

Production of Methyl Borate for Sodium Borohydride (NaBH₄): Hydrogen Storage Medium

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Abstract. The storage and production of hydrogen are the main problem for fuel cell applications. Hydrogen storage technologies can be separated into physical storage, where hydrogen is stored as a liquefied or compressed gas, and chemical storage, where metals and other materials adsorbed hydrogen. Chemical hydrides are a well-known class of compounds that have the high hydrogen capacity. Of these hydrides, sodium borohydride (NaBH₄), is more stable according to other chemical hydrides and more easily convert to H₂ in presence of catalysis. NaBH₄ can be produced in many different ways by using different materials such as various boron minerals, boron products, methyl borate esters, metal hydride...etc. In the present study methyl borate, used as a starting material in NaBH₄ production process, was synthesized from borax mineral. Obtained product was identified by Gas Chromatography and Mass Spectrometry (GC-MS). In addition, Fourier Transform Infrared Spectrometry (FT-IR) was used for characterization of methyl borate azeotrope and synthesized methyl borate.

Keywords: Methyl borate, NaBH₄, hydrogen storage, GC-MS, FT-IR.

1. Introduction

Hydrogen is a secondary energy which produced from primary and renewable energy sources such as wind, water, solar etc. It is considered as future energy carrier to be used in transport, such as automotive applications [1], [2]. Moreover, hydrogen is an ideal candidate to replace the present energy carriers used in both mobile and stationary applications so that it will also change the harmful effects to the environment and reduce the dependence of the countries on imported oil [3], [4].

Hydrogen can be stored as pressurized gas, cryogenic liquid and as a solid combined with a metal hybrid. However, due to the low volumetric and gravimetric efficiency of hydrogen storage and safety issue none of the methods above are suitable for portable applications. Instead, liquid hydrocarbons (propane, methanol, gasoline, etc.) and chemical hydrides (NaBH₄, KBH₄, LiBH₄, etc.) could be employed as hydrogen sources for portable PEMFC [5], [6].

Methyl borate is widely applied as a solvent or catalyst in the production of resins, waxes, paints and varnishes, in organic reaction to produce biocides, flame retardants, anti-oxidants, corrosion inhibitors, tackifiers for elastomers and rubbers, cross-linking agents for polymer, dehydrating agents and plastic stabilizers as a methylation agent or as a boron source [7]. Moreover, methyl borate is used in production of NaBH₄, has a great hydrogen storage capability, as a starting material [8], [9].

The production of methyl borate esters have been investigated for many years. There are a few studies about TMB and TMB-M azeotrope in the literature except patents [10]-[13]. Generally, boric acid is used as a boron source in methyl borate production. The purpose of this study is to investigate the methyl borate production from borax mineral. The production process of methyl borate will be structured in three parts such as synthesis of azeotrope, breaking of azeotrope to obtain pure product and increasing of the purity of

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product. The obtained product was identified by GC-MS analysis. In addition, FT-IR analyses were performed to determine the structural properties of the azeotrope and obtained product.

2. Experimental

2.1. Materials and characterization

Borax used as a boron source in methyl borate production was provided by Eti Mine Works, Turkey. The chemical and physical properties of the mineral are shown in Table 1. After cleaning the mineral manually of visible impurities, it was ground and sieved to give a particle size of 250 mesh by ASTM standard sieves. The sample was analyzed using X-ray diffraction (XRD) and was found to be borax.

Table 1: The chemical and physical properties of borax

Chemical formula	$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$
$\text{B}_2\text{O}_3\%$	36.6%
Crystal system	Monoclinic
Hardness	2 – 2.5 Mohs
Specific gravity	1.715 g/cm^3
Color and transparency	Colorless, white, grayish, transparent-translucent

Sulfuric acid (with 99.5% purity) and methanol (with 99.5% purity) were purchased from Merck. Calcium chloride-2-hydrate (with 97% purity) purchased from Riedel de Haën. Calcium chloride-2-hydrate was heated to 150°C to obtain anhydrous calcium chloride in an oven. Also, commercial methyl borate (with 99% purity) purchased from Merck was used as a reference material to investigate the characteristic properties of methyl borate.

The obtained product was analyzed by using a Perkin Elmer Clarus 500 GC-MS equipped with a SGE ID-BPX5 capillary column (30 m×0.25 mm ID×0.25 μm) for identification. The operating conditions were as follows: The sample was manually injected into the column in split mode (50:1) at 250°C. Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The oven temperature was held at 70°C for 10 min. The identification was performed using the Wiley and Nist mass spectral library available on the data system. Infrared spectra were recorded using a Perkin Elmer Spectrum One mark FT-IR spectrometer with ATR Sampling Accessory at 4 cm^{-1} resolution in the 4000–650 cm^{-1} range.

2.2. Methods

2.2.1 Characterization of reference material

In order to compare characteristic properties of reference methyl borate and product methyl borate FT-IR analysis was performed. FT-IR spectrum of reference material was given in Figure 1 and absorbance band regions were listed in Table 2.

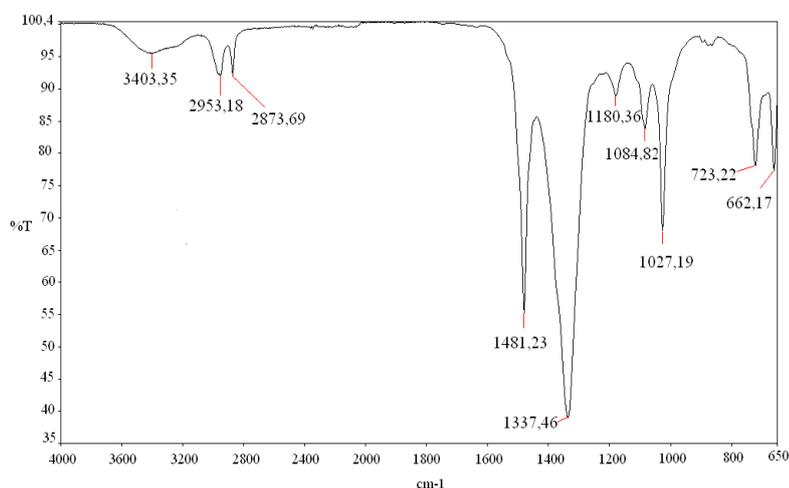


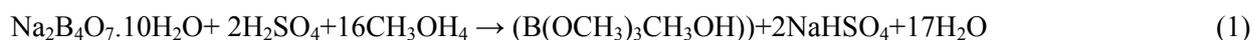
Fig. 1: FT-IR spectrum of reference material.

Table 2. Absorbance band regions

Wavelength (cm ⁻¹)	Band Regions
3403	O-H band
2953-2873	C-H stretching bands
1481	C-H stretching band
1337	B-O band
1180-1027	C-O stretching bands

2.2.2 Synthesis

Methyl borate is synthesized from the reaction of borax, methanol and sulfuric acid in an esterification reaction (Eq.(1)). The overall reaction is as follows:



The devices used in methyl borate production consist of a temperature resistant still pot, magnetic stirrer with a heating plate, and a condenser. The borax, sulfuric acid, and methanol mixture was prepared according to (1) and it was heated to adjusted temperature based on the boiling points of azeotrope. The mixture was fractionally distilled and as a result of heating, the methyl borate-methanol azeotropic mixture was formed. Then, it was broken by treating it with calcium chloride to obtain methyl borate. The obtained product was distilled again to increase of purity. After the production process was completed, the obtained product was analyzed by GC/MS. According to analysis result, the product was identified as methyl borate (B(OCH₃)₃). The production procedure was given in Figure 2.

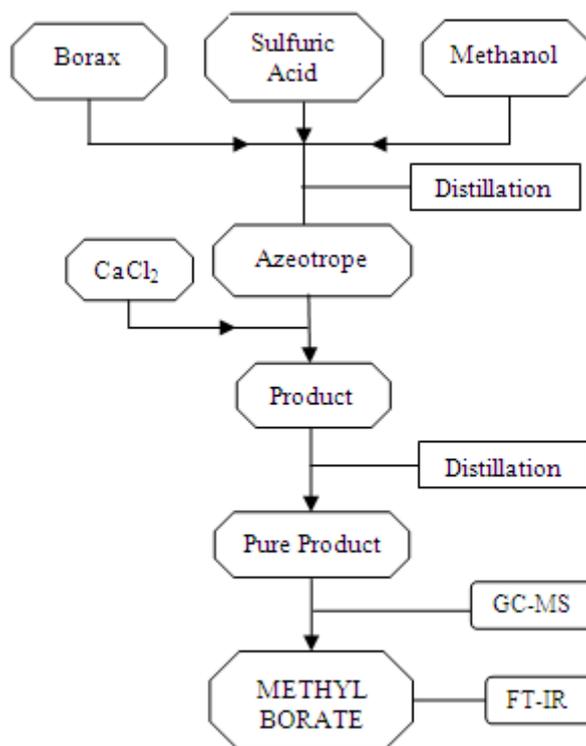


Fig. 2: Flow chart of methyl borate production.

3. Results and Discussion

3.1. FT-IR analysis of azeotrope

FT-IR spectrum of methyl borate and methanol azeotrope is given in Figure 3. It is observed that intensity of characteristic B-O band for methyl borate and methanol azeotrope was smaller than reference material as expected.

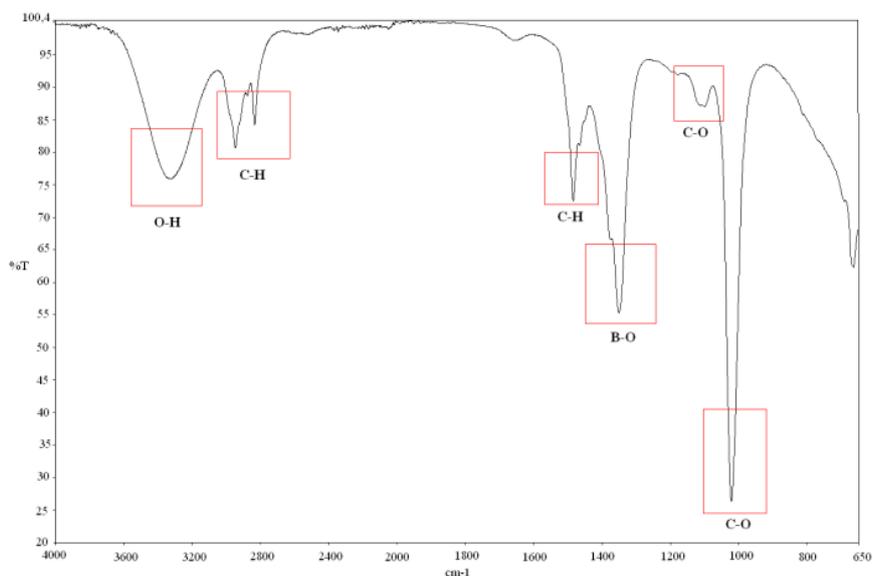


Fig. 3: FT-IR spectrum of azeotrope.

3.2. GC-MS analysis of methyl borate

Qualitative analysis of pure product was performed by GC-MS analysis after separating from methyl borate and methanol azeotrope. Resulted pure product was identified as methyl borate based on the Wiley and Nist mass spectral library (Figure 4).

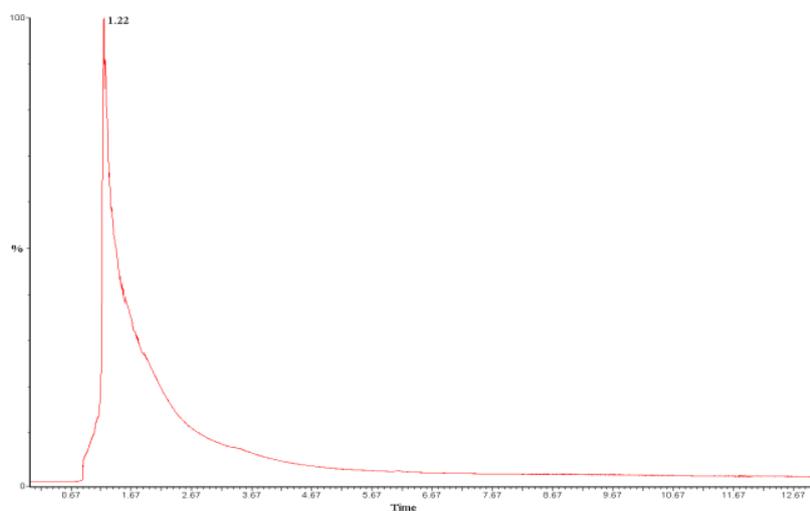


Fig. 4: Chromatogram of methyl borate.

3.3. FT-IR analysis of methyl borate

FT-IR spectrum of methyl borate exhibited the following absorption bands and they were assigned referring to literature. The band at 3298 cm^{-1} is the stretching vibrations of the O-H group. The bands at 2948 cm^{-1} , 2835 cm^{-1} , and 1484 cm^{-1} assigned to the C-H stretching mode. The band at 1348 cm^{-1} is assigned to the characteristic B-O band. The bands at 1101 cm^{-1} and 1017 cm^{-1} are C-O stretching modes (Figure 5).

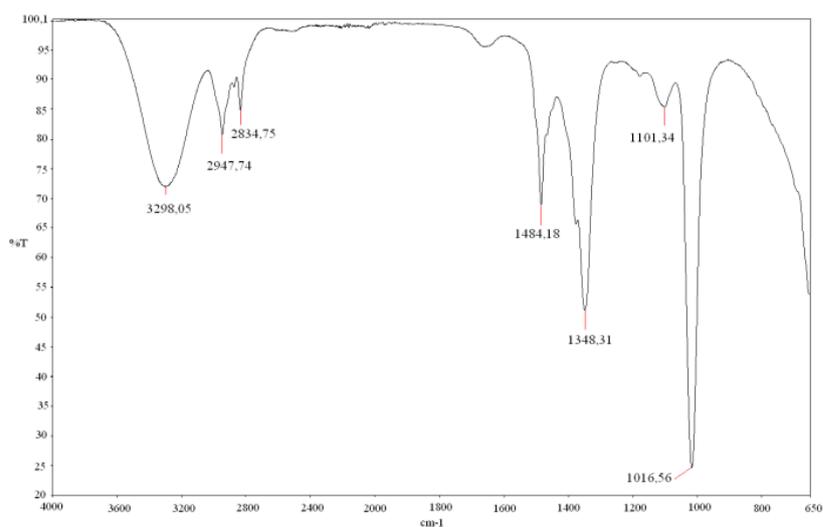


Fig.5: FT-IR spectrum of methyl borate.

4. Conclusion

In the present study, methyl borate was synthesized according to an esterification reaction. The production process consists of three stages: a) Borax, sulfuric acid and methanol were all reacted to produce azeotrope b) The azeotrope treated with calcium chloride to obtain pure product c) The obtained product was distilled again for increasing purity. The resulted product was identified as methyl borate by GC-MS analysis. In addition, the structural properties of methyl borate were determined by FT-IR spectroscopy.

5. References

- [1] T.N. Veziroglu. Hydrogen movement and the next action: fossil fuels industry and sustainability economics. *Int. J. Hydrogen Energ.* 1997, 22: 551–556.
- [2] I. Dinçer, Environmental impacts of energy. *Energ. Polic.* 1999, 27: 845–854.
- [3] S. Fernández-Valverde. *Hydrogen: The Ecological Fuel for Mexican Future; Towards a Cleaner Planet.* Springer Berlin Heidelberg, 2007.
- [4] B. Sakintuna, F. Lamari-Darkrim, M. Hirscher and B. Dogan. Metal hydride materials for solid hydrogen storage: A review. *Int. J. Hydrogen Energ.* 2007, 32 (9): 1121-1140.
- [5] J. Kim, H. Lee, S. Han, H. Kim, M. Song and J. Lee. Production of hydrogen from sodium borohydride in alkaline solution: development of catalyst with high performance. *Int. J. Hydrogen Energ.* 2004, 29: 263.
- [6] S.U. Jeong, R.K. Kim, E.A. Cho, H.J. Kim, S.W. Nam, I.H. Oh, S.A. Hong and S.H. Kim. J. A study on hydrogen generation from NaBH₄ solution using the high-performance Co-B catalyst. *Power Sources.* 2005, 144: 129-1341.
- [7] I. Girgin and A. Obut. Trimetil Borat [B(OCH₃)₃] Üretim Yöntemleri. *Madencilik*, 2003, 42: 37-42.
- [8] H. I. Schlesinger, H.C. Brown. US Patent 2,534,533, 1950.
- [9] H. I. Schlesinger, H.C. Brown and A. E. Finholt. Sodium borohydride, its hydrolysis and its use as a reducing agent and in the generation of hydrogen. *J. Amer. Chem. Soc.* 1953, 75: 205-209.
- [10] H.I. Schlesinger, H.C. Brown, D.L. Mayfield and J.R. Gilbreath. Procedures for the preparation of methyl borate. *J. Am. Chem. Soc.* 1953, 75: 213.
- [11] C.O. Jr. Wilson. Process for the preparation of lower alkyl borates. 1959, US 2880227.
- [12] C.M. Bowman and E.J. Watson. Method for the preparation of trimethyl borate. 1961, US 2976313.
- [13] G.N.Jr. Tyson. Preparation of borate esters. 1959, US 2884440.