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1,4-ButaneDiol (BDO) synthesis by Cu-Chromite catalyzer

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Abstract
Cu-Chromite catalyzer is an important catalyzer in chemical reactions. Among reactions that act under this catalyzer can point variety of oxidation, hydrogenation reactions, dehydrogenation, alkylation, alcohols decomposition and other useful reactions in petroleum industries include: reforming. Recyclable is one of advantages of this catalyzer.1, 4-BDO can use as solvent in coatings. Also uses as primary material for producing tetra hydro Furan, polyButylene Terephthalate (PBT), gamma-Butyrolactone(GBL), polyurethane and other materials. This paper study the synthesis of this compound by Cu-Chromite nano catalyzer.

Keywords: nano Cu-Chromite, 1,4- ButaneDiol, catalyzer

Introduction
1,4-BDO is a colorless liquid with formulation of HOCH2CH2 CH2 CH2O. Other names of this compound are, 4-Butylen Glycol, 1,4-Di Hydroxide Butane, Butane Diol, 1,4-Tetra Methylene Glycol and Diol 14B [1]. 1,4-BDO could be used as solvent for coatings.
Physical and chemical properties of this compound showed in table 1.

Table 1: 1,4-BDO properties

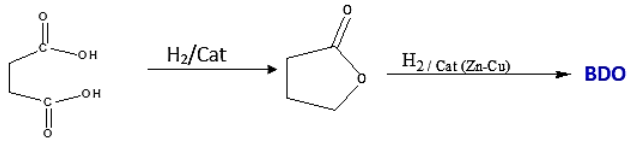
Property	Value and specification
Appearance	Colorless and viscous liquid
Molecular weight	90.12 g/mole
Melting point	19oc
Boiling point	230oc
Vapor density	3.1 g/cm3
Density	1.02 g/cm3
Flash point	121oc
Water solution ability	Aqueous
Vapor pressure	0.014 hpa in 25oc
Self-burning point	402.5oc

1-1 ,4-BDO synthesis methods
According to mentioned methods, BDO's synthesis methods can classify in to 4 groups:

1-2-Synthesis by Aldehyde and Acetylene as primary material
This method is industrial synthesis method of 1,4-BDO that acts in 3 steps [1]. In first step, Formaldehyde and Acetylene act together in presence of on organic catalyzer and synthesis 1,4-BDO. Next step, possible to perform on a small sample aliquot. The limit of quantification value in fish tissue was 0.083 mg g^{-1} and the limit of detection was 0.016 mg g^{-1}.
Acetylene-Diol reduce in presence of a reducer catalyzer like H2/Pd and convert to 1,4-BDO. Finally, the material is separated by distillation column.

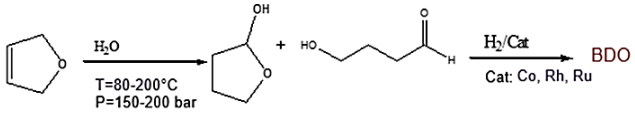
1-3-Synthesis by 4-carbon Di-Carboxylic acid or its derivations as primary material.
By this method, catalytic hydrogenation of 4-carbon Di-Carboxylic acid act in presence of Cu and Cr catalysts in gas phase that leads to synthesis of GBL. GBL converts to BDO in presence of Cu-Chromite catalyzer [2].

GBL vapor and water vapor and Hydrogen gas transition above the Cu-Zn catalyzer cause increasing efficiency.



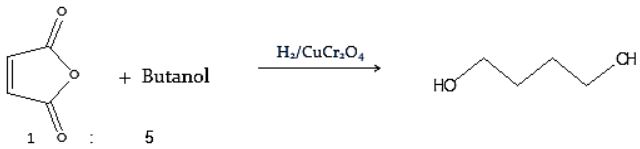
1-4-Synthesis by Di-Hydro Furan as primary material

By this method, 2,3- Di-Hydro Furan hydrogenate catalytic in presence of water and Hydrogen in 20-300oc and pressure of 1-300 bar in neutral or acidic conditions and mixture of 4-Hydroxi Butyr Aldehyde and Isomer of 2-Hydroxi Tetra Hydro Furan synthesized [3]. This productions in first step, convert to 1,4-BDO in presence of Hydrogen and Rhodium, Ruthenium and cobalt catalyzers with Phosphine or phosphide ligands.



1-5-Synthesis by Maleic Anhydride as primary material

By this method, a solution of Maleic anhydride converts to 1,4-BDO in presence of Mono-Hydric Aliphatic alcohol and catalyzer [4].This process is a single step process and temperature is 15-60oc.



So the conditions are

1. This process is a single process.
2. Reaction acts in room temperature and catalytic hydrogenation conditions. 3-Using single group alcohols cause increasing efficiency.

As the table 2 shows each of mentioned methods has advantages and disadvantages in synthesis of BDO:

In synthesis method by Aldehyde and Acetylene, primary materials are available. Formaldehyde has environmental problems due to toxicity. Because of process complexity, bench and pilot synthesis scales aren't suitable, but is able to industrial scale synthesis. By 4-carbon Di-Carboxylic acid synthesis, primary materials are available. Because of using metallic oxides catalyzers, this method is complex and for its high condition of temperature and pressure isn't economical efficiency. Although this method has no environmental problems but because of mentioned problems, it isn't an appropriate method. In synthesis by Di-Hydro Furan, used catalyzers are expensive and isn't economical efficiency. The synthesis efficiency is low and it isn't need to separate the main product from intermediate products. Work conditions of temperature and pressure are relatively high but hasn't much environmental problems. So this method isn't an appropriate method. Method of synthesis BDO by 2-Halo Ethanol's, primary materials aren't available. The efficiency is low and using Octa Carbonyl Di-Cobalt isn't economical. The process of electrical reduction has complexity and isn't compatible with industrial structures. According to that didn't reported any environmental problems, but this method isn't appropriate method. Among presented methods of synthesis of BDO, method of Maleic anhydride using, is a relatively good method because of availability of primary materials, single step process, suitable reaction conditions and no environmental problems.

Table 2: BDO synthesis methods compare

Number	Synthesis method	Primary materials availability	Efficiency	Process complexity	Environmental problems	Economical efficiency	Increasing production scale
1	Aldehyde and Acetylene	Available	Relatively high	Complex	Yes	Yes	No
2	4-carbon Di- Carboxylic acid	Available	Relatively low	Complex	No	No	No
3	2,3-Di-Hydro Furan	Not available	Relatively low	Complex	No	No	No
4	Maleic Anhydride	Available	High	Simple	No	Yes	Yes
5	2-Halo Ethanol	Not available	Low	Complex	No	No	No

1-5-1-Empirical section

The used equipment for synthesis BDO, preparing, sample producing, casting, cutting and mechanical tests are below:

Steel reactor, autoclave 500ml for catalytic reduction reaction and FT-IR (Nicolet 860) device for infrared tests, FT-NMR device Bruker,500MHZ-DPX3300 model with DMSO solvent and Tetra-methyl silane (TMS) as standard case, Digital melting point IA 8103 device for measuring melting point also used Thin Layer Chromatography (TLC) for studying reaction progress.

2-Cu-Chromite nano catalyzer synthesis

First, mix 0.1 mole of Cu-Nitrate and 0.1 Cr-Nitrate in 100 ml of Deionized water and metal-Nitrate produce then add 100 ml of 2 molar Citric acid slowly that should act in 50oc for 30 mins6 after that, heat the plate in 95oc till the water vaporize and observe a transparent viscous gel then place the gel into a container in 160oc for 2 hrs7 to produce a black powder then calcinate the black powder in 600oc for 2 hrs in furnace till nano catalyzer synthesize. Size of synthesized nano particles are measured by TEM8 and SEM9 microscopes about 75 nm.

2-1-1, 4-BDO synthesis

By this method, a solution of Maleic anhydride converts to 1,4-DBO in presence of Hydrogen and Mono Hydric Alcohol. First, prepare the catalyzer in 900 psig and 120oc in presence of Hydrogen then reaction acts in 55oc. The FT-IR and Hydrogen spectrum results are below. As in image 1 shows, totally there are three peaks in compound. The first one is for two of Hydrogen of OH groups that has 4.5 ppm peak in H-NMR test. The second peak is for the type of 4 Hydrogen groups that relates to Methyl connected groups and has 1.4 ppm peak.

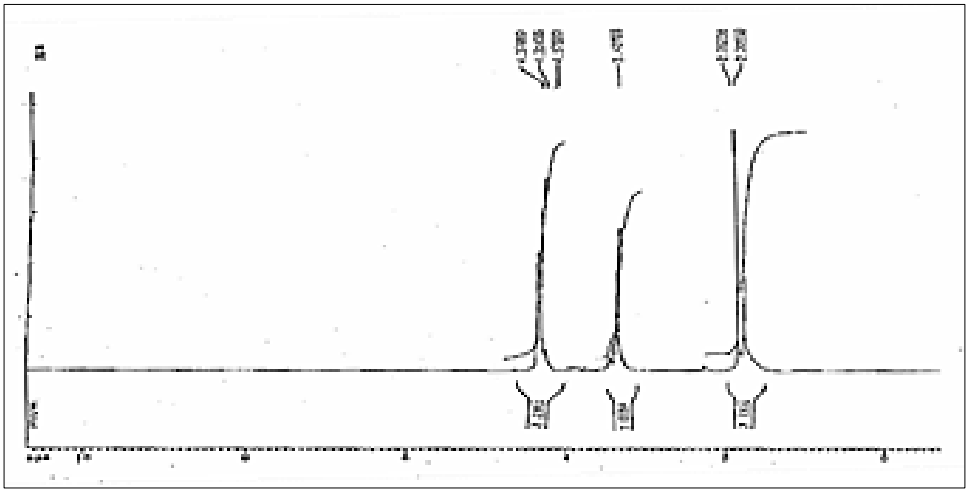


Fig 1: 1,4-BDO H-NMR results

Because of OH group there is a wide peak in FT-IR spectrum that is higher than 3000 and about 3300-3400 cm-1. Also because of first type of alcohol, there is a peak in 1050cm-1 area. Results shows that using catalyzer cause increasing efficiency of 1,4-BDO synthesis reactions.

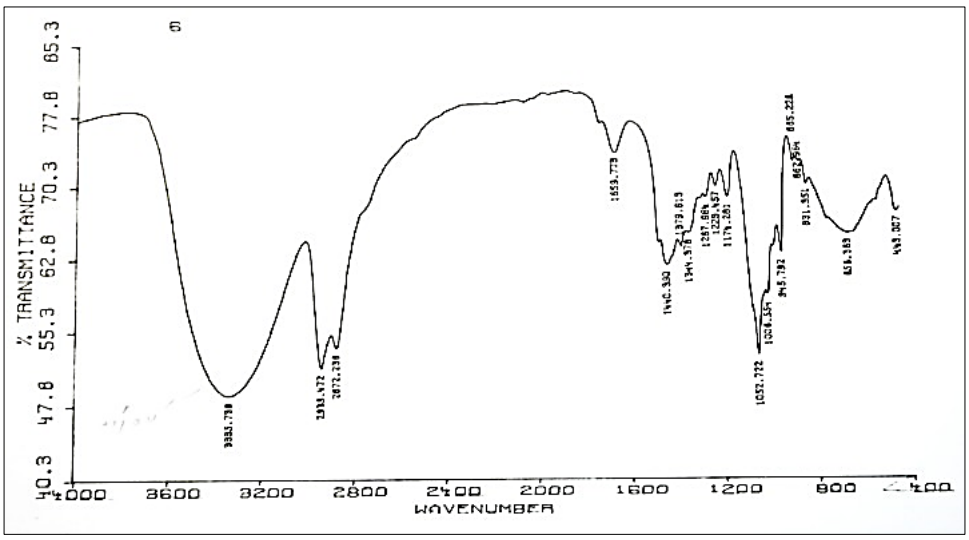


Fig 2: FT-IR test results of 1,4-DBO

Conclusion

The results shows that when use the Cu-Chromite catalyzer, the efficiency increase significantly. This reaction acts by Cu-Chromite catalyzer macro scale and the efficiency was 70-75 percentages but by using nano scale catalyzer the efficiency is about 100%.

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