Kolbe electrolysis also called as kolbe reaction is an organic reaction named after German chemist Adolph Wilhelm Hermann Kolbe.

This reaction is a electrochemical decarboxylation of the salts of carboxylic acid which produces radicals. This reaction is also called as decarboxylative dimerisation, since it proceeds with radical reaction mechanism. This reaction is used in synthesis of symmetrical dimers. It can also be employed for a mixture of carboxylic acid in order to furnish unsymmetrical dimers.

For example, consider the following reaction

 $\begin{array}{cccc} \text{RCOONa} & \longrightarrow & \text{RCOO}^- + \text{Na}^+ \\ \hline \text{Reaction at Anode} \\ \text{R}-\text{C}-\text{O}^- & \stackrel{-\text{e}}{\longrightarrow} & \text{R} \stackrel{>}{\underset{\scriptstyle \bigcup}{\overset{\scriptstyle \end{array}}{\overset{\scriptstyle \end{array}}}}}}}}}}}}}}}}}}}}}}}}}}}}} } \\ \end{array}}$

Free radicals always undergo disproportionation or auto oxidation and dimerization. Because of these reaction in kolbe electrolysis, the mixture of hydrocarbons are formed.