyl chloride to obtain a fuel-soluble product, palmitoyl-hyperbranched polyglycerol (PHPG). The thermogravimetric analyses show that the long-alkyl chains rupture first from the matrix at about 200 °C, and then the HPG core breaks around 400 °C during the cracking of PHPG, which indicates a high decomposition temperature for this "macroinitiator". The cracking processes of *n*-tridecane with PHPG in different molecular weights and addition quantities are performed in an electrically heated tube reactor under supercritical conditions (3.5 MPa, and 600–720 °C). PHPG can promote the cracking of *n*-tridecane with significant improvements of the conversion and heat sink. The conversion of *n*-tridecane is improved as high as 17.6% at 690 °C, and the corresponding heat sink is improved from 3.0 MJ/kg to 3.5 MJ/kg. Furthermore, the optimum addition quantity and molecular weight range of PHPG are chosen for the practical application to an aviation kerosene under 600–700 °C, and the increases of heat sink in comparison with those from the thermal cracking confirm the potential application of PHPG to endothermic hydrocarbon fuels.

1. Introduction

Several decades have witnessed the great developments of supersonic and hypersonic aircrafts with the cruising speed increased to Mach 5 or higher [1]. At hypersonic flight speeds, great cooling capability for the engine structure is demanded because of the severe aerodynamic heating of the aircrafts [2]. Using endothermic hydrocarbon fuels is considered to be an effective way to meet the requirement of thermal management [3]. The onboard fuel not only functions as the propellant, but also plays an important role of coolant in the regenerative cooling systems of advanced hypersonic aircrafts [4].

The endothermic capability of a hydrocarbon fuel is usually defined as heat sink [5], which is a key indicator and contributed by the sensible enthalpy change and endothermic cracking reactions of the fuel. At high Mach number speeds, the lack of sufficient endothermic heat sink capability from aviation kerosene has limited the development of regenerative cooling systems. To solve the problem, several strategies have been investigated such as changing the fuel compositions to control the endothermic properties of hydrocarbon fuels [6], developing additive packages to enhance the upper limit of the available operation temperature range [7], and using catalysts to enhance the endothermic reactions of hydrocarbon fuels [8].

For the thermal cracking of any hydrocarbons, the free radical chain reaction is a widely accepted mechanism [9], and the rate-determining step is the formation of free radicals. Appropriate initiators can help to generate great amounts of reactive free radicals at relatively low temperatures, and then result in an increase of the overall rate of thermal cracking [10]. Hence, the soluble initiators might promote the heat sink of hydrocarbon fuels, and be beneficial

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http://dx.doi.org/10.1016/j.fuel.2015.08.066
0016-2361/

to solve some difficulties that the application of heterogeneous catalysts is often faced with, such as catalysts deposition, deactivation, and regeneration [11,12].

Oil-dispensable palladium nanoparticles [13] and nanozeolites [14] were reported to be used as “quasi-homogeneous catalyst” to catalyze the cracking of hydrocarbon fuels. A little amount of palladium (0.05 wt%) or nanozeolites (100 ppm) could enhance the heat sink of hydrocarbon fuels significantly. However, the palladium nanoparticles or nanozeolites are apt to aggregate and deposit when used at the high cracking temperatures, and the expensive palladium-contained residues after cracking might cause environment pollution. Soluble initiators are then chosen to solve the deposition problem of heterogeneous or quasi-homogeneous catalysts. Triethylamine and tributylamine were found in the previous work [15] to be effective homogeneous initiator in accelerating the cracking of heptane. Some commercially available initiators, such as azobis-isobutyronitrile or peroxides, can work well in polymerizations, but cannot work well in promotion of the cracking of hydrocarbon fuels because of their low decomposition temperature (60–100 °C) [16].

Hyperbranched polymers [17], have received much attention in recent years because of their unique properties mainly from the highly-branched architecture and convenient synthesis by one-pot polymerization of AB_m ($m \geqslant 2$) monomers [18]. Glycidol, an important AB_2 monomer, can be polymerized in a controlled manner by ring-opening multi-branching polymerization (ROMBP) to give hyperbranched polyglycerol (HPG) [19], which is structured with a hyperbranched polyether “core” and terminated with hydroxyl groups (Fig. 1) [20]. HPG has been applied in many fields such as biocompatible microgels [21], catalysis entrapment [22] and nanomaterials [23] because of good biocompatibility and easy functionalization. HPG can be esterified with long-chain chlorides, and the obtained product is soluble in nonpolar solvents [24]. At a certain temperature, the polyether core breaks into a number of free radicals, hence the esterified HPG might be used as a promising initiator to promote the cracking of hydrocarbon fuels. Compared with the “hard” metallic nanoparticles, the hyperbranched macromolecules can be treated as “soft” nanoparticles which are well dissolved in hydrocarbon fuels. We can also consider the macromolecule as a “radical package”. Once the cracking of “radical package” releases thousands of radicals, the environment filled with radicals can be treated as a “radical pool” [25].

In this work, HPG is synthesized by anionic polymerization, and the molecular weights are regulated by different initiator/monomer ratios, as that was reported by Sunder et al. [26]. Higher molecular weights of HPG are obtained by Kainthan’s method of emulsion polymerization [27]. Palmitoyl hyperbranched polyglycerol (PHPG) is synthesized from HPG esterification with palmitoyl chloride [28]. To investigate the heat sink enhancements of hydrocarbon fuels with the addition of PHPG, a series of cracking reactions of the PHPG-contained fluids of *n*-tridecane and aviation kerosene under different operation conditions are carried out in an electrically heated tube system. The investigations are expected to provide fundamental information to the design of a novel macromolecular initiator and the preparation of an advanced hydrocarbon fuel with high heat sink.

2. Materials and methods

2.1. Materials

(±)glycidol (96%), potassium methylate (95%), 1,1,1-tris(hydroxymethyl)propane (98%), palmitoyl chloride (96%), *n*-tridecane (99%), magnesium sulfate anhydrous (99.5%) were purchased from Aladdin Chemical Reagent Corporation. Toluene (99.5%), methanol (99.5%), pyridine (99.5%) and dichloromethane (99.5%) were purchased from Sino-pharm Chemical Reagent Corporation. The aviation kerosene were provided by China National Petroleum Corporation.

2.2. Preparation of hyperbranched polyglycerols

Glycidol was purified by vacuum distillation before use, 1,1,1-tris(hydroxymethyl)propane (0.187 g, 1.39 mmol) was partially deprotonated (10%) by potassium methylate under 65 °C for 15 min. The generated methanol was distilled off from the melt in vacuum. Then a 50 mL aliquot of glycidol was added slowly for 24 h with a peristaltic pump. The molecular weight of HPG was controlled according to the monomer/initiator ratio. After

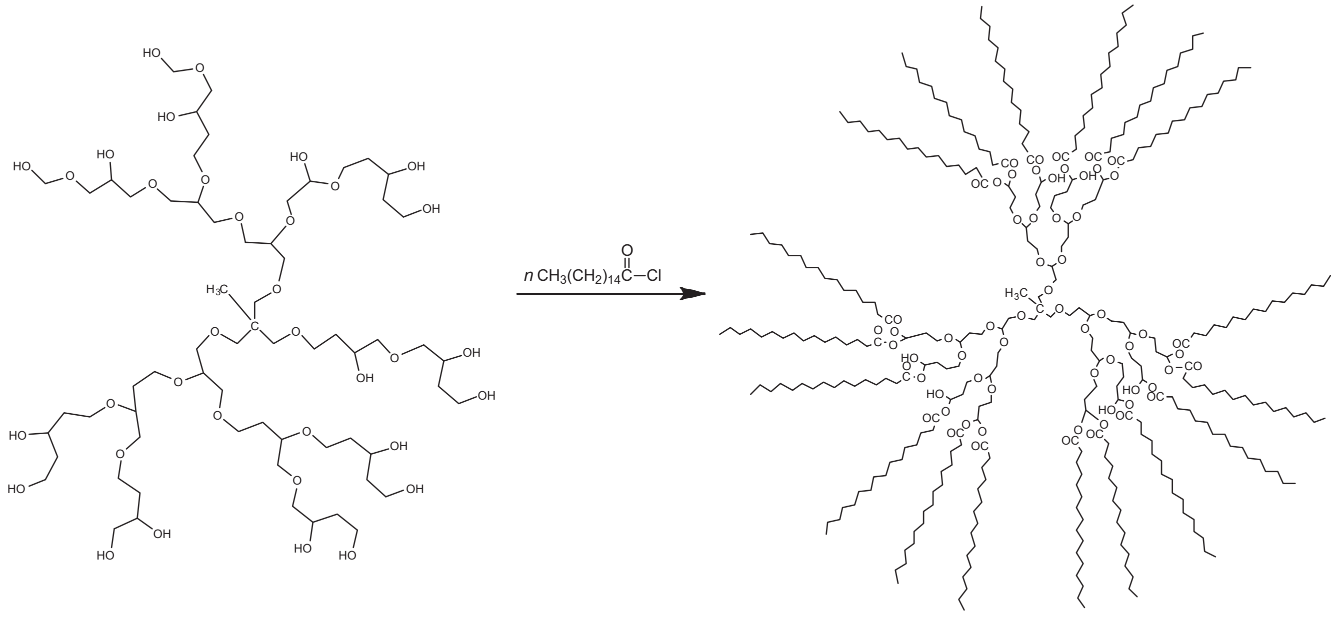

Fig. 1. Synthesis of PHPG from the esterification of HPG with palmitoyl chloride.