

Kinetic Modeling For Transformation of Bioethanol into Ethylene and Diethyl Ether: A Review

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Abstract: Biomass is a significant renewable energy source for the process plant, which can be used as fuel, or it can be converted to ethanol. Ethylene and Diethyl ether (DEE) are produced through dehydration of ethanol. Two distinct adsorption-desorption models have explained the stop-effect (SE) to characterize the catalyst's experimentally observed transition behavior. This review provides a critical assessment of biomass and focuses on ethanol's kinetics to produce ethylene and DEE through the 'Stop effect' process.

Keywords- Bioethanol, Kinetic modeling, Ethylene, DEE, Stop-effect.

I. INTRODUCTION

Climate changes and the depletion of fossil fuel resources are increasingly significant global concerns. The reduction of greenhouse gas emissions is due to the replacement of fossil fuel resources. Several articles have already shown that biomass crops play an essential role as bioenergy sources to produce heat, electricity, or biofuels via thermochemical or biochemical processes [1].

Many centuries took place for fossil fuels to create, whereas biomass can be used as raw material to produce renewable fuel. Biomass energy, or bioenergy, corresponds to sources of energy from plants and plant extracted materials. Today, wood is the predominant source of biomass energy, but it is also known that it is possible to use the other biomass resources as fuel. It included food crops, grass, woody plants, agricultural or forestry residues, algae rich in oil, and the organic materials of municipal - industrial waste [2].

Currently, various types of biomass sources are available and used (Fig. 1). It involves everything immediately from primary sources of crops as well as residues produced from the land. The gases resulting from anaerobic digestion of animal manures or organic materials in landfills also include biomass resources [3].

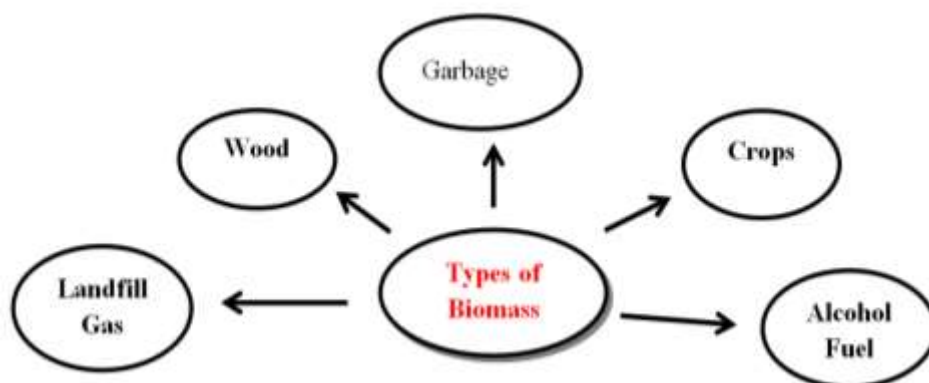


Figure 1. Types of Biomass

In general, biomass is defined as all organic matter that could be used as energy sources, including crops, food, plants, and agricultural and forestry residues (Fig. 2). The use of biomass, a renewable energy source, also has many key benefits: it helps to reduce the chemical industry's dependency on non-renewable resources, which are regarded CO₂ neutral, and also produces biofuels like methanol, ethanol, dimethyl ether (DME), synthetic natural gas (SNG), hydrogen, etc. [4][5].

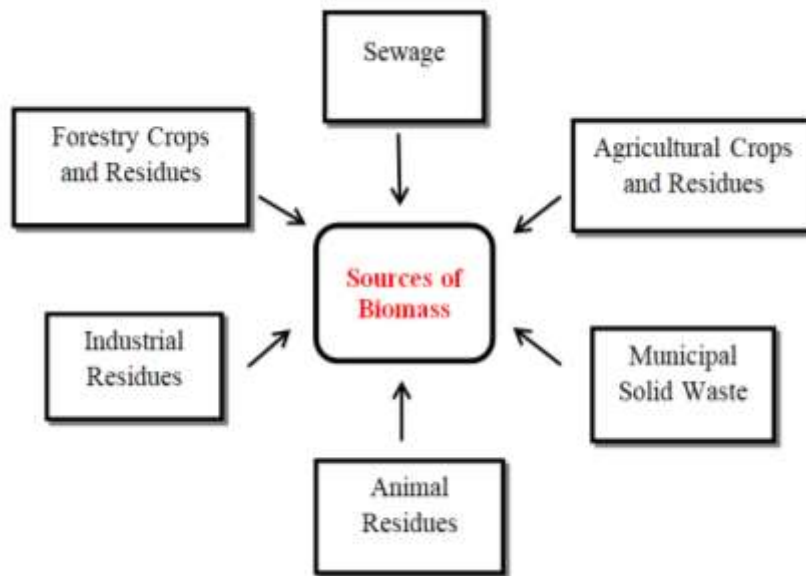


Figure 2. The production of biomass from various sources.

The overall conversion efficiency of biomass to bioethanol is reduced due to significant biological, chemical, and physical reactions. Bioethanol is usually used as a blendstock for gasoline up to 20%. The investigations to transform biomass-derived alcohols into long-chain hydrocarbons are also ongoing. [6].

The schematic diagram for the biomass conversion route is shown in Fig. 3. Biomass is directly converted into biofuels through the thermochemical process, including gasification, pyrolysis, and liquefaction. A wide range of products such as gaseous, condensable vapors, and solids are produced through thermochemical routes. The biological processes convert biomass to bioethanol or biodiesel, whereas thermochemical functions convert all biomasses into synthetic fuel [25].

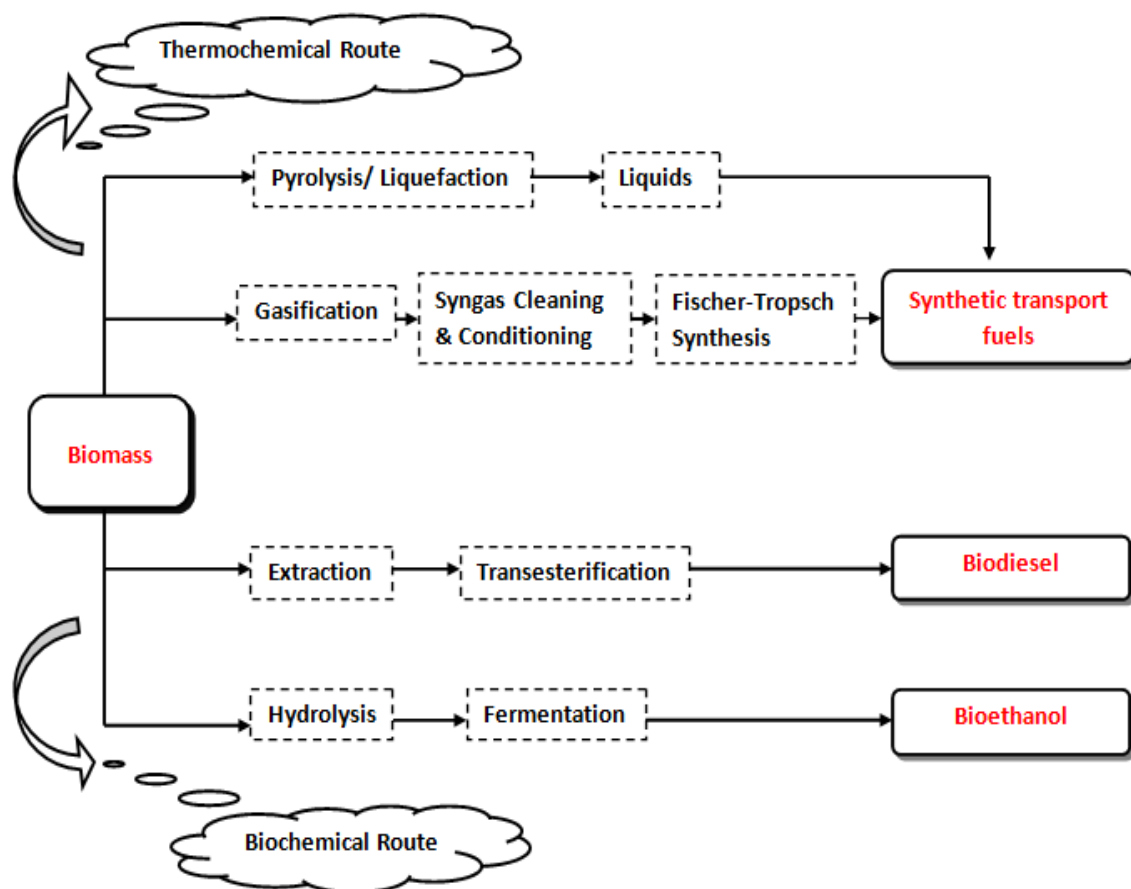


Figure 3. The schematic illustration of biofuels production pathways.

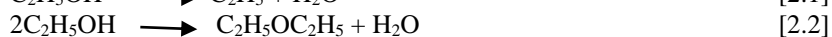
Ethanol can be produced in two ways: either through fermentation of biomass or from petroleum feedstock. Ethanol production depends on cellulosic biomass fermentation[7][8][27][28]. The alcohol obtained in this way is usually called bio-ethanol [9]. Fermentation of biomass to ethanol usually contains about 95% water and 5% ethanol. This route is to satisfy the increasing ethanol demand for a world with a growing population[10]. More than half a million products are produced today due to the

petrochemical industry's development and oil processing [11]. Catalytically transformed feedstock into high-value-added products [12], such as the production of olefins [13], fuels[14], and aromatics[15], from ethanol.

The main objective is to review biomass production is to obtain ethanol from biomass. Ethanol is converted to ethylene and diethyl ether. Further, ethanol's kinetics through the 'Stop effect' process produces ethylene and DEE through dehydration.

II. KINETIC MODELING

The ethanol conversion to ethylene and diethyl ether (DEE) is through the dehydration process. Two reactions are occurring as follows:



Scheme 1. Dehydration route for the production of ethylene and diethyl ether from ethanol.

Equation 2.1 is an endothermic reaction that produces ethylene from ethanol via a unimolecular mechanism. Equation 2.2 is an exothermic reaction that produces DEE from ethanol via a bimolecular mechanism. An increase in temperature promotes an endothermic reaction, according to Le Chatelier's theory, whereas a decrease in temperature promotes an exothermic reaction. Hence, High temperature favors ethylene production, whereas low temperature favors DEE production [26].

The stop-effect is the significant increase in the reaction rate when the reactant's feed concentration is reduced to zero [16]. Koubek et al. 1980; Koubek et al. 1981[17][18] observed the dehydration of alcohol phenomenon and the deamination of primary amines on acid-base oxide catalysts and offered their observations as "Stop- Effect." Two distinct adsorption-desorption models have explained the stop-effect (SE) to characterize the catalyst's experimentally observed transition behavior [19]. Ethanol dehydration in the vapor phase is followed by overall second-order kinetics compared to the predicted first-order kinetics for lightly adsorbed species[20].

Two basic models explained this effect such as Ist Model assumes there was only one type of active site, and it was proposed by Koubek et al. 1980[17]; Koubek et al., 1981[18] to study an approximate observation description. The second model considered (II) two types of active sites involved in the process and was proposed by Nowobilski and Takoudis, 1986 [21]. Thullie and Renken 1991 studied both the models under forced concentration oscillations (FCO), and it was often difficult to distinguish under steady-state conditions [22].

The model I match their experimental findings suggested by Koubek et al. 1980; Koubek et al. 1981[17][18]. According to Model I, the reactant adsorbed on an occupied site, creating a second layer of 'A' molecules and restricting the surface reaction. It summarizes Model I is summarized as follows:



The "second layer" blocked the surface after stopping the reactant feed and would desorb the releasing active "AS" species. Consequently, the reaction rate will rise, go through a maximum, and ultimately tend to zero.

Nowobilski and Takoudis1986 [21] present a scheme assuming two distinct active sites, where its reactant (amine or alcohol) is firmly adsorbed on the catalyst's acid site (S_1), and the reaction involves an empty basic site (S_2). The necessary steps for the model (Model II) were:



Active sites 'S' is blocked by 'A' molecules when the adsorption of 'A' is high on both sites, and the production rate is low in the steady-state. It desorbs from the surface after a stop in the flow rate of 'A.' The concentration of empty sites increases rapidly, which increases the rate of reaction before it absorbs the accumulated surface compound 'AS', Assuming that the desorption proceeds much rapidly from the basic sites than from the acid ones.

Golay et al., 1997 [16] the reaction mechanism suggests that S_1 is an acid site where the alcohol or amine is heavily adsorbed. S_2 is a simple site where the reactant is adsorbed more weakly characteristic property of γ -alumina.

Rouge et al.,2001, [23]studied alumina and amphoteric metal oxides for catalytic dehydration of alcohol and amines to produce olefins. If the reactant feed was reduced to zero, a sharp rise in the reaction rate is detected. The scheme suggested:

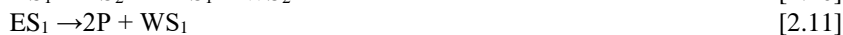


A = Alcohol (Isopropanol, iPrOH), E = Olefins (Propene), W = Water

As an inhibitor, A adsorbed on S_2 works. The reactant A desorbs rapidly from S_2 when the reactant feed is stopped and the concentration of free sites increases, leading to a dramatic increase in the reaction rate. Since water released during iPrOH adsorption and removed iPrOH from the S_2 sites, an instantaneous adsorption equilibrium between iPrOH and water on these sites had replaced the adsorption stage on S_2 . This explained the assumption of reversible water adsorption at S_2 sites.

Yadav and Murkute, 2004 [24] investigated the stop effect model (Model-2) on UDCaT-4 catalyst for dehydration of 2-propanol and alkylation of Mesitylene. Two cases considered here:

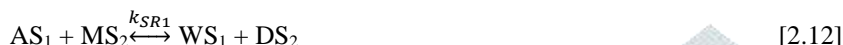
(a) IPA dehydration gives propylene and water



A = IPA, E = Diisopropyl ether (DIPE), P = Propylene, and W = Water.

The second-order kinetics is including individual alcohols. A combination of n-propanol and 2-propanol has also been found to be followed by dehydration of n-propanol. This also implies no association between IPA isomerizes of 2-propanol and n-propanol and n-propanol, which is dehydrated to produce propylene.

(b) Mesitylene alkylation with IPA



A = IPA, M = Mesitylene, D = Mono alkylated mesitylene, and W = Water.

IPA dehydration was individually found to follow second-order kinetics by adsorption of IPA at two adjacent sites S_1 and S_2 . The ether (E) product formed was instantly broken down to propylene (P).

The reaction mechanism indicated that for 2-propanol dehydration and methyl dealkylation with 2-propanol, these two types of sites were responsible. The high energy of activation for DIPE cracking for 2-propanol dehydration showed that DIPE was generally more reactive than 2-propanol. The large values of the apparent activation energy indicate that all reactions are kinetically regulated spontaneously.

Bokade and Yadav 2011 [20] investigated the kinetic model using 30% m/m DTPA/montmorillonite catalyst to research the significant process parameters. The ethanol dehydration mechanism indicated that there were two types of sites responsible. A model based on two catalytic sites was suggested according to which two different sites S_1 and S_2 , adsorbed by ethanol (A):



In the reaction, these two adsorbed species participated. In this case, the rate-determining step is AS_1 and AS_2 reactions as the surface complexes (DS_1) and (WS_2), to form diethyl ether (D) and water (W), respectively. As shown below, DS_1 broke down immediately to ethylene (E) in the gas phase.



Ethanol dehydration and diethyl-ether cracking were second-order reactions with low species adsorption. The high activation energy for DEE cracking for ethanol dehydration indicated that DEE indeed was more reactive than ethanol.

III. CONCLUSION

Biomass is a significant renewable energy source used in the future as a fuel in process plants and transportation. The stop-effect is the considerable increase in the reaction rate when the reactant's feed concentration is reduced to zero. Two distinct adsorption-desorption models have explained the stop-effect (SE) to characterize the catalyst's experimentally observed transition behavior. The mechanism of the ethanol dehydration process reaction suggests that two catalytic sites are responsible for ethylene production. The Kinetic model represented the simplicity and reality of the process.

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