At 480°C., a conversion of 18.99% to total water soluble acids, 13.29% to maleic acid, 4.70% to aldehyde and 2.47% to quinone is obtained with the fused V₂O₅ catalyst at space velocity 5680 and air:xylene ratio 262 (Table 27). The conversion to water soluble acids is more at lower air:xylene ratios.

A comparison of these values with the results reported by Parks and Allard⁵⁵ shows that the conversion to total acids obtained in the present investigation are more both for the fused and unfused catalysts. These authors reported a maximum conversion of 18.2% to total acids at 530°C. with the alfacx supported unfused V₂O₅ catalyst, while with unsupported granular fused V₂O₅, they got a conversion of only 9.8% at 510°C. The air:xylene ratio employed by these workers was, however, quite low and the exact composition of their xylene mixture is not known.
SUMMARY

OXIDATION OF XYLENES

The first part of this thesis deals with the catalytic vapour phase oxidation of ortho, para and meta xylene, individually using air (and in some cases oxygen also) as the oxidising gas. The reaction products formed on the oxidation of each of these xylene over typical oxidation catalysts have been identified and estimated. The three oxidation reactions have been studied, over a series of catalysts comprising mainly of oxides of vanadium, molybdenum or cobalt either alone or in conjunction with each other. In each case, experiments have been conducted under different reaction conditions to assess the potentiality of each catalyst and determine the optimum working conditions for particular desired end product.

The chief products of oxidation of ortho xylene are phthalic and maleic anhydrides. A comparative study made with single catalysts containing oxides of vanadium, cobalt, molybdenum or vanadates of tin, silver or copper showed that for the oxidation of ortho xylene to phthalic anhydride, the catalyst containing oxides of vanadium has the highest activity. As a catalyst support, kieselguhr was found to be superior to silica gel and a concentration of 31.01% of $V_2O_5$ on the weight of kieselguhr was found to be optimum.

The activity of vanadium pentoxide-kieselguhr catalyst is notably affected by the addition of oxides of molybdenum, cobalt, uranium or curium, though in most cases the addition of a promoter makes the catalyst so highly active that the oxidation to maleic anhydride increases appreciably. A catalyst containing both cobalt oxide and molybdenum oxide as promoters for the $V_2O_5$ was found to be quite active and gave high space-time-yields of phthalic anhydride.
The vanadium oxide catalysts, heated to fusion temperature of V₂O₅ were found to give higher conversion of ortho xylene to phthalic anhydride than the unfused catalysts. With the fused catalysts, the conversion to phthalic anhydride is greater by about 15-18% and the selectivity is also higher. The working temperature for these catalysts is about 100°C more than in case of unfused catalysts, but there is no excessive rise of the catalyst bed temperature during the reaction. With ortho xylene, the unsupported fused V₂O₅ catalyst gave a conversion of 61.73% per pass to phthalic anhydride and 9.57% to maleic anhydride, while with a pumice supported fused catalyst, 51.8% and 9.31% conversions, to phthalic and maleic anhydrides respectively, were obtained. Fused catalysts supported on kieselguhr or silica gel gave lesser yields and the incorporation of cobalt oxide with the fused catalyst did not improve its activity. No loss in the activity of pumice supported fused catalyst was noticed on use for about one month. The process yield of phthalic anhydride obtained with this catalyst was 72.31%, while the space-time-yield was 84.76 gm./hr./l.

Another distinct advantage of the fused catalysts is that the complete oxidation to carbon dioxide is about 8% less than obtained with the unfused catalysts. Employing oxygen in place of air, space-time-yields as high as 190 gm./hr./l. could be obtained keeping the conversion and selectivity practically the same as with air.

Para xylene does not undergo oxidation in the vapour phase in a way similar to the oxidation of ortho xylene. Para toluic aldehyde, maleic anhydride and carbon dioxide were the main products of catalytic oxidation of para xylene. Besides these, small amounts of terephthalic acid, p-toluic acid and benzquinone were also formed. The conversions to terephthalic acid and p-toluic acid were just about 1% each with the various catalysts studied. The vanadates of silver and tin had very little activity for the oxidation of para xylene, while vanadium oxide catalysts gave good conversion to maleic anhydride.
The behaviour of the meta xylene was similar to that of the para isomer. The vapour phase oxidation employing catalysts containing oxides of vanadium, molybdenum and cobalt gave mainly maleic anhydride, \( \alpha \)-toluic aldehyde and carbon dioxide. Small quantities of quinone were also formed. Isophthalic acid was found in the reaction products in some of the experiments. The conversion to maleic anhydride was about 20–22%.

The oxidation of mixed xylenes (ortho 30%, para 20% and meta 50%) gave mainly aldehydes and maleic anhydride. About 18–20% of the xylenes passed were converted to maleic anhydride, while the total conversion to all water-soluble acids was 22–25%.