



Kinetics of furfuryl alcohol condensation over acid catalyst for preparing diesel precursor



Shaohui Sun^{*}, Ruishu Yang, Peiqin Sun, Chunsong Ma, Junwu Chen

Research Center of Heterogeneous Catalysis & Engineering Science, School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou City, China

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ABSTRACT

C₉–C₂₅ oxygen-containing compounds formed via the condensation reaction of furfuryl alcohol (FA) can be used as fuel intermediates for the production of bio-fuel. In this paper, the condensation reaction of FA was carried on over sulfuric acid catalyst in a batch aqueous phase reactor, in which the produced oligomers were separated from aqueous reaction system automatically before they went on further to form polymers. Reaction kinetics experiments showed that the values of reaction order of FA and sulfuric acid all were 1. The molecular structure and content of short chain-length oligomers B (C₉–C₂₅) were analyzed by gas chromatography-mass spectrometry (GC-MS) and gas chromatography (GC) respectively. The molecular weight of FA condensate was determined by gel permeation chromatography (GPC). According to the information provided by GC/MS and GPC, we revealed that two polymerization mechanisms, step-growth polymerization and chain-growth polymerization, coexist in FA condensation reaction process in aqueous system. A simplified kinetics model based on the present mechanisms was established, and condensation products were divided into short chain-length oligomers B (C₉–C₂₅) and long chain-length oligomers C (>C₂₅).

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1. Introduction

With the rapid socio-economic development taking place in China, the excessive consumption of fossil fuels has resulted in a large amount of carbon dioxide emissions, leading to the overloading of global air atmosphere with greenhouse gases and thus to the climatic change in the environment. There has been great interest in the conversion of biomass to fuel and chemicals. First-generation biofuels, such as biodiesel (fatty acid methyl esters: FAMES) or ethanol from sugar cane or starch, are being reconsidered because their production engrosses crop land and competes with food production. Hence, the second generation of biofuels should be produced from non-edible biomass (waste) that does not require crop land to grow. For example, the renewable cellulosic ethanol is produced through the fermentation of monosaccharides, which is the production of lignocellulose hydrolysis reaction. China is relatively rich in biomass energy resources. The Chinese government has paid high attention to the development of biomass energy industry, and explicitly calling for the development of

renewable energy and clean energy to replace fossil fuels and reduce greenhouse gases emissions. Chinese Academy of Sciences (CAS) Wang proposed a dual-bed aqueous catalysis system with Ru/C as catalyst for the liquid alkane (pentane/hexane: C₅/C₆) production from acid biomass hydrolysate, for cassava and corncob hydrolysate, C₅/C₆ alkane yield of 38.8% and 44.1% were obtained, respectively [1]. Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry (ICIFP-CAF) Zhang used the conical fluidized-bed, with biomass (such as: saw dust, rice husk, straw etc. soft biomass materials) as raw materials of gasification to produce hot coal gases [2]. In recent years, a new approach to produce hydrocarbon transportation fuels from lignocellulosic biomass by chemical catalytic reaction of monosaccharides has proposed by researchers [3–10]. Monosaccharides from the hydrolysis of cellulose are not biochemical conversion to produce ethanol, but forming alkane molecules within gasoline, diesel or jet fuel fraction from hexose- and pentose-derived biomass platform molecules, such as furfural, 5-hydroxymethyl furfural, levulinic acid through stepwise chemical catalytic reactions. The major challenges of chemical catalytic route are: 1) How to extend the length of carbon chain of C₅ and C₆ monosaccharide to produce the fuel intermediates whose carbon number distribution range from C₉–C₂₅

^{*} Corresponding author.

E-mail address: shaohui99@zzu.edu.cn (S. Sun).

appropriate the requirements of the petrol and diesel. 2) How to remove oxygen atoms in fuel intermediates to produce alkanes for fuels efficiently. Fortunately, some strategies for the production of fuel intermediates whose carbon number is more than 9 have been proposed. Such as, the aldol condensation reaction catalyzed by base using 5-hydroxymethyl furfural or furfural with ketones containing α -H atom as reactants [3,4], the alkylation reaction catalyzed by acid using 2-methyl furan and butyraldehyde as reactants [5,6], the pathway of levulinic acid through γ -valerolactone to produce butene catalyzed by a solid base [7,8], and the condensation of furfuryl alcohol catalyzed by acid [9,10]. Then alkanes fitting for transportation fuels are converted through the hydrodeoxygenation of these fuel intermediates. Furfuryl alcohol (FA) origin from biomass can polymerize in acidic conditions via the condensation of the hydroxyl group and the hydrogen atom of the heterocycle at carbon 5 to produce a polymer with methylene linkages. As shown in Scheme 1, the diesel was produced starting only from FA, derived from pentosan-rich hemicellulose. The oligomers of FA condensation can be hydrogenated with a Ni/Al₂O₃ catalyst at 100 °C. The product of this hydrogenation was distilled and the diesel fraction (boiling in the range from 170 to 370 °C.) was isolated [9,10]. It is important to control the degree of condensation of FA to form C₉-C₂₅ fuel intermediates for the purpose of producing transportation fuels. Kim studied characterizations of molecular structure and thermodynamic properties of FA condensation reaction [11], effects of solvent, catalysts on the products [12–14]. Understanding the mechanism and reaction kinetics of FA condensation is critical but still challenging for developing attracting technique for biofuels production.

In this research, the condensation reaction of FA in aqueous solution under sulfuric acid catalyzed reaction was studied. The reaction mechanism of condensation reaction of FA was proposed. This paper revealed that two polymerization mechanisms, step-growth polymerization and chain-growth polymerization, coexist in FA condensation reaction process in aqueous system. Chain-growth polymerization is a polymerization technique where unsaturated monomer molecules add onto the active site of a growing polymer chain one at a time. Polyethylene, polypropylene, and polyvinyl chloride (PVC) are common types of plastics made by chain-growth polymerization. Step-growth polymerization refers to a type of polymerization mechanism in which bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers. E.g.

preparation of poly(*p*-phenylene oxide) (PPO). A model of condensation reaction process was established to simulate the distribution of condensation oligomers with different molecular weights in the quasi-homogeneous system.

2. Experimental

2.1. FA condensation reaction

Furfuryl alcohol ($\geq 98\%$) was purified by rotary vacuum distillation. *N,N*-Dimethylformamide ($>99.9\%$), pyridine ($\geq 99.5\%$), NaHCO₃ ($\geq 99.8\%$). Oligomerization of FA was performed with an aqueous solution containing FA (25 g) and given different concentrations sulfuric acid (75 g) at different temperatures (30–70 °C) and reaction 90min in a three-necked flask of 300 ml, under reflux and stirring at 300r·min⁻¹, which excluded the effect of interfacial mass transfer because it is a quasi-homogeneous (Fig. S1), and put nitrogen into flask during the reaction.

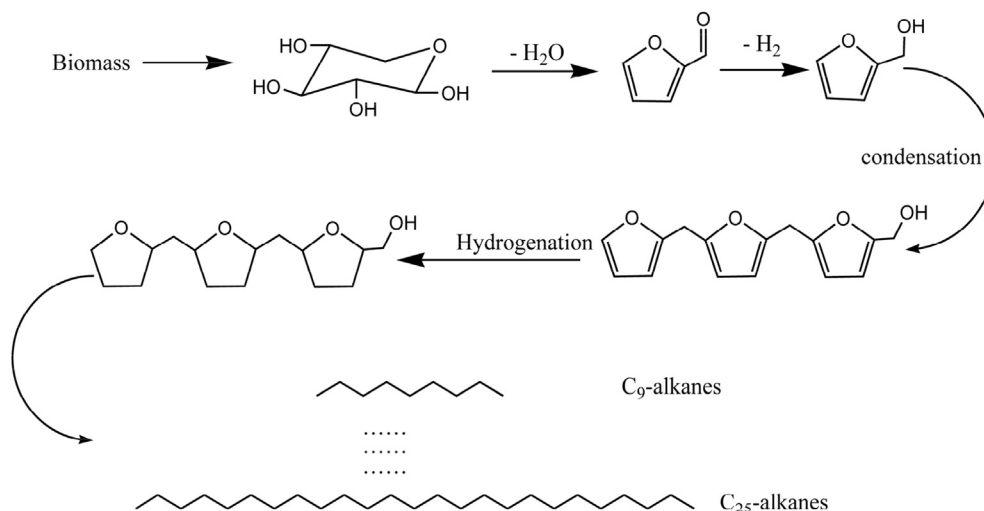
2.2. The characterization of FA condensation products

GC chromatographic conditions: A gas chromatograph SHIMADZU GC-14B equipped with a flame ionization detector (FID) and Agilent DB-5 capillary column (0.25 mm \times 0.25 μ m, 30 m). The GC temperature profile used was as follows: injector Temp. 250 °C; FID Temp., 250 °C; oven Temp., 100 °C held for 3 min, ramp rate, 6 °C·min⁻¹, and final Temp., 300 °C held for 3 min. An injection volume of 0.4 μ L was employed. High purity nitrogen was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. The split ratio was set to 30:1. To calculate the oligomers' conversion and selectivity, response factor was applied.

GC/MS chromatographic conditions: Capillary chromatography equipped with SHIMADZU GC-2010 capillary chromatograph. Chromatographic operating conditions same with before except the carrier gas is high purity helium with a split ratio of 80:1.

GC/MS mass spectrometry conditions: Electron impact ion source: 70eV; ion source temperature: 250 °C; scanning range (*m/z*): 30u~500amu; scanning mode is for full scan monitoring.

Gel permeation chromatography (GPC) conditions: Agilent 1100 Infinity gel liquid chromatograph, G1362A difference detector, mobile phase for *N,N*-dimethylformamide (Chromatographic purity) with a flow rate of 1.0 mL min⁻¹ at room temperature, polystyrene as reference compound.



Scheme 1. The reaction pathway for the conversion of biomass into liquid alkanes.

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