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Chemical Conversion of the Oil Palm Wastes

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ABSTRAK

Penghasilan 2-furaldehid (furfural) daripada sabut mesokap dan cecair buangan dari kilang kelapa sawit menggunakan asid protik telah dikaji. Kesan rendaman sabut kelapa sawit dalam asid sebelum pemanasan telah juga dikaji. Penghasilan furfural sempurna dalam masa 3–4 jam apabila asid hidroklorik (HCl) dan asid sulfurik (H_2SO_4) digunakan sebagai mangkin, sedangkan masa yang lebih lama diperlukan apabila asid fosforik (H_3PO_4) atau asid oksalik ($H_2C_2O_4$) digunakan. Kajian ini juga menunjukkan kadar penghasilan dapat dipercepat apabila kepekatan asid ditinggikan. Perendaman sabut dalam asid selama 24 jam sebelum tindak balas dilakukan dapat meninggikan penghasilan furfural. Pengubahan kimia atas cecair buangan dari kilang pemprosesan kelapa sawit telah dilakukan juga. Hasil kajian menunjukkan kesan kepekatan asid terhadap kadar tindak balas serupa dengan kesannya terhadap sabut mesokap.

ABSTRACT

The production of a 2-furaldehyde (furfural) from mesocarp fibre waste and oil palm sludge from a palm oil mill using protic acids was investigated. The effect of immersion of fibre in acid prior to heating was also studied. Production of furfural was completed in 3–4 hours when hydrochloric (HCl) or sulfuric (H_2SO_4) acids were used as the catalyst whereas a longer reaction time was required in the case of phosphoric (H_3PO_4) or oxalic ($H_2C_2O_4$) acids. The experiment showed that the rates of furfural production were increased when higher acid concentrations were applied. Immersion of fibre in the acids for 24 hours prior to reaction increased the furfural yield. The chemical conversion of sludge from the palm oil mill was also investigated. A similar acid concentration effect on the rate was observed.

INTRODUCTION

Malaysia is the world's largest palm oil producer (Khor, 1983) and therefore the industry has become one of the country's major economic resources. In view of its importance, research aimed at further diversifying the use of oil palm products and by-products was thought to be highly desirable. As a contribution to this general theme, a study on the production of furfural by chemical treatment of oil palm wastes has been undertaken at this laboratory. It is hoped that the study of the chemical treatment of oil palm wastes will also contribute to information on waste treatment. In this report some findings on the acid treatment of oil palm wastes are presented.

MATERIALS AND METHODS

Fresh mesocarp fibre wastes and and sludge were obtained from Kilang Kelapa Sawit Lee Chin Cheng, Dengkil, Selangor. The fibre wastes were sun-dried upon arrival from the mill and used

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without prior grinding. The sludge was separated from its fatty residue before use in these experiments.

Common table salt was used. AR Grade Chloroform was used for all extractions and sample dilutions. In monitoring furfural production the UV absorption at λ max = 276.0nm (Madden, 1971) was measured using an Hitachi model 200–20. The Infrared (IR) Spectra of the purified products were obtained using an Acculab 3 IR Spectrometer. The absorption at 1601 cm^{-1} was used as the callibrating band. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WP.80 NMR instrument with tetramethylsilane (TMS) used as the internal standard (0.0ppm). All acid concentrations used are presented in terms of weight/weight.

The continuous extraction apparatus shown in *Figure 1* was used in all of these procedures.

Production of Furfural from Oil Palm Mesocarp Fibre

In all of these experiments, approximately 100 g of mesocarp fibre was weighed and transferred into a single-neck, round bottomed flask. The acid catalyst (100 ml) and salt (400 g) were then added and the flask was heated to boiling (120°C). Chloroform (25 ml) was then introduced into the extraction chamber on the side-arm of the modified Dean Stark trap. The chloroform was drained into a sample bottle at one hour intervals and the U.V. absorption readings were taken after the experiment was completed.

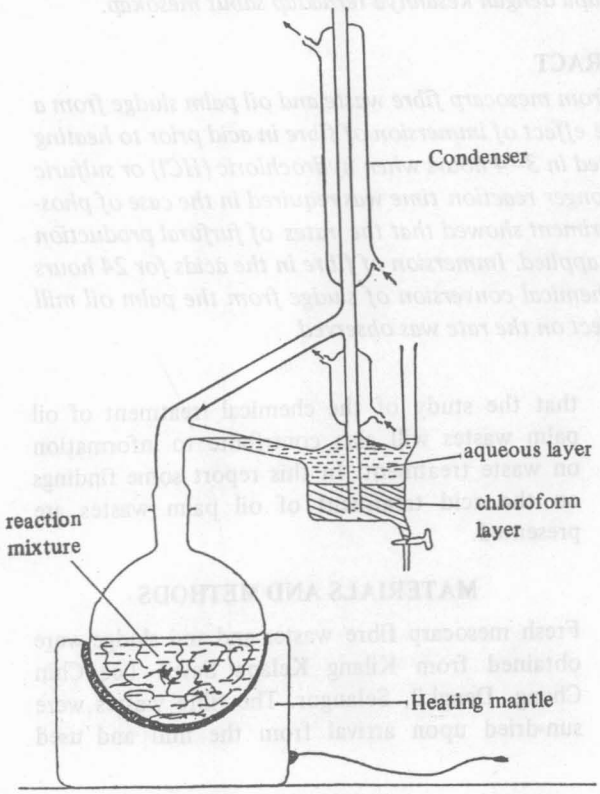

Fig. 1. Reaction apparatus for the production of furfural

The yield of furfural was obtained by combining all the extracts and then concentrating under reduced pressure. The crude product was later distilled under reduced pressure and the liquid evaporated at 64–68°C (15–17 mmHg) was collected (CRC Handbook of Chemistry and Physics, 1980; b.p. 90°C (165 mmHg)). The IR and NMR spectral analyses were consistent with the expected furfural (Grassell, 1971). IR NaCl; μ max 3130, 2840, 2800, 2760, 1690, 1570, 1460, 1390, 930, 830 cm^{-1}. NMR CCl_4; δ (ppm); 9.9 (1H, s), 7.8 (1H, s), 7.4 (1H, d), 6.8 (1H, m).

Production of Furfural from Pre-immersed Oil Palm Mesocarp Fibre

In a similar manner as above, approximately 100 g of dried mesocarp fibre was weighed and transferred into a 2 L single-neck, round bottomed flask. The flask was then filled with 1 L of sulfuric acid to immerse the fibre. After immersing the fibre for specific lengths of time, 400 g of salt was added and the heating was commenced (120°C). Collection of chloroform extracts at hourly intervals was also carried out in this experiment and the adsorption was measured upon completion of four collections.

The previously described procedure was employed to obtain the yields of furfural in each experiment.

Production of Furfural from Oil Palm Sludge

For these experiments, 1000 ml of the sludge was poured into a 2L, single-neck, round bottomed flask. Concentrated acid was later added into the liquid to make the desired concentration. After adding 400 g of salt, the flask was fitted with the extraction apparatus and the heating commenced (120°C). As in the previous experiments, the collection of chloroform extracts was at hourly intervals.

The yield of each experiment was obtained as previously described.

RESULTS AND DISCUSSION

Production of furfural from oil plam mesocarp fibre wastes was studied using four different acids as catalysts. The progress of product formation was monitored for each acid at three acid concentrations. By plotting the total U.V. absorptions versus time, the progress of furfural production was followed as shown in *Figure 2**. Comparison of the plots in this figure showed that the production of furfural was complete in three to four hours when using hydrochloric or sulfuric acids as the catalyst whereas a longer time was required in the case of phosphoric or oxalic acids. In addition, the experiment also showed that the reaction rates were increased by increasing the acid concentration. Similar results were also observed in the hydrolysis of padi husks (Nordin *et al.*, 1984) and other agrowastes (Villar *et al.*, 1984, Barale *et al.*, 1982, Scott *et al.*, 1983).

The use of phosphoric acid in this experiment did not give a complete conversion even at 15% concentration and for oxalic acid, the reaction was complete only when 15% acid concentration was used. It is possible that these acids were too weak to effect the complete reaction at lower concentrations in the time allowed.

The yield of furfural in each experiment is presented in Table 1. The best yield was obtained using either hydrochloric or sulfuric acids at 10% concentration. Even though a higher acid concentration shortened the reaction time, it failed to increase product yields. These results have also

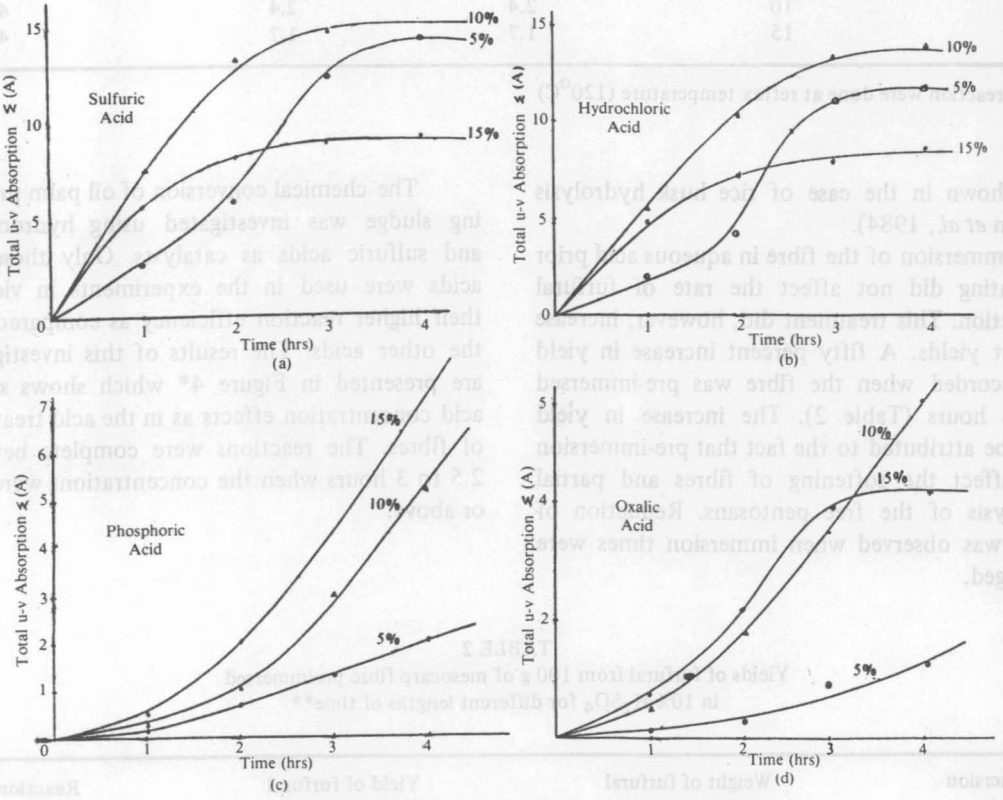

Fig. 2. Plots of the total u-v absorption versus time for oil palm mesocarp fibre using a) H_2SO_4 b) HCl c) H_3PO_4 and d) $(COOH)_2$ at 5, 10 and 15% concentrations.

*It should be noted that the total absorption was measured at different dilution factors, thus the total absorption should not reflect the real concentration of product.

TABLE 1
Yields of furfural from 100 g mesocarp fibre using various acids at 5, 10 and 15% concentration**

Acid	Acid concentration %	Weight of furfural (g)	Yield of furfural %	Reaction time (hrs)
HCl	5	4.0	4.0	4
	10	5.9	5.9	4
	15	3.1	3.1	4
H_2SO_4	5	4.9	4.9	4
	10	6.3	6.3	4
	15	4.2	4.2	4
H_3PO_4	5	0.9	0.9	4
	10	2.1	2.0	4
	15	2.6	2.6	4
$(COOH)_2$	5	1.7	1.7	4
	10	2.4	2.4	4
	15	1.7	1.7	4

** The reaction were done at reflux temperature (120°C)

been shown in the case of rice husk hydrolysis (Nordin *et al.*, 1984).

Immersion of the fibre in aqueous acid prior to heating did not affect the rate of furfural production. This treatment did, however, increase product yields. A fifty percent increase in yield was recorded when the fibre was pre-immersed for 24 hours (Table 2). The increase in yield could be attributed to the fact that pre-immersion may affect the softening of fibres and partial hydrolysis of the free pentosans. Reduction of yields was observed when immersion times were prolonged.

The chemical conversion of oil palm processing sludge was investigated using hydrochloric and sulfuric acids as catalysts. Only these two acids were used in the experiments in view of their higher reaction efficiency as compared with the other acids. The results of this investigation are presented in Figure 4* which shows similar acid concentration effects as in the acid treatment of fibres. The reactions were complete between 2.5 to 3 hours when the concentrations were 10% or above.

TABLE 2
Yields of furfural from 100 g of mesocarp fibre preimmersed in 10% H_2SO_4 for different lengths of time**

Preimmersion (hrs.)	Weight of furfural (g)	Yield of furfural (%)	Reaction time (hrs.)
12	8.7	8.7	4
24	9.4	9.4	4
72	7.0	7.0	4
360	6.3	6.3	4

** The reactions were done at reflux temperature (120°C)

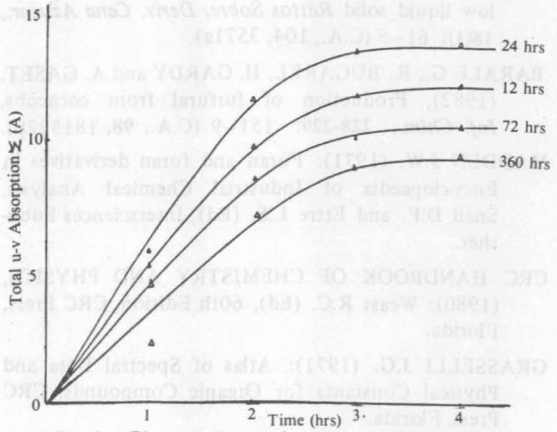

Fig. 3. Plots of the total u-v absorption versus time for preimmersion experiment using H_2SO_4 as catalyst.

Though higher acid concentrations have allowed the shorter reaction times, lower yields were obtained for both catalysts. The yields are shown in Table 3. The best yield of furfural was obtained when 5% sulfuric acid was used.

CONCLUSION

This investigation showed that furfural can be produced from the mesocarp fibre wastes and sludge from oil palm processing plants. Whereas a 10% acid concentration effected the most efficient production from fibre, a 5% acid concentration is more appropriate for the treatment of sludge. A slightly better yield of furfural was shown using sulfuric acid as catalyst. It is also noteworthy that preimmersion of fibre resulted in a large increase in product yields. Further work should be done on preimmersion.

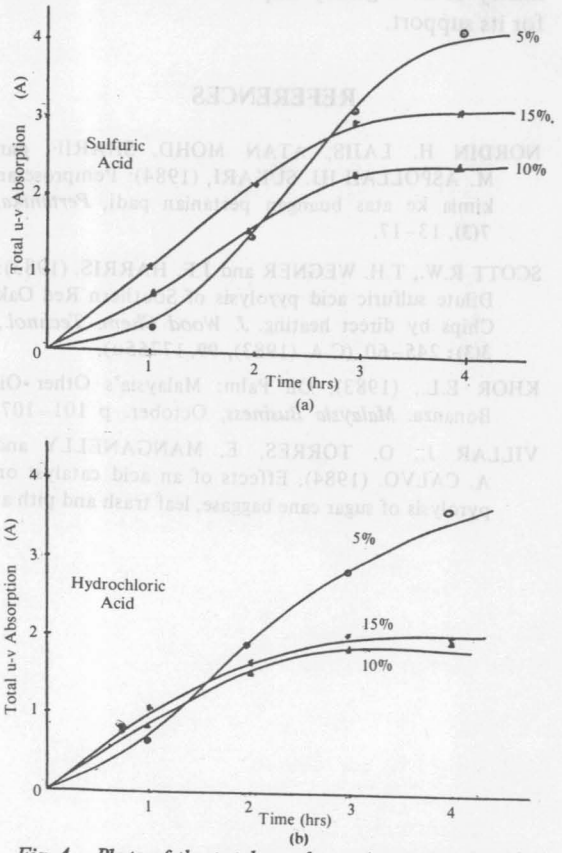

Fig. 4. Plots of the total u-v absorption versus time for 1000 ml palm oil sludge using a) H_2SO_4 and b) HCl at 10 and 15% concentrations.

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TABLE 3
Yields of furfural from 1000 ml of palm oil sludge**

Acid	Acid concentration %	Weight of furfural (g)	Reaction time (hrs.)
H_2SO_4	5	2.5	4
	10	1.6	4
	15	1.5	4
HCl	5	2.0	4
	10	1.2	4
	15	1.2	4

** The reaction were done at reflux temperature (120°C)

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