IMAGE ANALYSIS OF LIQUEFIED OIL PALM TRUNK RESIDUE SOLVOLYSIS IN GLYCEROL AND ETHYLENE GLYCOL

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ABSTRACT

A 2^{4-1} fractional factorial design of experiment by software Stat–Ease Inc., Design–Expert® Version 7 was used to study the solvolysis of oil palm trunk particles (OPT) in ethylene glycol and glycerol. The solvolysis variables including; raw material loading, types of solvents, percentage of H_2SO_4 catalyst and solvolysis retention time. The solvolysis residues were examined under stereomicroscope and field emission scanning electron microscope. The result showed that the generated response surface methodology model for this study is found to be significant. Generally, solvolysis of OPT in glycerol gave higher amounts of liquefied yield if compared to that in ethylene glycol. The morphology of the residues revealed that the changes in appearances and sizes, if compared to raw OPT feedstock, can be seen as early as 10 min solvolysis time. With 6% catalyst in 120 min solvolysis time, the OPT component greatly disintegrated regardless of its initial loading quantity. This condition also gave darker solid residues that possibly associated with the formation of char component. The micrograph of the filtrate showed scattered OPT fibres with diameter measured less than 50 µm, silica granules and the OPT feedstock was not completely macerated.

Keywords: Fractional factorial design, image analysis, oil palm trunk, RSM, solvolysis.

INTRODUCTION

Many studies of biomass solvolysis have been conducted by other researchers including tree species like poplar (*Populus ssp.*), alder (*Alnus ssp.*), linden (*Tilia ssp.*) and chestnut wood (*Castanea sativa Mill.*) [1], bagasse and cotton stalks [2], oil palm (*Elaeis guineensis*) empty fruit bunch (EFB)[3] cotton wool and filter paper [4] and waste paper [5]. Liquefied biomass can be used for resol-type phenolic resin in phenolic foam [6], novolak phenol formaldehyde resin [7], liquefied wood/ polyurethane films[8] and various polymer composites [9].

Malaysian palm oil industry generates large quantities of palm biomass waste each year. This waste is a good source of renewable raw material. There are several solvolysis studies of oil palm wastes that have been conducted previously such as on EFB fibre, mesocarp fibre and palm kernel shells which later were used in phenolated EFB resin and as bio oil [10, 11]. Considerably, no solvolysis of waste oil palm trunk (OPT) ever conducted by any researchers. Therefore, the objective of this study was to assess the solvolysis of waste OPT in ethylene glycol and glycerol to obtain a liquefied product.

The solvolysis study was conducted based on response surface methodology (RSM), 2^{4-1} fractional factorial design. This design is useful for estimating linear model terms, where each factor was varied over two levels; highest or lowest values. Besides, this design also enables to find the possible significant variables for the experiment as well as estimating main effect and interactions among factors [12].

METHODOLOGY

The OPT sample of a 25 year-old felled OPT was obtained from an oil palm plantation in Ara Kuda, Kedah, Malaysia. Sulphuric acid (H_2SO_4) brand QRëC® with 95-97% purity grade was used as catalyst. Analytical grade of glycerol and ethylene glycol brand of Sigma-Aldrich® were used as solvolysis reagent. Aqueous solution of sodium hydroxide (NaOH) was used to neutralize the liquefied product. Ethanol (Sigma-Aldrich®) was used to rinse the liquefied OPT. The OPT was cut into debarked discs, chopped, ground, screened to specific sizes between 250-1000 µm and were oven dried for 24 hours before it ready as feedstock.

The study adopted a 2^{4-1} fractional factorial design aided by software Stat-Ease, Inc. Design-Expert® Version 7. The four variables were OPT loading (A), solvolysis time (B), percentage of H_2SO_4 catalyst (C) and solvolysis solvents (D). The summary of the variables used is shown in Table 1. Based on fractional factorial designs (2^{4-1}), the number of runs generated were eight (16/2 = 8 runs) but each run was duplicated for more precise estimation. Total number of runs were 16. The number of runs, the actual and coded value of independent variables is shown in Table 2. The low limit value of the solvent that is 0, meaning that 100% glycerol was used as solvolysis solvent and no ethylene glycol presented while at 100 high limit value meaning that 100% ethylene glycol was used with no glycerol presented.

The OPT feedstock, solvent and catalyst (H_2SO_4) were mixed according to the formula ratio as described in Table 2. The solvolysis reaction was carried out in a 500 ml four-neck glass flask, equipped with a stirrer, reflux condenser, temperature probe and heating mantle. Mixture of solvent and catalyst was initially heated to 150 °C before the OPT feedstock was added. The reaction time was recorded once all the OPT feedstock had been added into the flask. When completed, the flask that contained a dark brown mixture (liquefied OPT) was immersed in an ice bath to stop the reaction. The excessive amount of catalyst was neutralized with an equivalent sodium hydroxide (NaOH) aqueous solution. The liquefied OPT was then diluted with excessive amount of ethanol and stirred continuously for 5 min. The solid residue of unliquefied OPT feedstock was obtained by vacuum-filtration with grade 1 Whatman® qualitative filter paper. It was then rinsed thoroughly using ethanol until colourless filtrate and was oven dried overnight at 105°C.

The following Eq. (1) calculated the solvolysis yield:

$$Liquefaction\ yield\ (\%) = \left(1 - \frac{Weight\ of\ solid\ residue\ (OD)}{Weight\ of\ OPT\ feedstock\ (OD)}\right) \times 100 \qquad (1)$$

Table 1. The independent variables used during the oil palm trunk (OPT) solvolysis

Component	Name	Units	Actual		Coded	
			Low	High	Low	High
A	OPT Loading	g	30	60	-1	1
B	Time	min	10	120	-1	1
C	Catalyst	%	2	6	-1	1
D	Solvolysis solvents	%	0	100	-1	1

Stereomicroscopic imaging and Field-Emission Scanning Electron Microscopy (FESEM)

Dried solid residues after filtration were digitally examined under Olympus SZX10 stereomicroscope. This stereomicroscope is equipped with the DP27, a 5-megapixel micro imaging digital camera that is capable to capture images up to 2448 x 1920-pixel resolution. Sample images were captured at 1000 ms exposure time.

The surface topographic details and microstructure analysis of the solid liquefied OPT residues was visualized using a general-purpose ultra-high resolution field-emission scanning electron microscope (FESEM). The FESEM used was Carl Zeiss Leo Supra 50 VP Field Emission. The operating voltage was 15kV. The samples were oven dried overnight at 105 °C before coated with thin layer (±200 Å) of gold using a vacuum sputter coater.

RESULTS AND DISCUSSION

The amount of liquefied OPT yields obtained as a response to the different parameters of OPT loading (A), solvolysis time (B), catalyst (C) and solvolysis solvent (D) are presented in Table 2. The experiment implemented the 2^{4-1} fractional factorial design. The 16 experimental runs were conducted in random order to avoid the effect of lurking variables. The final response (liquefied OPT yield) obtained ranging between 51.36% (min) and 81.76% (max). The predicted OPT liquefied yields were calculated based on Eq. (2) and Eq. (3). It was found that the predicted yields were in the acceptable range with the experimental/actual values.

Table 2. Liquefied oil palm trunk (OPT) yields as response to the multiple solvolysis variables

Run	Factor Levels								Actual yield (%)	Predicted yield (%)
	Actual				Coded					
	A	B	C	D	A	B	C	D		
1	30	10	2	0	-1	-1	-1	-1	57.24	58.04
2	30	10	2	0	-1	-1	-1	-1	58.83	58.04
3	30	10	6	100	-1	-1	1	1	51.36	53.32
4	30	10	6	100	-1	-1	1	1	55.28	53.32
5	30	120	2	100	-1	1	-1	1	59.12	59.46
6	30	120	2	100	-1	1	-1	1	59.80	59.46
7	30	120	6	0	-1	1	1	-1	79.37	80.56
8	30	120	6	0	-1	1	1	-1	81.76	80.56
9	60	10	2	100	1	-1	-1	1	54.65	55.58
10	60	10	2	100	1	-1	-1	1	56.50	55.58
11	60	10	6	0	1	-1	1	-1	57.70	58.69
12	60	10	6	0	1	-1	1	-1	59.68	58.69
13	60	120	2	0	1	1	-1	-1	62.29	62.55
14	60	120	2	0	1	1	-1	-1	62.81	62.55
15	60	120	6	100	1	1	1	1	64.66	65.88
16	60	120	6	100	1	1	1	1	67.09	65.88

A = OPT Loading (g); B = Time (min); C = Catalyst (%); D = Solvent (%)

The analysis of variance (ANOVA) of the model is presented in Table 3. It shows the reliability and the significance of the model and the variables involved. The F-value for the model is 61.97 indicates that the model terms are significant. With the "Model F-Value" this large, there is only a 0.01% chance that it could occur due to noise. The model terms were selected or excluded based on the p-value with 95% confidence level. The p-value for the model, factors (A, B, C and D) or its interaction (AB, AC and AD) are less than 0.05 implies that the terms are significant. The predicted R^2 (Pred R-Squared of 0.9276) is in reasonable agreement with the adjusted R^2 (Adj R-Squared of 0.9660), which is good. The adequate precision (Adeq Precision) statistically calculates the signal to noise ratio. A ratio greater than 4 is desirable. The adequate precision of 25.143 obtained from the experiment indicates an adequate signal. This model can be used to navigate the design space.

In Fig. 1, the RSM model for liquefied OPT yield in glycerol and ethylene glycol shows the effect of main factor and their interactions to the final yield. It can be seen that solvolysis of OPT in glycerol gave higher yield compared in ethylene glycol. In a study done by Jasiukaitytė et *al.* [13], they also found that lignin has less solubility in ethylene glycol with

H_2SO_4-catalyzed solvolysis. In glycerol, the OPT loading of 30 and 60 g at time 10 min had less significant effect on the liquefied yield. The 60 g OPT loading tend to give lower yield due to the thick viscosity of glycerol that prevent proper mixing during the initial solvolysis process. However, as the solvolysis time increased, the amount of yield also increased because the OPT feedstock started to liquefy. At 120 min solvolysis time, 30 g OPT loading gave higher yield due to the higher ratio between solid and liquid. In ethylene glycol, 60 g OPT loading gave higher yield compared to 30 g OPT loading at 10 min solvolysis time. As the solvolysis time increased, the amount of yield obtained from 30 g OPT loading also increased and eventually surpassed that of 60 g. This happened probably due to thinner viscosity of ethylene glycol permitted the OPT feedstock to mixed well, even during the initial phase of the solvolysis process. In terms of catalyst, 6% H_2SO_4 gave higher yield compared to 2%. One thing in common in all the solvolysis conditions is the yield could be obtained as quick as 10 min solvolysis time. This finding is in agreement with a study by Kurimoto and Tamura [14]. In a study conducted by Yao [15], they reported that rapid solvolysis in initial phase was due to degradation of lignin components, hemicelluloses and some reachable cellulose. The yield conversion ratio became slower due to hard-to-access cellulose. The early solvolysis phase affected the conversion rates of the subsequent solvolysis stages.

Table 3. Analysis of variance (ANOVA) for oil palm trunk (OPT) solvolysis model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	1018.38	7	145.48	61.97	< 0.0001	Significant
A (OPT Loading)	18.90	1	18.90	8.05	0.0219	
B (Time)	458.61	1	458.61	195.33	< 0.0001	
C (Catalyst)	130.27	1	130.27	55.49	< 0.0001	
D (Solvent)	163.87	1	163.87	69.80	< 0.0001	
AB	52.59	1	52.59	22.40	0.0015	
AC	24.73	1	24.73	10.53	0.0118	
AD	169.40	1	169.40	72.15	< 0.0001	
Pure Error	18.78	8	2.35			
Cor Total	1037.16	15				

Standard Deviation	1.53	(R^2) R-Squared	0.9819
Mean	61.76	($R^2_{Adj.}$) Adj R-Squared	0.9660
C.V. %	2.48	($R^2_{Pred.}$) Pred R-Squared	0.9276
PRESS	75.13	Adequate Precision	25.143

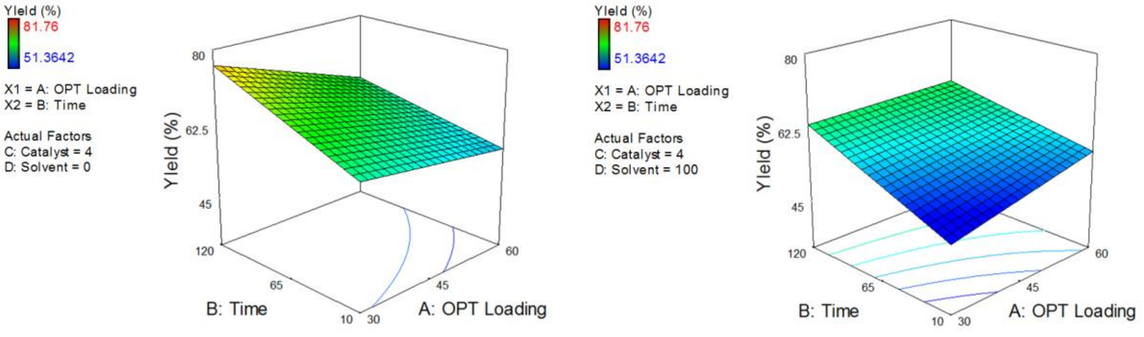
The final empirical models in terms of coded factors for percentage of liquefied OPT yield (***y***) is shown in Eq. (2):

$$\boldsymbol{y} = 61.76 - 1.09A + 5.35B + 2.85C - 3.20D - 1.81AB - 1.24AC + 3.25AD \qquad (2)$$

While the final equation in terms of actual factors is shown in Eq. (3):

$$\boldsymbol{y} = 52.06 + 0.02A + 0.2B + 3.30C - 0.26D - (2.20 \times 10^{-3})AB - 0.04AC + (4.34 \times 10^{-3})AD \qquad (3)$$

Therefore, for any A, B, C and D we can predict the percentage of liquefied OPT yield (***y***). The predicted ***y*** is a function of A, B, C and D. For the equation terms in coded factors, the coefficients are unitless.



(a) (b)

Figure 1. 3D surface view of the yield obtained after oil palm trunk (OPT) solvolysis. (a) – solvolysis in glycerol; (b) – solvolysis in ethylene glycol.

Stereomicroscopic imaging

Morphology of raw OPT feedstock used in this study is shown in Fig. 2. Once the solvolysis process completed, the dried solid residues from liquefied OPT in glycerol were examined under stereomicroscope and the images captured are presented in Fig. 3. The stereoscopic images revealed that the decrease in size of OPT feedstock appearances, if compared to raw OPT can be seen as early as 10 min solvolysis time. At 6% catalyst for 120 min solvolysis time, the OPT particles were harshly disintegrated regardless of its initial loading amount. This condition also gave darker solid residues that possibly associated with the formation of char component. This formation of char is linked to the degradation of weak bonds, such as alkyl-aryl ether bonds in lignin [16]. Fig. 4 shows the condition of OPT solid residues that were liquefied in ethylene glycol. Similar like solvolysis of OPT in glycerol, 6% catalyst with 120 min solvolysis time disintegrated the OPT component significantly. The amount of feedstock or the ratio of feedstock to the solvents has less significant effect especially at 10 min solvolysis time. The catalyst percentage and solvolysis time have great effect in the solvolysis of OPT feedstock.

Figure 2. Raw oil palm trunk (OPT) feedstock prior to the solvolysis process.

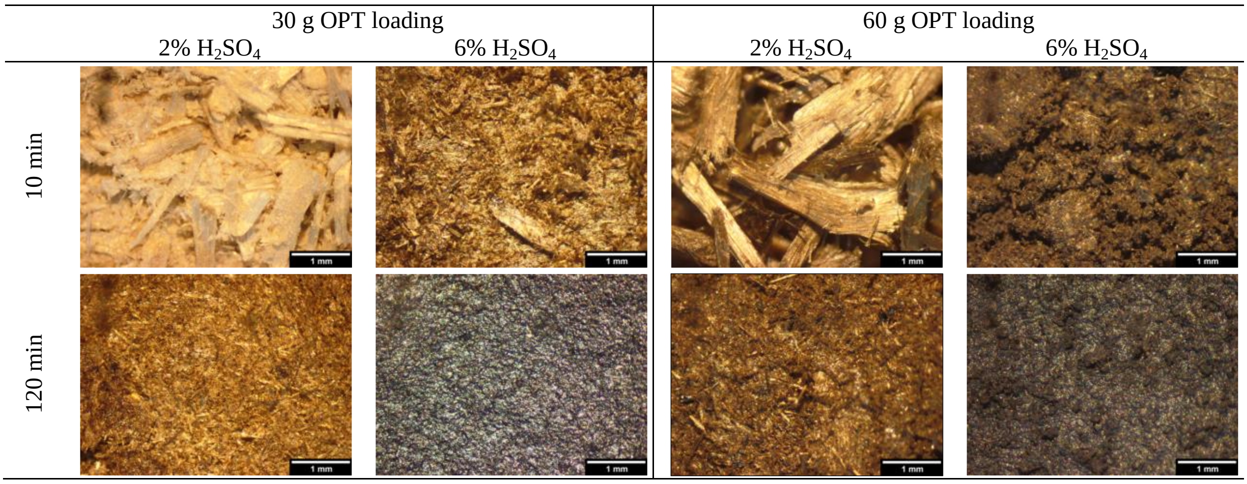


Figure 3. Morphology of oil palm trunk (OPT) residues solvolysis in glycerol.

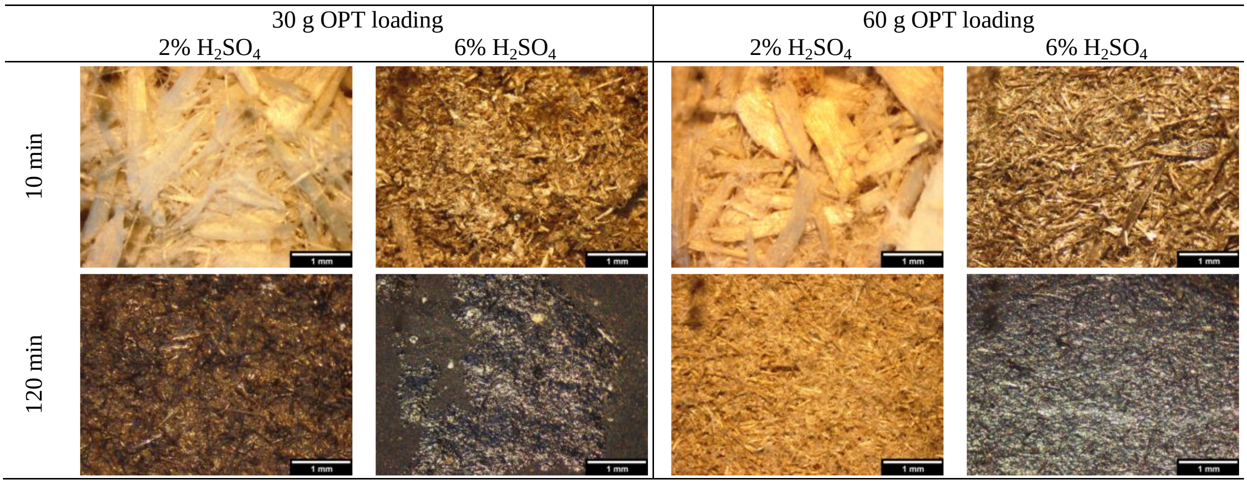


Figure 4. Morphology of oil palm trunk (OPT) residues solvolysis in ethylene glycol.

Micrographs of field-emission scanning electron microscopy

Micrograph of raw oil palm particles prior to the solvolysis process is shown in Fig. 5. It has been observed that at 50× magnification, the micrograph of raw OPT feedstock shows aligned OPT fibres and a collection of silica granules embedded in OPT parenchyma. Fig. 6 shows the micrographs of residue from 30 g OPT liquefied in ethylene glycol with 6% H_2SO_4 catalyst for 120 min solvolysis time. The Fig. 6-A is the micrograph at 50× magnification with working distance (WD) of 16 mm while Fig. 6-B is the same sample but at 300× magnification with WD of 15 mm. The filtrate shows scattered OPT fibres with diameter measured less than 50 µm. The OPT component was not completely disintegrated. Generally, the lignin components and hemicelluloses congregated those fibres [17]. Lignin also situated in middle lamellas of the fibres. From the micrograph, we assumed that lignin is one of the components that had been attacked and decomposed during solvolysis process. This finding is based on the EFB solvolysis study by Ahmadzadeh and Zakaria [18].

The liquefied OPT residue at 6% H_2SO_4 catalyst for 120 min in glycerol is shown in Fig. 7. Fig. 7-C is the micrograph at 50× magnification with working distance (WD) of 16 mm while Fig. 7-D is the same sample enlarged at 300× magnification with WD of 15 mm. It shows the formation of nearly flat surface topography with the presence of silica granules. Images of silica granules in this work are identical with those found in studies conducted by Ahmad et *al.* [19] and Wirasnita et *al.* [20]. Silica granules appeared and clearly be seen because fibres were macerated into smaller sizes compared to the silica granules. The fibres decomposed up to microfibrils. Solvolysis of OPT in glycerol disintegrates the lignocellulosic OPT components better, if compared to that in ethylene glycol.

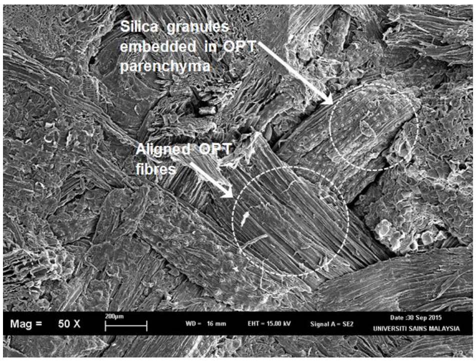


Figure 5. Micrograph of raw oil palm (OPT) particles prior to the solvolysis process.

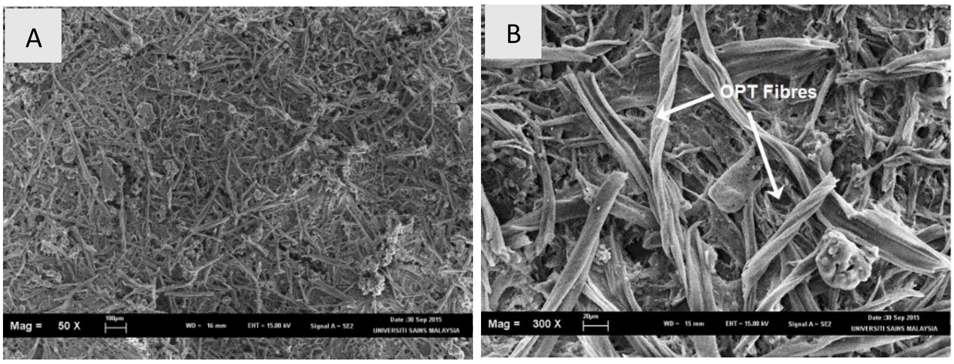


Figure 6. Micrographs of solid residue from 30 g oil palm trunk (OPT) feedstock solvolysis in ethylene glycol at 6% catalyst for 120 min. A – 50× magnification; B – 300× magnification.

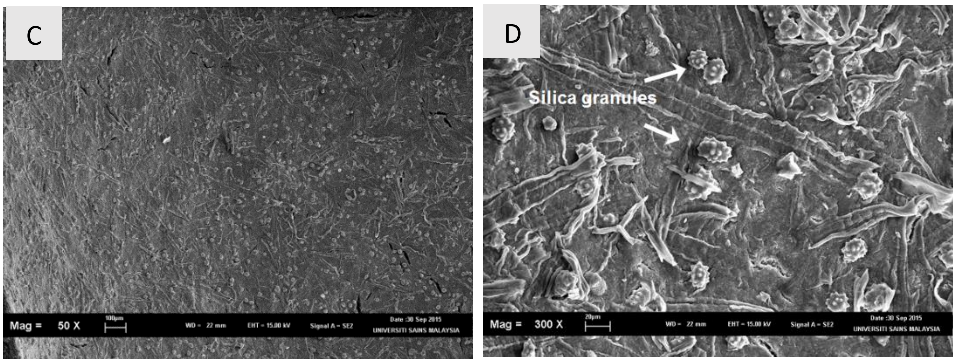


Figure 7. Micrograph of solid residue from 30 g oil palm particles feedstock solvolysis in glycerol at 6% catalyst for 120 min. C – 50× magnification; D – 300× magnification.

CONCLUSION

Response surface methodology (RSM) through 2^{4-1} fractional factorial design was useful to determine the significant variables of OPT solvolysis process. In the solvolysis study, factors like solvolysis time, the solvent used and percentage of H_2SO_4 catalyst significantly influenced the final liquefied OPT yield. In comparison, between ethylene glycol and glycerol as solvents, solvolysis of OPT in glycerol gave higher amounts of liquefied yield. The use of higher percentages of H_2SO_4 catalyst simultaneously with longer solvolysis time contributed to higher yields too.

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