Catalytic Vapor-Phase Oxidation of FATTY OILS

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The combined thermal decomposition and catalytic vapor-phase oxidation of fatty oils in a one-step process presents many technical difficulties which prevent high conversions. The optimum conversion of red oil to maleic acid was 24.2 mole per cent at 425° C. and a space velocity of 28 reciprocal hours. The glycerides (sardine and soybean oils) gave much smaller conversions and caused considerable fouling of the catalyst because of premature ignition. These results indicate that, to obtain maximum conversion of maleic anhydride from unsaturated acids, the acid should be capable of vaporization without appreciable decomposition. The glycerides are even less suitable for this reaction than the acids themselves.

IN RECENT years the manufacture of dibasic acids has become extremely important, chiefly because of the increasing demands of the plastics and solvent industries. Any process which will produce a cheap dibasic acid is therefore of great interest to industry. One of the cheapest dibasic acids that may be made from a wide variety of raw materials is maleic acid (or maleic anhydride). At present it is produced chiefly as the by-product of phthalic anhydride manufacture and by the catalytic oxidation of benzene and of butane-butene mixtures.

The patent literature and technical publications show that it can be produced from practically any organic compound, other than paraffin hydrocarbons, containing at least four carbons in a straight chain and capable of being vaporized as such. Among the most satisfactory compounds from the standpoint of conversion are the unsaturated acids, such as crotonic (*1*), and the pentenoic acids (*4*). These, of course, are too expensive to be considered as industrial raw materials. In normal times the cheapest related compounds, although of high molecular weight, are the fatty oils. They are not easily vaporizable as such, but it was thought that by mild pyrolysis these oils might yield vapors suitable for vapor-phase oxidation. Economic considerations demanded that the pyrolysis and oxidation take place in a series of steps rather than in two separate steps.

In the work reported here, a study was made of the effect of different variables upon the production of maleic anhydride from three representative oils: red oil, sardine oil, and soybean oil.

OXIDATION EQUIPMENT

Equipment was designed for the process by means of which pyrolysis and oxidation could both be effected in one pass through the apparatus (Figure 1). It consisted essentially of an air preheater, a vaporization chamber, and a converter (all constructed of ordinary black steel pipe), followed by the usual type of glass product-recovery system. Dry metered air was preheated by passing it over heated chromel resistance wire and then led into the vaporizer, where it came in contact with an oil spray from a Monel metal atomizer. The heated air caused the oil to decompose sufficiently for vaporization. The resulting mixture of cracked oil vapor and air was then passed in downward flow over a vanadium pentoxide catalyst deposited on Alfrax pellets in the converter. The converter temperature was controlled by a bath of boiling mercury which surrounded it. The boiling point of the mercury was controlled by pressure exerted upon it from a tank of carbon dioxide.

PRODUCT ANALYSIS AND CATALYST PREPARATION

The solid and soluble products of oxidation were removed from the gases leaving the converter by cooling and water absorption. In this way all maleic anhydride, unreacted oil, and soluble products were recovered. Maleic acid was determined by the barium maleate monohydrate method (*3*), other acids by titration with 0.1 *N* sodium hydroxide, and aldehydes by the neutral sodium sulfite method (*5*).

The carbon dioxide in a portion of the exhaust gases was absorbed in a barium hydroxide solution, from which the precipitated barium carbonate was determined by conversion to barium sulfate in the usual manner.

The catalyst was prepared by adding an oxalic acid solution to a solution of ammonium metavanadate in the presence of Alfrax pellets, $^3/_{16}$ inch long and $^3/_{16}$ inch in diameter. The resulting mixture was evaporated to dryness and placed in the converter where dry air was passed over it for 7 hours at 450° C. The resulting catalyst was then used in an actual vapor-phase oxidation process for 6 hours at 375–450° C. before data were taken. In this manner the early abnormal behavior of the catalyst was avoided. The actual runs usually lasted 6 hours.

The ammonium metavanadate was C. P. grade furnished by the Vanadium Corporation of America. The Alfrax pellets were commercial grade (alkalinity less than 0.0002 per cent calculated as Na_2O). After activation the catalyst contained 12.4 per cent vanadium oxides by weight.

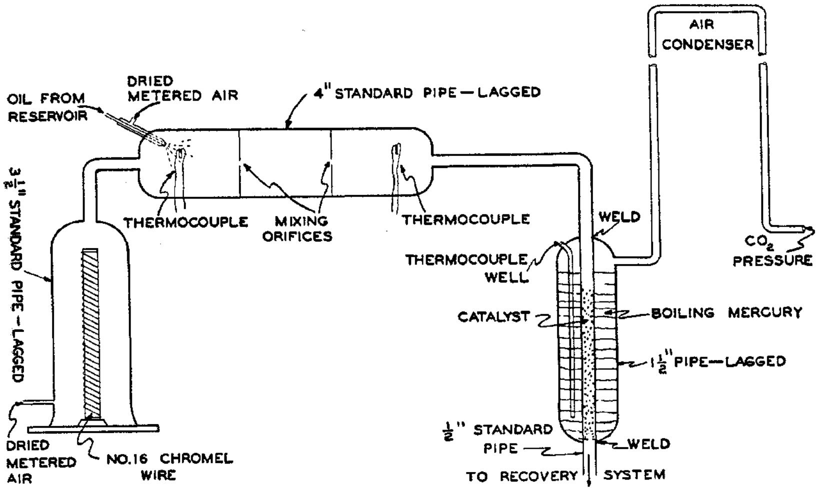

Figure 1. Apparatus for Catalytic Vapor-Phase Oxidation of Fatty Oils

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CATALYTIC OXIDATION OF RED OIL

The red oil was a purified grade similar to U.S.P. oleic acid. The effects of temperature and space velocity were the chief variables studied. The molar air-oil ratio was never less than 364 to 1, and in one run was as high as 920 to 1. Usually the ratio was in the neighborhood of 500 to 1. In previous runs with other materials (*2*) it was found that variations in this ratio, particularly in these high values, had little effect on conversions. Accordingly, no effort was made to control the ratio.

Data and results for a typical run are as follows:

Red oil vaporized, grams (lb.)	376 (0.828)
Time of run, hr.	6
Temp. of boiling Hg in converter, ° C.	425
Flow of primary air, lb./hr.	5.4
Flow of secondary air, lb./hr.	2.0
Molar ratio, air to oil	520
Weight ratio, air to oil	53.7
Vaporization temp. in mixer, ° C.	275
Temp. of gases leaving mixer, ° C.	250
Pressure in mixing chamber, lb./sq. in. gage	3
Mixture passed over catalyst (remainder by-passed), %	54.5
Red oil passed over catalyst, grams (lb.)	205.0 (0.45)
Length of catalyst, in.	19
Vol. of catalyst, cu. in. (cu. ft.)	5.77 (0.00334)
Space velocity, cu. ft. oil vapor/hr./cu. ft. catalyst	28.8
Maleic acid obtained (by analysis), grams	20.5
CO_2 obtained (by analysis), grams	87
Aldehydes obtained (by analysis), gram mole	0.252

Conversion	*Mole %*	*Weight %*
Maleic acid	24.2	10.0
Carbon dioxide	271	42.4
Aldehydes	34.4	..

Effect of Temperature. The influence of temperature on the catalytic oxidation of red oil is shown in Figure 2 for three different space velocities. The highest conversion of oleic acid to maleic acid was 24.2 mole per cent at 425° C. and a space velocity of 28 reciprocal hours[3]. This was the lowest space velocity used. At the higher space velocities, the optimum temperatures were not reached because of the excessive pressure necessary to raise the boiling point of the mercury above 525° C. Extrapolation of the high space velocity curves, however, indicates that the maximum conversions at higher temperatures would be less than that shown above.

The conversions to carbon dioxide were generally above 300 mole per cent, and varied with temperature and space velocity in approximately the same manner as in other catalytic vapor-phase oxidations.

Aldehyde conversions were generally in the neighborhood of 30 mole per cent, except at low times of contact when conversions were less.

Table I. Catalytic Oxidation of Fatty Oils

Oil	Catalyst[a] Temp., ° C.	Space Velocity, Reciprocal Hr.	Molar Air-Oil Ratio	Moles Products/Mole Oil		
				Maleic acid	CO_2	Aldehydes
Sardine	380	22.4	2030	0.11	2.71	0.18
	425	26.6	1400	0.11	0.60	0.12
	450	27.6	1565	0.07	..	0.17
Soybean	380	28.8	1030	0.03	1.53	0.02
	425	29.4	1000	0.04	0.79	0.01
	450	26.6	1100	0.02	0.27	0.01
Red	375	41.9	393	0.20	1.47	0.30
	425	28.8	565	0.24	2.71	0.34
	450	29.3	568	0.20	3.07	0.35

[a] Actually the temperature of the mercury surrounding the catalyst tube. Temperatures in pyrolytic chamber: sardine oil 260–300°, soybean oil 230–290°, red oil 230–275° C.

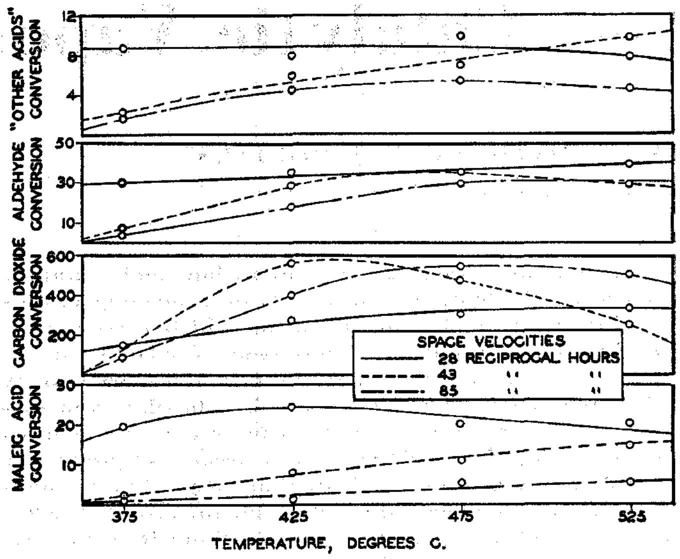

Figure 2. Catalytic Vapor-Phase Oxidation of Red Oil (Mole Per Cent Conversion *vs.* Temperature)

Unreacted oleic acid and acids other than maleic, formed either in the pyrolytic or oxidation reaction, were never present in amounts greatly exceeding molar conversions of 8 per cent.

Effect of Space Velocity. A study of the curves in Figure 2 indicates that, at low temperatures, low space velocities were most favorable to maleic acid production. At higher reaction temperatures, an optimum space velocity existed.

Preliminary Pyrolysis. Considerable difficulty was encountered in controlling the preliminary pyrolysis. If the temperature in the pyrolytic chamber was allowed to fall below about 230° C., incomplete vaporization resulted and liquid formed in the chamber. When the temperature of pyrolysis rose above 280° C., carbon was formed during the thermal decomposition with subsequent fouling of the catalyst. Slightly above 280° C. the gases would ignite and burn. It is probable that in no case did complete vaporization take place, since fog was present in the exhaust gases from all runs. Pyrolysis of a portion of this fog undoubtedly took place in the converter, inasmuch as the fog became less dense as the oxidation temperature increased.

OXIDATION OF GLYCERIDES

For comparison, runs were also made on a West Coast sardine oil (iodine number 188) and a technical grade of soybean oil (iodine number 133). Table I shows the results obtained on these oils in a series of runs comparable to those made with red oil. Figures for the oxidation of red oil are included for comparison.

Conversions using the glycerides did not approach those using red oil, and operating difficulties were considerably greater. The temperature range that could be used in the vaporizer was limited, and in every case unvaporized liquid was found in the vaporizer at the end of the run. All attempts to raise the vaporization temperature resulted in the formation of carbon and a viscous semisolid, part of which was carried into the catalyst chamber. If anything, the soybean oil was more difficult to handle than the sardine oil.

LITERATURE CITED

(1) Drossbach, Otto, U. S. Patent 1,880,991 (Oct. 4, 1932).
(2) Faith, W. L., and Dendurent, M. S., *Refiner Natural Gasoline Mfr.*, 18, 393–6 (1939).
(3) Faith, W. L., and Schaible, A. M., *J. Am. Chem. Soc.*, 60, 52–4 (1938).
(4) Faith, W. L., and Yantzi, M. F., *Ibid.*, 60, 1988–9 (1938).
(5) Kingscott, P. C. R., and Knight, K. S. G., "Methods of Quantitative Organic Analysis", p. 245, New York, Longmans, Green and Co., 1914.

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[3] Space velocity was calculated as cubic feet of oil (assumed to be uncracked vapor) at standard conditions per hour per cubic foot of catalyst (reciprocal hours). It was varied by varying the amount of catalyst in the converter.