

catalysts could not retain their activities more than 15—20 hrs. and their industrial application would be impossible. (H. Shingu, T. Tsuchihara: Reports of the Institute for Chemical Research, Kyoto University, 18, 65 (1949)).

We studied further the catalytic dehydrogenation of aliphatic primary alcohol by passing the gaseous mixture of air and isoamyl, octyl and lauryl alcohol respectively over a copper gauze catalyst activated by silver, and the catalyst was found to be effective for a long duration and prospective for the industrial application. Upon the investigation of the influence of air-alcohol ratio, space velocity of the alcohol, the reaction temperature and the life of the catalyst, we obtained the best results when the alcohol and the air, the amount of the latter being 80—100% of that quantity necessary for the oxidation of the alcohol to the corresponding aldehyde, were passed over the catalyst at 340°—360°C. Generally speaking, the space velocity of the alcohol were found to influence little on the yield of aldehyde, within the range of our experiment (0.30—0.98/cc. hr.), only a slight decrease of yield was observed at the large space velocity. In the optimal conditions the conversion of isoamyl-alcohol was 55.3 mol%, the yield of aldehyde 44.0 mol % of the theoretical value based upon the amount of alcohol passed over the catalyst, or the selectivity for the aldehyde production 82.7%, and the yield of high boiling products 5.8% by weight. The catalyst retained its activity unchanged after the use for 55 hrs.

We confirmed further that this method, being conducted under reduced pressure, was as much effective for the octyl and lauryl alcohol as for the isoamyl alcohol as described above.

66. Study on the Preparation of Vanillin from Lignin.

Yusaku Fukuda.

The purpose of this study is to clarify the theory of kraft pulping process as well as the practical problem of obtaining vanillin from waste lignin.

Alkali lignin and thiolignin were oxidized by heating with nitrobenzene in the presence of caustic alkali under the conditions as suggested by Freudenberg and the yield of vanillin from two sorts of lignin were compared with each other.

About 15 g of alkali lignin prepared from wood powder of red pine, was heated for 3 hrs. at 160°C with nitrobenzene (35 cc) and 2N-NaOH solution (600 cc) in an autoclave. After removal of excessive nitrobenzene and aniline by means of steam distillation, the reaction mixture was extracted with ether repeatedly. Vanillin in the extract was determined by converting it into *m*-nitrobenzohydrazone.

The yield of vanillin was found to be 10.5% based upon the lignin used in

average for five experiments repeated. This figure is lower than that obtained by Freudenberg (20–25%). It was found, however, that vanillin once produced was decomposed under the condition of oxidation of lignin, and only about 55% of vanillin was actually recovered from reaction mixture. Therefore, the total yield of vanillin from alkali lignin might be accounted to be about 20%.

On the other hand, the thioglignin which was obtained from meal of red pine by cooking with NaSH has resulted in giving a smaller yield of vanillin amounting in average to 6.61%.

The sulfur content of the thioglignin prepared by us is 5.71%. If the elementary composition of lignin is assumed to be C 65%, H 6%, and OCH_3 15%, the sulphur content of the thioglignin as mentioned corresponds to the atomic ratio of 1 S to 30 C. In other words, it results that one sulfur atom is combined with every three building units of lignin ( c.c.c). If the sulfur atom or its radical hinders the formation of vanillin from lignin by any means, the yield of vanillin from the thioglignin should be $\frac{2}{3}$ the yield from alkali lignin, namely about 7%. The actual yield obtained by us, that is 6.61% agrees fairly good with this.

We are now investigating the chemical nature of the combined sulfur atom in the lignin molecule.

67. Studies on Biocatalyses. (XI)

On the Absorption of Carbon Dioxide by Plant.

Kinsuke Kondo, Shigeki Mori and Fumio Kawai.

In the previous paper (This Report 18, 33 (1949); 19, 68, 69 (1949)) we reported the presence and distribution of carbonic anhydrase in various plants. In this paper we mention on the nature of the enzyme relating to carbon dioxide absorption by plant. The enzyme was prepared from pepper plant leaves, the material was ground and the juice was pressed out, after separating chloroplasts by centrifuge, the supernatant liquor was purified by adsorption with kieselguhr and elution was repeated by the cake with sodium phosphate buffer, pH 7.2.

The enzyme solution thus prepared has the activity of carbonic anhydrase causing decomposition of substrate, bicarbonate, but no potency of absorption of carbon dioxide, while on adding minute amount of histidine or other $-\text{NH}$ compound it catalysed the absorption of carbon dioxide strongly. In the second experiment we have ascertained that carbon dioxide absorption is catalysed by the enzyme on adding chlorophyll b. The added chlorophyll b was isolated from the same plant material.