

A Review of Acetol: Application and Production

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Abstract: Problem statement: Acetol is used as organic intermediates because it contains both hydroxyl and carbonyl functional groups and mainly use to produce polyols and acrolein. It also widely uses as reduced dyes and skin tanning agent. The commercially used acetol is made from petroleum-based that leads to high cost of production. **Approach:** This review highlighted applications of acetol and established methods and factors affecting acetol selectivity. Global market of acetol and its contribution in Malaysia were also surveyed. **Results:** Multiple ways which was through dehydration of glycerol or dehydrogenation of polyols and sugar alcohols could be applied to produce acetol. **Conclusion:** The approach using glycerol as feedstock since its economic viable in the presence of metal supported acidic catalyst is the very promising and reliable because it's high conversion and selectivity. The production under optimum conditions still remained as an open challenge to all researchers.

Key words: Dehydrogenation process, glycerol, acetol, propylene glycol, molecular catalysis, economic viable, both hydroxyl, dehydrogenating catalyst, methyl alcohol

INTRODUCTION

Acetol is a ketone compound which is also known as hydroxyacetone. Its IUPAC name is 1-hydroxy-2-propanone. Acetol is extremely reactive as it contains both hydroxyl and carbonyl functional groups. It is hygroscopic and miscible with ethanol and ethyl ether. The first synthesis of acetol has been made by reacting bromoacetone and sodium or potassium formate or acetate, followed by hydrolysis of the ester by methyl alcohol. Treatment of glycerol or propylene glycol at 200°C to 300°C with a dehydrogenating catalyst leads to the formation of acetol, while the direct oxidation of acetone with Bayer and Villager's acetone-peroxide reagent produces acetol together with pyruvic acid.

Reportedly, acetol plays a role as an organic synthesis intermediates or starting materials. It is widely used in the industries as the structure of acetol itself can promote variety of reaction including dehydration, hydrogenation, oxidation and polymerization (Dasari *et al.*, 2005). Acetol is mainly used to produce products such as propylene glycol via hydrogenation reaction and acrolein through dehydration. It is also used to synthesize compounds such as propionaldehyde, acetone and furan derivatives.

In food industry, acetol has been extensively used to give aroma to foods. It gives strong odour to the bread which is almost identical to proline, valine and isoleucine i.e. constituents that are frequently used as bread flavors. Moreover, it is also used to induce flavor compounds in heated milk. The taste of acetol is characterized by many descriptors depending upon the medium. In aqueous solutions, acetol is described as sweet and roasted. In contrast, acetol is described as yogurt-like in emulsions. Acetol is formed as the product of carbohydrate fragmentation or degradation that occurs during nonenzymatic browning reactions or known as the Maillard Reaction.

Meanwhile in textile industry, acetol can be used as a substitute to sodium dithionite which is usually used to reduce dye to a water soluble compound. Usually in textile industry, vat dyes are used to give color as it is water insoluble and generally based around anthraquinone or indigo. As the dyes displayed excellent color fastness and UV stability, they are often used for fabrics that must withstand frequent, harsh washing such as military uniforms and hospital textiles or those continuously exposed to daylight such as furnishings. However as the dyes are water insoluble, redox chemistry need to be employed to allow fixation in which the dye stuff is initially reduced to a water

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soluble compound using sodium dithionite, but this has results in sulphur salts in the waste water (Lacasse and Baumann, 2004). In order to overcome this problem acetol can be used as a substitute, though there is some limitation as it can only reduce some of the dyes.

Apart from that, acetol is also used as main constituent of skin tanning agent in cosmetic industry (Pathak, 2005) as well as to provide expedient access to both natural carbohydrates and unnatural polyhydroxylated molecules of significance in medicine. For a long time, the direct catalytic asymmetric aldol reaction of α -hydroxylated ketones with aldehydes had only been achieved with protein-catalysts such as aldolases and catalytic antibodies (Machajewski and Wong, 2000).

Conversion of glycerol to acetol: The production of acetol from glycerol is greatly influenced by the presence of catalyst. The most famous catalyst used in the production of acetol from glycerol is the metal supported acidic catalyst. This phenomenon maybe due to the acidic catalysts favours the elimination reaction while the transition metal catalyst involves in promoting the carbonylation reaction.

The acid-base properties of support materials play role in the selectivity of the acetol. According to Sato *et al.* (2008), the addition of acidic oxide support such as Al_2O_3 , ZrO_2 , Fe_2O_3 and SiO_2 to copper effectively promoted acetol selectivity while basic support shows low selectivity towards acetol. They study the production of acetol by using reduced and unreduced copper supported by aluminum oxide ($\text{Cu-Al}_2\text{O}_3$) catalyst in the presence of gaseous using fixed-bed down-flow glass reactor. In nitrogen flow, unreduced $\text{Cu-Al}_2\text{O}_3$ decreases the conversion and increases acetol selectivity with time on stream. Meanwhile when $\text{Cu-Al}_2\text{O}_3$ was subjected to hydrogen reduction, it is fully converted to glycerol and acetol selectivity increases with time on stream for the first 5 hours. In hydrogen flow, acetol selectivity decreases because 1,2-propanediol was produced during the hydrogenation of acetol over $\text{Cu-Al}_2\text{O}_3$ after reduction. At temperatures below 250°C , acetol selectivity was as high as 90 mol% while at 300°C , the catalyst was deactivated and the conversion decreases with time on stream. This indicates that the selective dehydration proceeds at temperatures below 250°C .

Based on a research reported by Suprun *et al.* (2009), acetol can be yielded in the presence of moderate acidic support catalyst, Fig. 1. In their preliminary work, several tests were performed with

selected catalysts at 280°C by using fixed-bed reactor. Pure alumina and titanium supports with low acidity showed a very low conversion of glycerol (10–15%) at 280°C . In contrast, the used of strong acidic support catalyst decreases the conversion of acetol and increases the yield of acrolein. They compared the catalysts reactivity of Al_2O_3 and TiO_2 supports by PO_4^- ions, Silico-Alumino-Phosphate-11 (SAPO) and SAPO-34. Based on the results, the optimum catalyst was found to be SAPO-11 with 70% glycerol conversion and 65% acetol selectivity while the least reactive catalyst was the SAPO-34 with 50% glycerol conversion and 50% acetol selectivity Research by Kinage *et al.* (2010) using continuous fixed-bed reactor with the presence of sodium-doped metal oxide catalysts. The selected metal oxide catalysts which are CeO_2 , Al_2O_3 , ZrO_2 and Ga_2O_3 were doped with 5% wt. of sodium. They found that the formation of acetol from glycerol need moderate acid-base site of catalyst. Catalyst with high basic site will leads to produce allyl alcohol while excess basic site give further cracking of acetol and form ethylene glycol as by-product. The results showed that the Na-doped CeO_2 gave highest selectivity of acetol (68.6%) followed by $\text{Na/Al}_2\text{O}_3$ (57.3%), Na/ZrO_2 (49.8%) and $\text{Na/Ga}_2\text{O}_3$ (35.2%).

A study by Chiu *et al.* (2006) has been carried out using reactive distillation operated in batch and semi-batch mode with the presence of copper-chromite catalyst. In their preliminary catalyst screening, they found that copper-chromite catalyst showed superior acetol selectivity compared to Ru, Pt, Pd and Ni catalysts. 90% acetol selectivity was achieved over copper-chromite catalyst at 240°C and 98 kPa. It's known that copper-chromite catalyst exhibit poor hydrogenolytic activity toward C-C bonds and efficient activity for C-O bond hydro-dehydrogenation. They continued their study by batch and semi-batch mode in order to obtain the optimum production of acetol and found that semi-batch mode increases glycerol conversion (92.71%) and acetol selectivity (90.62%). They concluded that catalytic conversion of glycerol to acetol via semi-batch reactive distillation exhibits higher yield, higher selectivity and lower-residue formation than batch due to the semi-batch operation has a higher catalyst loading to glycerol ratio in the reaction (Chiu *et al.*, 2006). However, they did not clarify the active species of copper although chromium seems to be the active species. In another work, the same catalyst was also used in their new approaches using vapor-phase and liquid-phase packed bed reactor. The vapor-phase packed bed reaction carried out in a stainless steel tube and the reactor packed with pellets

of copper-chromite catalyst. The study showed that vapor-phase packed bed reaction has higher glycerol conversion (22.1%) and higher acetol selectivity (61.99%) than liquid-phase packed bed reaction with 20.4% glycerol conversion and 29.90% acetol selectivity. They clarified that the residence time for the gas is much less than for the liquid. The density of the acetol is lower in the gas phase which dramatically reduces polymerization reactions that contributed to higher order reaction (Chiu *et al.*, 2008).

The conversion of glycerol to acetol also can be obtained without using acidic supported catalyst. This research has been done by Yamaguchi *et al.* (2010) using high-temperature liquid water in the presence of carbon dioxide at 573K. In the absence of carbon dioxide, the conversion of glycerol is reported to be as low as 40% with 0.5% acetol selectivity. The glycerol conversion increases from 40 to 50% by the addition of carbon dioxide and the acetol yield also increases from 0.5 to 1% at 1.5 hours by the addition of carbon dioxide. This indicates that carbon dioxide enhanced the yields of the solid substance and acetol. The increase in acetol yield can be explained by the increase in acidity of the solvent. This is due to the formation of carbonic acid when the carbon dioxide is dissolved in the high-temperature liquid water.

Acetol from other resources: Acetol also can be synthesized from propylene glycol via dehydrogenation process. However, this type of reaction is less popular reaction due to the minimal economic viability of the process. In prior work, Disselkamp *et al.* (2008) used aqueous propylene glycol and hydrogen peroxide with the presence of Pd-black catalyst under reflux conditions at 368K to synthesize acetol. Unfortunately, acetic acid was also found to be the second major products apart from a lesser abundant compound formed which was the lactic acid. From the study, it is seen that the yield of acetol is 38% and does not vary greatly with increasing addition of H₂O₂. It is proved that at 5 equivalents H₂O₂ a 65% conversion exists and acetol:acetic acid ratio of 2:1 is seen. The experiments also revealed that although the product distribution in chemistries is similar, the amount of reactive oxygen is greatly enhanced with co-addition of O₂/H₂O.

Research by Sato *et al.* (2008), showed that the dehydrogenation of 1,2-propanediol with the presence of Cu-Al₂O₃ catalyst at 250°C can be carried out using vapor-phase reaction. In this process, alcohols are dehydrogenated to form corresponding carbonyl compounds and copper is used as it is a well-known dehydrogenation catalyst. The dehydrogenation of 1,2-Propanediol has resulted in a 60.8% conversion and 71.3% acetol selectivity with a small amount of acetone (5.2%) and propanoic acid (2.2%) generated as by-products.

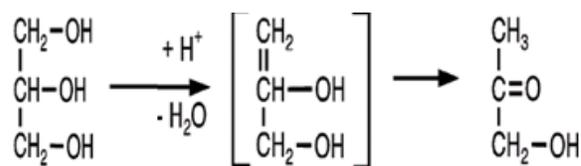


Fig. 1: Schematic suggested by Suprun *et al.* (2009) for dehydration of glycerol to acetol

From the prior research reported, acetol can be produced from C6 sugar such as glucose, sucrose and sorbitol. The synthesis of acetol from sugar using reactive distillation technique has been studied by Dasari (2006). In his study, the use of nickel-based catalyst has converted sorbitol to lower polyols with the selectivity's of C3 derivatives to be more than 80%. The C3 derivative consists of propylene glycol, glycerol and acetol. However, they did not state the selectivity of the products obtained. The reaction was performed at 230°C and 250 psi hydrogen pressure for 12 hours with the presence of 5% catalyst. The conversions of glucose and sucrose are nearly as effective as the use of sorbitol. Glycerol dissolves and stabilizes sorbitol in a manner much like water which consequently allows the reactions to be conducted without the presence of water. The preliminary results of the study illustrate that high selectivity for conversions of C6 feedstock can be maintained even at lower water contents. The yield remained high which was up to 75% sugar was found to be present in the water. This indicates a more effective use of reactor volumes at 75% sugar relative to 25% sugar. These findings have created opportunities to use reactive distillation for sorbitol conversion to achieve higher yields.

In earlier work by Yan (2008) they describe that acetol can be obtained from C6 sugar (sorbitol) under batch mode gas phase heterogeneous. They identified copper chromite as effective catalyst than palladium catalyst. The optimum conditions of the hydrogenolysis were at 290°C and 0.3 bar with 2.5% sorbitol aqueous feed. These conditions yielded a 25% acetol. The by-products such as acetone and 1-hydroxy-2-butanone were also formed in this process.

Industrial producer of acetol: United States is the major producer country of acetol since the technology was discovered by a group of local researchers in 2006. However, they exploited it as a building block to produce propylene glycol. The Senergy Chemical from U.S claims that the propylene glycol can be produced under novel conditions which are low temperature and low pressure. In this process, glycerol is initially catalytically converted into acetol and subsequently

hydrogenated into propylene glycol. The process is efficient, as it produces small to negligible amount of waste and it only generates a non-toxic chemical derived from a natural material. Senergy Chemical is a global license holder of this technology. The technology converting glycerol to propylene glycol was developed by researchers Suppes and Sutterlin at the University of Missouri in United States. In this technology hydrogen is used as a co-reagent to perform a hydrogenolysis conversion of glycerine, in the presence of a copper-chromite catalyst. Initially, water molecules are removed from the glycerine and this process is then followed by the addition of hydrogen molecules. This process yields two products which are acetol and propylene glycol as well as some water as by-product. According to Suppes, the formation of ethylene glycol in this process is undesirable because of its toxicity as well as every pound of ethylene glycol produced has resulted in the formation of another 0.5 pound of unwanted by-products (Special Report Chemical Processing, 2008).

Global market and local market of acetol: Biodiesel economics strongly depend on the market of glycerol and biodiesel's by-product generated from the transesterification of vegetable oils. To date, the U.S. biodiesel industry is expected to introduce 1 billion pounds of additional glycerol into the market exceeded the currently annual demand of only 600 million pounds. This has leads to the needs of finding a high-value use of glycerol. One of the solutions is to use propylene glycol (1,2-propanediol), a less toxic compound as an alternative to ethylene glycol in antifreeze production. Propylene glycol can be produced from glycerol and this can reduce the cost of biodiesel manufacturing to as much as \$0.40 per gallon. Dehydration of glycerol via catalytic reactive distillation offers a number of advantages, such as lower operating temperature and pressure, more efficient conversion and fewer by-products, compared to conventional conversion routes. The same technology also can be used to convert glycerol to acetol as intermediate followed by the production of polyols.

Acetol made from petroleum costs around USD 12.5 per kilogram while using biomass-sourced glycerol could cut production cost to as little as USD 1.25 per kilogram, opening up markets for glycerol and benefiting biodiesel production (Special Report Chemical Processing, 2008). Current market of acetol prices is USD 231.1 per kilogram in United States. The profit margins of acetol attract the industries mainly to invest in the production of acetol which has higher

selectivity to produce propylene glycol. It is because the production of propylene glycol from acetol comprising low costs of production.

Currently, Malaysian selling price of acetol is about MYR 853 per kilogram in 2009. The market price range of glycerol in Malaysia is about MYR 1204 to MYR 1273 per tonne. The theoretical maximum 100% yield of glycerol dehydration would be achieved if 1 kilogram of glycerol would form a maximum of 804 gram acetol. This means in every kilogram of glycerol which cost only MYR 1.20 could yield 0.8 kg of acetol that could sell MYR 682 in market if the condition is achieved. However, the estimation profit of production excluded processing cost which contains of catalyst and other resources.

CONCLUSION

Acetol could be obtained through multiple ways as described above but by referring to some reasons stated, the best method in producing acetol is by dehydration of glycerol as feedstock with the presence of metal supported acidic catalyst. Any new use of glycerol will increase it demands, therefore improve its economic value. Furthermore, it could help in lowering down the biodiesel production cost which had been a big issue as years goes by.

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