



ALTERNATIVE ENERGY STORAGE KEY COMPONENT TRIMETHYL BORATE: SYNTHESIS, DEHYDRATION AND KINETIC PARAMETERS

Çetin ÇAKANYILDIRIM* and Metin GÜRÜ**

*Department of Chemical Engineering, Engineering Faculty, Hitit University,
19030 Çorum, Turkey, cetincakanyildirim@hitit.edu.tr

**Department of Chemical Engineering, Engineering Faculty, Gazi University,
06570 Ankara, Turkey, mguru@gazi.edu.tr

(Geliş Tarihi: 22.10.2013, Kabul Tarihi: 17.04.2014)

Abstract: The aim of this study was to investigate effects of dehydrants on the trimethyl borate reaction and determine the kinetic parameters. Thus, trimethyl borate was produced by reacting of boric acid with methyl alcohol in a rotary evaporator. Evaporator was programmed to operate at 65 °C temperature and 150 rpm. Formed water at this reaction affects the reaction rate and trimethyl borate formation, negatively. Therefore, water is necessary to be removed from the reaction media. Kinetic search of the process gives reaction rate and rate constant as, pseudo first order and 0.0613 min^{-1} , respectively. Consequently, the rate equation can be mentioned as $r=0,0613 C_{B(OCH_3)_3}$. Since the capacity and intensity properties changed with dehydrant type, various dehydrants at different amounts should be tested in the reaction. For this purpose CaCl_2 and LiCl were used as dehydrant in the reactor, separately. During the reaction, trimethyl borate was distilled in the form of an azeotrope with methanol. LiCl salt was also used to separate azeotrope into two layers. Top layer was rectified and determined as trimethyl borate compound by using GC-MS instrument. In addition, purity of trimethyl borate was determined by titrimetric method.

Keywords: trimethyl borate, calcium chloride, lithium chloride, rate equation.

ALTERNATİF ENERJİ DEPOLANMASI ANAHTAR BİLEŞENİ TRİMETİL BORAT: ÜRETİMİ, SU GİDERİMİ VE KİNETİK PARAMETERLERİ

Özet: Bu çalışmanın amacı trimetil borat üretimindeki kinetik parametrelerin ve su çekici kimyasalların sürece etkisinin belirlenmesidir. Bu maksatla üretim için borik asit ve metil alkol döner buharlaştırıcıda (reaktör) tepkimeye sokulmuştur. Reaktör 65 °C sıcaklıkta ve 150 tur/dakika dönme hızında çalıştırılmıştır. Tepkimede oluşan su trimetil borat üretim hızını olumsuz etkilemektedir. Bu sebepten dolayı suyun tepkime ortamından uzaklaştırılması gerekmektedir. Tepkimenin kinetik çalışmaları gerçekleşen tepkimenin sözde birinci dereceden ve hız sabitinin $0,0613 \text{ dakika}^{-1}$ olduğunu işaret etmektedir. Dolayısı ile hız denklemi $r=0,0613 C_{B(OCH_3)_3}$ şeklinde ifade edilebilir. Ürün miktarı ve özellikleri kullanılan su uzaklaştırıcılar ile değişim gösterdiği için farklı kurutucular, farklı oranlarda kullanılmalıdır. CaCl_2 ve LiCl tuzlarından su uzaklaştırıcı olarak tepkimede yararlanılmıştır. Tepkime sonrasında ürün trimetil borat ve metanolün azeotropu olarak toplanmış ve azeotropun iki tabakaya ayrılması maksadı ile LiCl kullanılmıştır. Üst tabaka zenginleştirilip trimetil borat bileşimi GC-MS ile belirlenmiştir. Trimetil boratın saflığı, ayrıca titrimetrik metot ile de analiz edilmiştir.

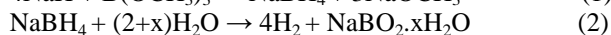
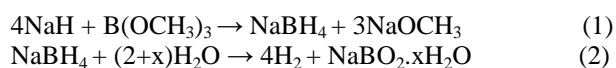
Anahtar kelimeler: trimetil borat, kalsiyum klorür, lityum klorür, tepkime hızı.

INTRODUCTION

Developing technology and industry increase energy consumption and air pollution, especially the decreasing natural gas and petroleum reserves increases the importance of clean and renewable energy. The consumption of fossil fuels is restricted because of the high CO_2 emission potential and sulfur contents. Consequently, environmental impacts arise from the emission such as acid rain, ozone depletion and global climate change have been grow up by the consumption of fossil fuels and must be stopped urgently by using clean

and renewable energy. In order to solve the above reported problems, hydrogen seems to be the most appropriate candidate because of its intrinsic properties (clean, renewable, high energy content etc.) (Chater et al., 2007). Practicable use of hydrogen energy extensively is related to the easy and feasible hydrogen producing process and its storage. As a matter of fact, elemental hydrogen has high volatility and the smallest in atomic diameter, it cannot be converted economically to liquid phase and stored in the pressurized steel container. Hydrogen gas can be hold in small spherical glass or adsorbed on the surface of porous metal and metal boride

by means of high pressure. Similarly, magnesium diboride was synthesized from its elements by solid phase reaction and hydrogen gas was stored on it by means of high pressure (Kaya et al., 2011). Also, other metal boride compounds can hold up hydrogen gas in the similar form. Sodium borohydride can be considered as one of those. It is the popular reducing chemical that serve in many area such as medical (Galvan et al., 2013) or nano-size catalyst production (Çakanyıldırım et al., 2012). NaBH₄ was produced by using dynamic behaviors of protide at the extreme surface of magnesium particles (Suda et al., 2005; Çakanyıldırım and Gürü, 2011). Since this method extremely depends on surface conditions, obtaining applicable results will probably need further developments. However, sorption of hydrogen in the metal borohydride by using of trimethyl borate (a part of Schlesinger process) (Bilici, 2004) is highly economic and advisable, because the high pressurized hydrogen gas or other hydrogen suppliers (such as MgH₂) is not necessary. In addition of metal borohydride synthesis, trimethyl borate is used as a solvent or catalyst for the production of resins, waxes, paints and varnishes. Also, it is used as a methylation agent or as a boron source in organic reaction to manufacture biocides, flame retardants, anti-oxidants, corrosion inhibitors, tackifiers for elastomers and rubbers, cross-linking agents for polymer, dehydrating agents and plastic stabilizers. Some of the recent studies are the synthesis of BN nanotubes from trimethyl borate and nitrogen gas (Lin et al., 2008) and the production of trimethyl borate-methanol azeotrope to be used as a volatile brazing flux (Lewicka et al., 2007). On the other side, trimethyl borate might be consumed at high quantities by reacting with sodium hydride in order to form sodium borohydride. Then, hydrogen gas can be generated by thermal and catalytic hydrolysis of sodium borohydride, (Pena et al., 2007; Harada et al., 2007; Cho and Kwon, 2007) according to the following reaction;



As can be seen from Eq. (3), trimethyl borate compound, which is necessary to form sodium borohydride, is synthesized by esterification reaction of boric acid with methyl alcohol in the presence of dehydrant.



A couple of decades ago trimethyl borate synthesis were searched in detail and most of these studies were published as patents. However, these studies were mainly considered in side products and azeotrope separation (Chiras, 1960; Schechter, 1954; Hartmann et al., 1984; Bowman and Watson, 1961; Cunningham, 1954). Dehydrant effect was briefly discussed by giving their name (calcium nitrate, aluminum nitrate or the chlorides of zinc, calcium, sodium and lithium) and some technical problems such as bump and spatter incase LiCl is in use (Cunningham, 1954). Alternatively, zeolites are offered to be used for dehydration process (Baloğlu, 2007). Thus,

it is necessary to perform comprehensive studies about the effect of various salts as water remover.

The purpose of this study is to investigate the synthesis of trimethyl borate used mainly in the metal borohydride production by reacting boric acid with methanol in the presence of dehydrant at the optimum conditions and characterize the product by means of GC-MS and titrimetric method. Also, kinetic study of this reaction was carried out and the reaction rate was determined.

EXPERIMENTAL

CH₃OH, CaCl₂ and LiCl were bought from Merck with purity of 99.5%, 99% and 99%, respectively. B(OH)₃ was provided by Eti Mine Works. Reagents mixed together in a molar ratio CH₃OH:B(OH)₃ = 6:1 and put in rotary evaporator (Büchi V800). Depending on the parameter, different amounts of CaCl₂ or LiCl were added into the mixture as dehydrant and evaporator was programmed to operate at 60-65 °C temperature and 150 rpm for the reaction. Early azeotropic liquid was carefully collected in the receiving flask. This process was completed while the condenser temperature was less than 50 °C. Then second azeotropic liquid was forced through cooling column by rising the water bath temperature of the rotary evaporator. Obtained azeotrope distillates were quantitatively analyzed in order to identify trimethyl borate existence by titrimetric method (Snell and Hilton, 1968). Also, products were characterized by GC-MS (Thermo Finnigan). Densities of the products were measured by Mohr-Westpall balance. Besides, amount of azeotropes taken at less and above than 50 °C were recorded by mass. In order to obtain more purified product, in a separation apparatus, LiCl salt was added to both of the azeotropes to separate trimethyl borate and methanol phases. Trimethyl borate rich upper phase was stored for further analysis.

Furthermore an experiment was performed to determine rate order of trimethyl borate formation reaction. During the reaction, samples were taken by pipette, transferred into the cell containers and cooled in ice bath in order to stop the reaction. Later, samples were determined immediately by means of GC-MS instruments. Integration of trimethyl borate peaks were used to calculate the rate order and rate constant by integral method.

RESULTS AND DISCUSSION

Trimethyl borate is stored and sold as an azeotrope of methyl alcohol. Generally, commercial product contains 70% trimethyl borate and the rest is alcohol. Density of pure trimethyl borate is 0.915 g/mL, whereas methyl alcohol density is 0.7918 g/mL. Thus, if the density of the product is closer to 0.915, it means product contains more trimethyl borate. Therefore purity of experimental products might be alternatively determined by their densities.

Figure 1 shows the density differences of the products. LiCl gives the best result if densities are considered. Especially, early azeotrope of the LiCl has the biggest

density values and the second azeotrope of LiCl is as denser as early azeotrope of CaCl₂. Although boiling temperature of the methanol is lower, trimethyl borate easily run to the condenser and accumulated in receiving flask more than methanol could achieve at lower temperatures. It was thought that this circumstance results from azeotropic effect of the product.

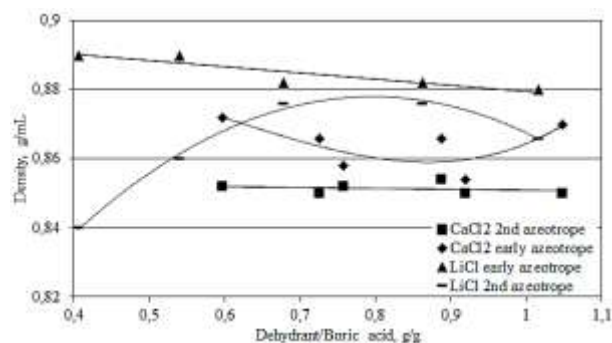


Figure 1. Effect of dehydrant on the azeotrope density; 60-65 °C, 6 CH₃OH/B(OCH₃)₃ molar ratio.

Besides, trimethyl borate was collected during the process at different time regimes. At the first stage, there was no water in the reaction vessel since the water absorber salts had big capacity to hold it. That proper condition supported rapid formation of the (early) trimethyl borate. At the beyond stage, formation of water cut off the condenser stream therefore temperature of the water bath needed to be raised in order to obtain further product which is called second azeotrope. Small density value of second azeotrope indicated that methanol concentration was high in the reactor since the water content was not suitable for producing trimethyl borate at all.

As can be seen from Figure 1, density of azeotrope was affected from dehydrant type and amount. Dehydrant amount becomes important when the economy of the process was considered. Excess using of dehydrant causes more water to be hold. Therefore at less than 50 °C, purer azeotrope could be condensed by fresh dehydrant addition. Conservation of mass is well known so, the early and second azeotrope amounts must behave oppositely. If trimethyl borate is less in the early azeotrope, second azeotrope must include the rest. Therefore choosing the effective dehydrant type would raise the early azeotrope amount and product quality. Moreover, intersection points of the experimental trend lines in Figure 2 may offer ideas about the real dehydrant amount selection. Figure 1 and Figure 2 demonstrate that LiCl is the reasonable one and can be used as dehydrant, successfully.

Purity of trimethyl borate products were firstly determined by titrimetric method. Figure 3 gives the B₂O₃ concentration and computed error values. Trimethyl borate concentration can be easily estimated by B₂O₃ amount of mother solution. In Figure 3, it is obvious that the concentration is rising with used amount of dehydrant. Especially for the second azeotropes, effect of LiCl on the trimethyl borate yield

is more remarkable in the graph. The value of LiCl is at about twice expensive than CaCl₂ price but less than half of CaCl₂ usage is adequate for a proper reaction. Besides, process operated with LiCl results in high efficiency, trimethyl borate quantity and purity.

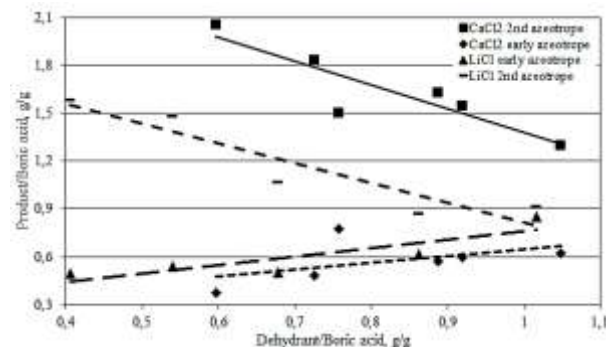


Figure 2. Effect of dehydrant amount on trimethyl borate yield; 60-65 °C, 6 CH₃OH/B(OCH₃)₃ molar ratio

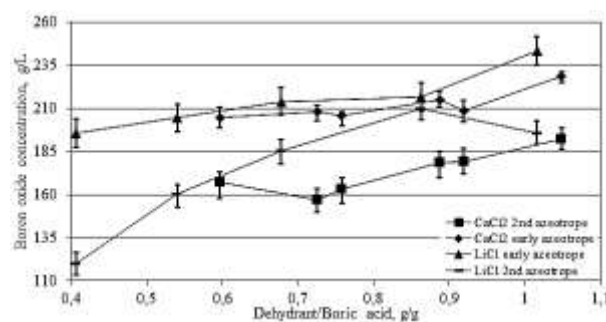


Figure 3. Effect of dehydrant on the boron oxide concentration; 60-65 °C, 6 CH₃OH/B(OCH₃)₃ molar ratio.

Figure 4 and Figure 5 show variation of the trimethyl borate as a function of methanol and dehydrant type and amount. All of these GC-MS graphs were executed by using the same experimental procedure. Results confirm that advantageous gains were obtained for LiCl. Analysis showed that it is always possible to obtain satisfactory results with LiCl dehydrant. Figure 4 demonstrates the 70% trimethyl borate azeotrope (most stable commercial product) and experimental result in which only 25.2 g of LiCl [LiCl/B(OCH₃)₃ by weight=0.406] was used. Even the amount is very small graph proves the product is pure enough to catch up with commercial product properties. In that way, LiCl seems to be very advantageous to serve as dehydrant, due to the high hygroscopic intensity. Figure 5 belongs to the studies achieved with 57 g and 37 g of CaCl₂ dehydrant, respectively. Peaks taken between 0.63-0.74 min are representing methanol and water while the peak between 0.85-0.94 min is mainly indicating trimethyl borate. Below sides of the graphs are giving the molecular weights of the trimethyl borate and its split atoms. Approximately, 104 g/mol is the molecular weight of trimethyl borate. Firstly, one of the -O-CH₃ bond is broken and molecular weight reduces to 73 g/mol value. This departure is followed by one of the oxygen and a methyl group and molecular weight reaches to 57 and 43 values, exactly. At this point, structure losses its boron atom, so at about 32 g/mol MS peak was appeared by that loss. Then, we guess the (-O-CH₃) molecule gave its

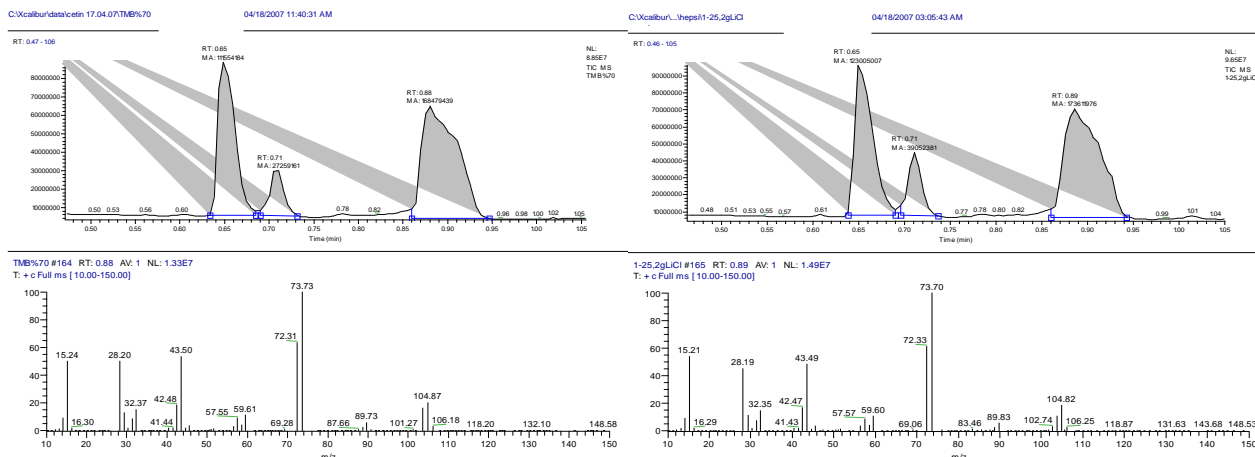


Figure 4. GC-MS analyses of commercial (on left) and experimental product ($\text{LiCl}/\text{B}(\text{OCH}_3)_3=0.406$)

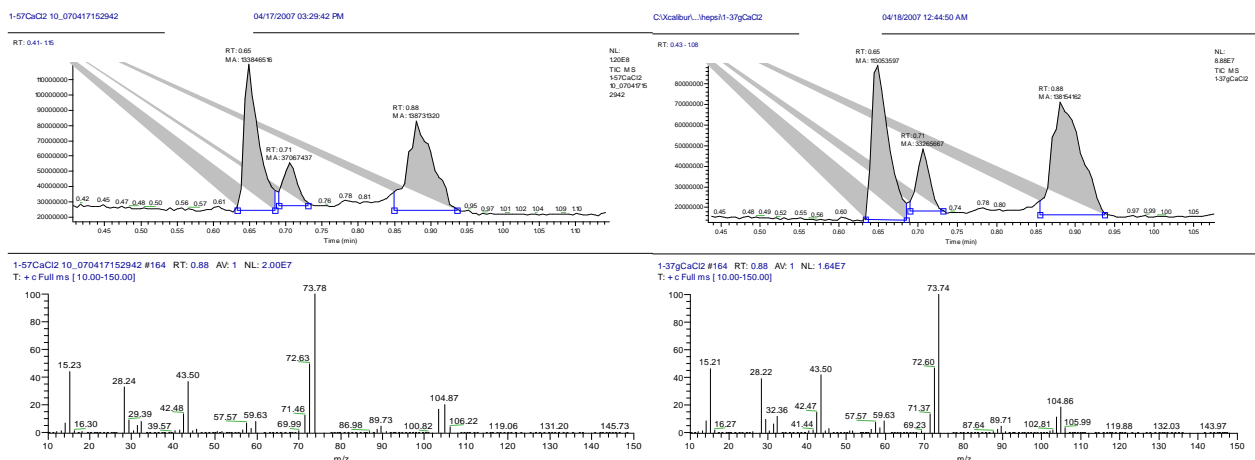


Figure 5. GC-MS analyses of the experimental product ($\text{CaCl}_2/\text{B}(\text{OCH}_3)_3=0.919$; 0.597)

hydrogens and carbon monoxide (28 g/mol) was formed. Peaks at 15 and 31 g/mol must be the result of detached $-\text{CH}_3$ and $-\text{O}-\text{CH}_3$ groups while the products were sweeping in the MS column.

GC-MS analyses of the second azeotropes have wider and shorter trimethyl borate peaks, so it can easily be concluded, they are poor about trimethyl borate content. These results were previously obtained in Figure 1 and Figure 3 in the manner of density and boron oxide concentration. In addition, second azeotrope graphs show water existence and full-grown methanol peaks. Therefore, it is well understood that early azeotrope contains more trimethyl borate. Furthermore, in Figure 2 it is obvious that amount of early azeotropes of LiCl were higher than CaCl_2 could achieve.

In order to investigate the trimethyl borate synthesis reaction kinetics, an extra experiment was carried out. Reactants were mixed in a reaction vessel located in a water bath at 63 ± 1 °C to result in trimethyl borate. After certain time, reaction vessel was transferred in ice bath to suppress the reaction rate and product concentration was immediately after measured by means of GS-MS and its peak area integration software. Figure 6 demonstrates the experimental results and rate order. Since the molar ratio was $(\text{CH}_3\text{OH}/\text{B}(\text{OCH}_3)_3)$ 6, this reaction was thought to be a pseudo type and common

kinetic approach was avoided. Reaction obeys pseudo first order kinetic ($R^2=0.9902$) and rate equation can be written as:

$$r = 0.0613 C_{\text{B}(\text{OCH}_3)_3}$$

Similarly, in another study it was reported that the reaction rate is 1.16th order and the equilibrium constants are 1.94×10^{-3} and 2.5×10^{-4} at 55 °C and 50 °C, respectively (Arslan, 2007).

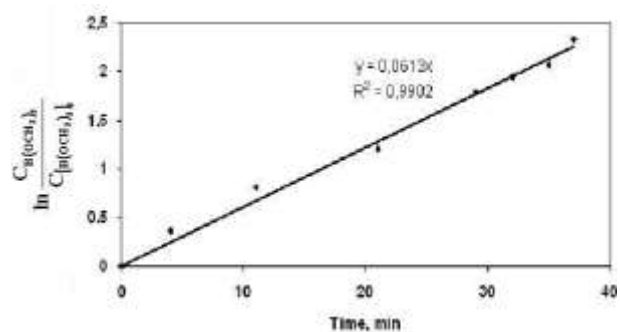


Figure 6. The change of $\ln(C_t/C_0)$ as a function of time for the formation of trimethyl borate; 63 ± 1 °C, 6 $\text{CH}_3\text{OH}/\text{B}(\text{OCH}_3)_3$ molar ratio.

CONCLUSION

Trimethyl borate is mainly used for synthesis of great number of chemicals and metal borohydrides that has importance for hydrogen storage technologies. In this study, methanol and boric acid were used to obtain trimethyl borate in the presence of dehydrants. In order to force the reaction, early and second azeotropes were taken away continuously from the reactor. Formed water was adsorbed by two types of dehydrants. Amount of dehydrants were investigated to determine the best values. Reaction rate and its constant were calculated as pseudo first order and 0.0613 min^{-1} . Since, trimethyl borate was taken in azeotropic form, LiCl salt was added to the azeotrope to get the phases separated. Performed analysis proves that, the product can be synthesized at higher efficiency and purity with less dehydrant consumption and methanol impurities, if LiCl was chosen as dehydrant.

ACKNOWLEDGEMENT

This study was supported by State Planning Organizing of Turkey under Project No: 2001 K 120590.

REFERENCES:

- Arslan R., 2007, Trimetil borat üretimi, MS Thesis, Gazi Ün., Ankara Türkiye.,
- Baloğlu H., 2007, Trimetil borat üretim prosesi geliştirilmesi, MS Thesis, İTÜ İstanbul, Türkiye.
- Bilici M.S.U., 2004, Sodyum borhidrür üretim yöntemleri, II. Uluslararası Bor Sempozyumu, Eskişehir Türkiye.
- Bowman C.M. and Watson E.J., 1961, Method for the preparation of trimethyl borate, Patent US2976313 A.
- Chater, P.A., Anderson P.A., Prendergast J.W., Walton A., Mann V.S.J., Book D., David W.I.F., Johnson S.R. and Edwards P.P., 2007, Synthesis and characterization of amide-borohydrides: New complex light hydrides for potential hydrogen storage, *J. Alloy. Compd.*, 446-447, 350-354.
- Chiras S.J., 1960, Process of preparing trimethyl borate, Patent US2947776 A.
- Cho, K.W. and Kwon H.S., 2007, Effects of electrodeposited Co and Co-P catalysts on the hydrogen generation properties from hydrolysis of alkaline sodium borohydride solution, *Catal. Today*, 120, 298-304.
- Cunningham G.L., 1954, Preparation of trimethyl borate, Patent US2830070 A.
- Çakanyıldırım, Ç., Demirci U.B., Şener T., Xu Q. and Mielle P., 2012, Nickel-based bimetallic nanocatalysts in high-extent dehydrogenation of hydrazine borane, *Int. J. Hydrogen Energ.* (37), 9722-9729.
- Çakanyıldırım Ç. and Gürü M., 2011, Production of NaBH_4 from its elements by mechano-chemical reaction and usage in hydrogen recycle, *Energ. Source., Part A*, 33, 1912-1920.
- Galvan, A.R., Contreras-Torres F.F., Basiuk E.V., Heredia A. and Basiuk V.A., 2013, Deposition of Silver Nanoparticles onto Human Serum Albumin-Functionalised Multi-Walled Carbon Nanotubes, *Can. J. Chem. Eng.*, 91, 264-270.
- Harada, T., Ikeda S., Miyazaki M., Sakata T., Mori H., and Matsumura M., 2007, A simple method for preparing highly active palladium catalysts loaded on various carbon supports for liquid-phase oxidation and hydrogenation reactions, *J. Mol. Catal. A-Chem.*, 268, 59-64.
- Hartmann H., Kabiell G., Kiener V.D. and Woerz O., 1984, Process for the preparation of trimethyl borate, Patent DE3324419 A1.
- Kaya, S., Gürü M. and Ar İ., 2011, Synthesis of magnesium borohydride from its elements and usage in hydrogen recycle, *Energ. Source., Part A*, 33, 2157-2170.
- Lin, F.H., Hsu C.K., Tang T.P., Kang P.L. and Yang F.F., 2008, Thermal-heating CVD synthesis of BN nanotubes from trimethyl borate and nitrogen gas, *Mater. Chem. Phys.*, 107, 115-121.
- Lewicka, L., Kulig-Adamiak A., Wisniewska A., Kaminski J., Dabrowski Z. and Cybulski J., 2007, Starting the production of trimethyl borate-methanol azeotrope to be used as a volatile brazing flux, *Przem. Chem.* 86, 48-50.
- Pena-Alonso, R., Sicurelli A., Callone E., Carturan G. and Raj R., 2007, A picoscale catalyst for hydrogen generation from NaBH_4 for fuel cells, *J. Power Sources*, 165, 315-321.
- Schechter W.H., 1954, Production of trimethyl borate, Patent US2689259 A.
- Snell, D.F. and C.L. Hilton, 1968, *Encyclopaedia of Industrial Chemical Analysis*, Vol. 7, Wiley, New York.
- Suda, S., Morigasaki N., Iwase Y. and Li Z.P., 2005, Production of sodium borohydride by using dynamic behaviors of protide at the extreme surface of magnesium particles, *J. Alloy. Compd.*, 404-406, 643-647.