

ACROLEIN FORMATION FROM GLYCEROL IN SUPERCRITICAL WATER.

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Glycerol reactions were conducted in high temperature and high pressure water (HHW: 573 to 673 K, 25 to 34.5 MPa) using a batch and a flow apparatus. To explore the reaction mechanism, the influences of temperature, H₂SO₄, glycerol concentration, and pressure, were examined. At the early stage of the reaction, the main products were always acrolein and acetaldehyde. The yield of acrolein was enhanced by higher glycerol concentration, higher concentration of H₂SO₄, and higher pressure. The experimental results revealed that ca. 80 % selectivity of acrolein was obtained at 90 % of glycerol conversion with acid catalyst in supercritical condition (673 K and 34.5 MPa). The dehydration of glycerol into acrolein was quite sensitive to pressure in supercritical condition because of the variation of proton concentration with respect to the pressure in supercritical water (SCW). We also developed a simple model of glycerol conversion into acrolein and analyzed the kinetic parameters. The rate constant of acrolein decomposition is always higher than that of acrolein formation in the absence of acid catalyst. On the other hand, it was revealed that the rate constant of acrolein formation overcame that of acrolein decomposition by adding acid in supercritical condition.

INTRODUCTION

A coming biomass community for sustainable societies demands to develop various biomass material conversion processes with high selectivity and high speed (efficiency). Waste vegetable oil has gained much attention because of its capability of being converted to bio-diesel as a sustainable energy resource. The bio-diesel is generally synthesized by methanolysis (transesterification) of triglyceride into methylester and the methanolysis was recently found to proceed without catalyst in supercritical methanol.[1]-[7] The byproduct of the methanolysis is glycerol and its effective utilization will be a key issue to promote this bio-diesel system.

Glycerol, a C₃ compound as same as propane and propylene, has been pointed out to convert into acrolein,^{8,9} which is commercially produced by partial oxidation of propane and a precursor of acrylic acid. Ramayya et al. [8] conducted the experiments of glycerol reactions in high temperature and high pressure water (HHW) at 573 K to 623 K of the reaction temperature and 34.5 MPa of the reaction pressure. They found that acrolein was obtained with high selectivity (84 % selectivity of acrolein at 40 % conversion of glycerol) by adding 5 mM H₂SO₄ at 623 K and 34.5 MPa. Bühler et al.[9] conducted the experiments of glycerol reactions using a flow apparatus in HHW at 622 to 748 K and 25 to 45 MPa without additives. They also conducted the simulation of the experiments using the detail kinetic model. Through these experimental and computational studies, they revealed that the glycerol reactions in HHW competitively progressed through both ionic and radical reactions. It was suggested that the predominance of the ionic or radical depended on temperature and pressure: the ionic reaction was preferred below the critical point of water (liquid state) and the radical was relatively favored at supercritical region. The kinetic model also indicated

that glycerol dehydration into acrolein mainly occurred through ionic reactions, on the other hand, another dehydration (into allyl alcohol) and the bond scission (into acetaldehyde and C1 compound such as formaldehyde) preferably underwent through radical reactions. Thus, the results by Ramayya et al.[8] and Bühler et al.[9] suggested that the acrolein formation from glycerol was controlled by proton and the high selective, high yieldable, and high efficient process of acrolein synthesis could be developed by means of HHW atmosphere, which is one of environmental benign “green” solvent.[10]-[12] In addition, glycerol is a simple model compound of carbohydrate and the data of the glycerol reaction would contribute toward the development of the other biomass conversion in HHW such as gasification.[9] The experimental data of glycerol in HHW was still low, in particular, the investigation of an acid catalyst on this reaction at wide reaction conditions must be demanded to explore the optimum condition for acrolein synthesis from glycerol.

In this study, glycerol reactions in HHW were examined using a batch reactor (for a long time reactions) and a flow apparatus (for a short time reactions). From the point of view of an organic synthesis, we focused on the acrolein formation from glycerol. The effects of temperature, H₂SO₄, and pressure on the reactions were investigated. A simple network model, of which rate constants were decided by fitting the experimental results, was used to know the effect of the parameters.

EXPERIMENTAL

Material

Glycerol was obtained from Aldrich. Acrolein and sulfuric acid (H₂SO₄, 1 mol/dm³ aqueous solution) were purchased from Wako Pure Chemical Co. These reagents were used as received. Pure water that was distilled after deionization was obtained by with a water distillation apparatus (Yamato Co., model WG-220).

Batch Experiments

The experiments without H₂SO₄ at 573 K were carried out by means of a SS 316 stainless steel tube bomb reactor with an inner volume of 6 cm³. The batch type reactor was constructed of an SS316 tube (105 mm length, 8.5 mm i.d., 12.7 mm o.d.) and Swagelok connectors (a reducing union and a cap) that are made of SS316. The reducing union was sealed by 1/16-inch plug. The loaded amount of glycerol was 0.1 g at all the batch experiments and it corresponded to 0.18 mol/dm³ of the concentration of glycerol in the reactor. The loaded amount of water was 4.3 g (ca. 720 kg/m³). The loaded amount of water correspond to the density of the saturated liquid phase at 573 K. The reactor containing the sample solution was purged air in it by Ar gas and sealed. The reactor then was submerged into the heating bath and the reaction started. Immersing the reactor in water bath stopped the reaction.

Flow experiments

Two HPLC pumps were employed to feed pure water and a sample solution. All the parts of the flow apparatus (the lines and the connectors) were made of SS316. The reaction cell was constructed of the 1/16-inch line (0.59 mm i.d., 1.59 mm o.d.) made of SS316 and its length ranged from 10 to 50 m as to the reaction times. The pre-heater and the reactor were heated to keep a desired temperature by electrical air ovens. In order to achieve a rapid

heating (milli-second order) at the mixing point, the pure water was heated up to more than 50 K higher than the reaction temperature in the pre-heater. A double piped heat exchanger was employed to cool down the reaction effluent rapidly. Pressure was maintained with a backpressure regulator. Temperatures of the several points of the apparatus (the outlet of the pre-heater, the inlet of the reactor, the mixing point, the outlet of the reactor, and the outlet of the heat exchanger) were measured by K-type thermocouples. The system pressure was measured by electrical pressure gauge at the points both before and after the reactor. Temperature and pressure were recorded by a data logger.

The concentration of glycerol in the reaction cell varied from 0.05 or 0.25 mol/dm³. When the effect of H₂SO₄ on the reaction was examined, glycerol was dissolved in H₂SO₄ solution and the acidic glycerol solution was fed to the apparatus. The glycerol concentration in the acidic solution was adjusted to be the same as the experiments without acid. The H₂SO₄ concentration in the reaction cell was set 1 or 5 mmol/dm³. The reaction time was controlled with changing the reactor length and the flow rate of the total influent.

The reaction temperatures were 573, 623, and 673 K. Pressure was set at 34.5 MPa as same pressure as the experiments by Ramayya et al.[8] The influent of the reactor was considered to be pure water when the reaction time was calculated because the density of the mixture at the reaction conditions could not be obtained. However, the assumption of influent as pure water would be reasonable because of the low-concentration of sample. The reaction time ranged from 5 sec to 80 sec. The experimental conditions of the flow experiments also listed in Tables 1 and 2 with the condition of the batch experiments and the experimental results.

Analyses and definition

Gas analysis was conducted only for the batch experiments. The gas product recovered in the system of the gas sampling, which was constructed of two GC-TCD and the cylinder, was measured its volume by the cylinder and analyzed its composition by the GC-TCD (Shimadzu, model GC-8A). One of the GC was operated with MS13X column and Ar gas (as the carrier) to detect H₂, CO, and CH₄. Another was operated with Porapak Q column and He gas to detect CO₂ and small hydrocarbons, which were alkane and alkene with carbon number ranging from 2 to 4 (C₂-C₄). Small hydrocarbons including CH₄ (C₁-C₄) were sometimes detected in the gaseous products. However, the total yields of the small hydrocarbons were always below 0.1 mol%. In addition, since the hydrocarbons formation was not discussed in this study, the yields of the hydrocarbons were not shown. The liquid products in the recovered solution were analyzed by HPLC (JASCO), which had RI and UV as detectors, with KS-802 column (Shodex) and GC-FID (Hewlett-Packard, model HP6890) with HP-5 column (Hewlett-Packard). The total amount of carbon in the water solution was evaluated by a total organic carbon detector (Shimadzu, model TOC-5000A). Product yield (mol%) of carbon compound was evaluated from carbon base.

RESULTS AND DISCUSSION

Tables 1 and 2 shows the experimental conditions and the results in the absence (Run # 1 to 9) and the presence (Run # 10 to 37) of H₂SO₄. The products that were identified and quantified in this study are acrolein, acetaldehyde, formaldehyde, hydroxyacetone, and allyl alcohol. We also observed the formation of methanol and ethanol, however, the yields of these compounds were always quite small and those were not shown in **Tables 1 and 2**.

Bühler et al.[9] reported that propionaldehyde was also main product. In the present study, this compound could not be detected at all the conditions.

Table 1 Experimental conditions and results (without H₂SO₄)

Run#	Conditions				TOC, Glycerol, and Products Yield							Selectivity of acrolein, %
	T, K	Pressure, MPa	Concentration, mol/dm ³	Time, s	TOC, mol%	Glycerol, mol%	Acrolein, mol%	Acetaldehyde, mol%	Formaldehyde, mol%	Hydroxyacetone, mol%	Allylalcohol, mol%	
1	573	Saturated	0.18	600	105.99	98.19	3.04	0.02				> 100
2	573	Saturated	0.18	1800	103.57	96.52	4.22	0.28	0.05	0.03		> 100
3	573	Saturated	0.18	3600	103.70	95.06	5.57	1.00	0.16	0.19	0.10	> 100
4	623	34.5	0.05	9.68	99.28	98.60	2.35				0.05	> 100
5	623	34.5	0.05	14.35	98.82	97.09	2.80				0.07	96.12
6	623	34.5	0.05	28.69	96.51	94.95	3.25				0.04	64.38
7	673	34.5	0.05	10.47	102.00	89.46	15.72				0.78	> 100
8	673	34.5	0.05	14.06	98.91	89.12	15.41				0.94	> 100
9	673	34.5	0.05	21.33	99.48	85.14	13.38				1.50	89.99

Table 2 Experimental conditions and results (with H₂SO₄)

Run#	Conditions					TOC, Glycerol, and Products Yield							Selectivity of acrolein, %
	T, K	Pressure, MPa	Concentration, mol/dm ³	H ₂ SO ₄ , mmol/dm ³	Time, s	TOC, mol%	Glycerol, mol%	Acrolein, mol%	Acetaldehyde, mol%	Formaldehyde, mol%	Hydroxyacetone, mol%	Allylalcohol, mol%	
10	573	34.5	0.25	5	16.60	103.27	95.61	2.80			0.17	0.03	64
11	573	34.5	0.25	5	22.41	103.26	95.05	3.45			0.19	0.04	70
12	573	34.5	0.25	5	33.26	103.11	94.41	3.90			0.19	0.06	70
13	573	34.5	0.25	5	41.35	102.52	93.87	4.44			0.14	0.05	72
14	573	34.5	0.25	5	55.54	102.06	92.39	4.82			0.17	0.06	63
15	573	34.5	0.25	5	82.62	105.01	90.95	5.13	0.07		0.24	0.06	57
16	623	34.5	0.05	1	5.86	105.59	97.82	6.87	0.14		0.25		> 100
17	623	34.5	0.05	1	7.29	104.62	96.50	7.97	0.14		0.36		> 100
18	623	34.5	0.05	1	9.73	103.38	95.49	8.67	0.28		0.46	0.03	> 100
19	623	34.5	0.05	1	14.51	104.95	86.67	9.34	0.54	0.07	0.88		70
20	623	34.5	0.05	1	19.48	96.59	78.03	10.00	0.74	0.11	1.08		46
21	623	34.5	0.05	5	7.38	105.03	84.97	12.92	0.53	0.05	1.29	0.03	86
22	623	34.5	0.05	5	9.86	104.25	83.48	14.52	0.88	0.05	1.48	0.04	88
23	623	34.5	0.05	5	14.67	104.38	77.70	17.00	1.61	0.10	2.08	0.03	76
24	623	34.5	0.05	5	19.71	101.11	73.25	19.32	2.31	0.28	1.93	0.03	72
25	623	34.5	0.05	5	29.09	95.74	56.62	23.04	4.60	0.40	3.08	0.04	53
26	623	34.5	0.25	5	14.58	106.87	73.43	26.97	1.98	0.67	1.98	0.04	> 100
27	623	34.5	0.25	5	19.46	106.08	65.02	32.10	2.92	1.08	2.66	0.06	92
28	623	34.5	0.25	5	29.59	104.15	54.65	39.09	4.79	1.88	3.04	0.08	86
29	673	25	0.05	5	5.05	98.19	59.85	22.09	2.88	0.89	0.28	2.75	55
30	673	25	0.05	5	9.54	97.08	45.13	41.96	8.50	2.13	0.42	1.46	76
31	673	25	0.05	5	12.67	95.99	36.69	52.95	10.46	2.49	0.67	1.09	84
32	673	30	0.05	5	8.06	98.52	28.72	61.08	9.21	3.44	0.00	3.71	86
33	673	30	0.05	5	10.88	95.85	26.43	60.31	10.54	3.81	0.02	3.44	82
34	673	30	0.05	5	15.75	82.95	22.72	42.72	12.31	3.84	0.08	2.55	55
35	673	34.5	0.05	5	10.32	88.42	7.85	74.29	14.30	5.59	0.04	4.46	81
36	673	34.5	0.05	5	13.70	85.63	6.02	74.11	18.22	6.59	0.05	3.18	79
37	673	34.5	0.05	5	20.20	79.77	4.12	66.18	22.86	7.78	0.06	1.94	69

Without catalyst

As shown in **Table 1**, TOC values at always around 100 % and glycerol conversion was quit slow reaction at 573 K (Run # 1 to 3) and only 5 mol% of glycerol disappeared even at 3600 s (Run # 3). The main product was acrolein, however, 1 mol% of acetaldehyde was obtained at 3600 s. Run # 4 to 6 were experiments at 623 K. The yield of acrolein was 3 mol% and the conversion of glycerol was 5 mol% at 29 s and 623 K (Run # 6) and the selectivity of acrolein was 64 %. In supercritical region (673 K, Run # 7 to 9), the quantitative acrolein formation was observed, that is, 14 mol% of acrolein was gained at 15 mol% of glycerol conversion (at 21 s, Run # 9). The high selectivity of acrolein was kept at 673 K (90 % at 21 s, Run # 9), however, the yield of acrolein was low, only 13 mol%. Furthermore, the yield of acrolein decreased with increasing the conversion of glycerol. This means that acrolein converted further.

With H₂SO₄

Table 2 shows the reaction conditions and the results in the presence of H₂SO₄. Addition of H₂SO₄ accelerated glycerol reaction at all the reaction time. The yield of acrolein

was always much higher than those of the other products and the primary product was always acrolein even in the presence of H₂SO₄.

Run # 10 to 15 were the experiments at 573 K. The conversion of glycerol at 573 K was 10 mol% at 83 s and then the yield of acrolein was 5 mol% (Run # 15). The selectivity of acrolein formation was then 57 % at 573 K (Run # 15).

The concentration of H₂SO₄ and glycerol was changed to explore the effect of these factors on the reaction at 623 K. Addition of 1 mmol/dm³ of H₂SO₄ to the reaction at 0.05 mol/dm³ of glycerol concentration slightly enhanced the reaction (see also Table 1, Run # 4 to 6). The yield of acrolein was 10 mol% was achieved at 20 % of glycerol conversion and the selectivity of acrolein was 46 % (at 20 s, Run # 20). Increase of H₂SO₄ concentration from 1 mmol/dm³ (Run # 16 to 20) to 5 mmol/dm³ (Run # 21 to 25) brought the only slight enhancement of glycerol conversion (26 mol% of glycerol conversion at 20 s, Run # 24). The increase of H₂SO₄ concentration improved the selectivity of acrolein: 19 mol% of acrolein was obtained at 26 mol% of glycerol conversion (Run #24, at 20 s, 0.05 mol/dm³ of glycerol concentration, 5 mmol/dm³ of H₂SO₄) and thus the selectivity of acrolein at this condition was 72 %, in contrast, 10 mol% of acrolein formed at 22 % of glycerol conversion at the same retention time (Run # 20, 0.05 mol/dm³ of glycerol concentration, 1 mmol/dm³ of H₂SO₄). The conversion of glycerol (45 mol%) at 0.25 mol/dm³ of glycerol concentration at 30 s (Run # 28) was almost the same as that at 0.05 mol/dm³ (43 mol%) at 30 s (Run # 25). On the other hand, the yield of acrolein was increased with increasing glycerol concentration, that is, 23 mol% of acrolein at 0.05 mol/dm³ of glycerol and 30 s of reaction time (Run # 25) was obtained and 40 mol% of acrolein at 0.25 mol/dm³ of glycerol and 29 s of reaction time (Run # 28) was yielded. Although 86 % of selectivity was obtained at 30 s (Run # 28), the selectivity of acrolein decreased with increasing reaction time (Run # 26 to 28), namely glycerol conversion (> 100 % selectivity of acrolein at 15 s, 92 % at 20 s, and 86 % at 30s, respectively).

At supercritical region (673 K), pressure effect was examined (Run # 29 to 31 were 25 MPa, Run # 32 to 34 were 30 MPa, and Run # 35 to 37 were 34.5 MPa). Figure 3 shows the results of the pressure effect on glycerol and acrolein yields. As the figure clearly shows, higher pressure enhanced glycerol conversion and acrolein formation. Finally, the high yield (74 mol%) and high selectivity (81 %) of acrolein were obtained at the experiments at 673 K, 10 s, 0.05 mol/dm³ of glycerol concentration, and 5 mmol/dm³ of H₂SO₄ concentration (also see in Table 2, Run # 35). Increase of reaction time lead the decrease of acrolein selectivity (Run # 35 to 37). As we confirmed the experimental results at 623 K, glycerol concentration positively affected the glycerol conversion and acrolein. This concentration effect will be seen at supercritical region and thus we are now studying further.

The selectivity and yield of acrolein reduced at longer reaction as shown in **Tables 1** and **2**. This means that the formed acrolein was converted into the other products. The formation of acrolein was sensitive for the concentrations of glycerol and H₂SO₄. Thus, the dependency of the formation rate on these concentration must be taken into consideration. However, there was not enough experimental data at this moment. Therefore, the concentration dependency of organics was set to first-order and the term of the proton concentration dependency was included in each rate constant as follows:

$$\frac{d[Acrolein]}{dt} = k_1'[Glycerol] - k_4'[Acrolein] \quad (1)$$

We decided the kinetic parameters (k'_1 and k'_4) by fitting the experimental data. **Table 3** lists the kinetic parameters. The activation energy (E_a) of k'_1 without H_2SO_4 was slightly higher than that of k'_4 . Thus, the formation rate of acrolein from glycerol would become higher than that of acrolein decomposition at higher temperature, however, the temperature where k'_1 overcomes k'_4 without H_2SO_4 is 1900 K, too high temperature. In contrast, the temperature where the rate constant of acrolein formation (k'_1) with H_2SO_4 conquered that of acrolein decomposition (k'_4) was 623 K. The formed acrolein was relatively stable because of the slower decomposition rate and thus the high selectivity and high yield of acrolein was achieved in supercritical water.

Table 3 Kinetic parameters of k'_1 and k'_4

k	A, 1/s	E_a , kJ/mol
without H_2SO_4		
k'_1	1.0E+19	247.5
k'_4	1.0E+17.6	231.6
with H_2SO_4		
k'_1	1.0E+11.7	146.4
k'_4	1.0E+2.1	1

CONCLUSION

In this study, it was revealed that 74 mol% of acrolein yield and 81 % of its selectivity was obtained with acid catalyst in supercritical condition (673 K). We developed a simple model of acrolein formation. The rate constant of acrolein formation overcame that of acrolein decomposition by adding acid in supercritical condition.

REFERENCES :

- [1]. Saka, S., Kusdiana, D., Fuel, Vol. 80, **2001**, p. 225.
- [2]. Kusdiana, D., Saka, S., Fuel, Vol. 80, **2001**, p. 693.
- [3]. Demirbas, A., Energy Conv. Manag., Vol. 43, **2002**, p. 2349.
- [4]. Kusdiana, D., Saka, S., Biores. Technol., Vol. 91, **2004**, p. 289.
- [5]. Madras, G., Kolluru, C., Kumar, R., Fuel, Vol. 83, **2004**, p. 2029.
- [6]. Warabi, Y., Kusdiana, D., Saka, S., Biores. Technol., Vol. 91, **2004**, p. 283.
- [7]. Cao, W., Han, H., Zhang, J., Fuel, Vol. 84, **2005**, p. 347.
- [8]. Ramayya, S., Brittain, A., DeAlmeida, C., Mok, W., Antal, Jr., M. J., Fuel, Vol. 66, **1987**, p. 1364.
- [9]. Bühler, W., Dinjus, E., Ederer, H. J., Kruse, A., Mas, C., J. Supercrit. Fluids, Vol. 22, **2002**, p. 37.
- [10]. Sasaki, M., Goto, K., Tajima, K., Adschiri, T., Arai, K., Green Chem., Vol. 4, **2002**, p. 285.
- [11]. Bicker, M., Hirth, J., Vogel, H., Green Chem., Vol. 5, **2003**, p. 280.
- [12]. Watanabe, M., Iida, T., Aizawa, Y., Ura, H., Inomata, H., Arai, K., Green Chem., Vol 5, **2003**, p. 539.