Characterization and Exergy Analysis of Triphenyl Borate

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Summary: In this study, unlike from the literature, boron oxide, borax decahydrate, boric acid and borax pentahydrate as boron sources were used to synthesize Triphenyl Borate (TPB). The reactions of TPB were carried out by using both phenol and various boron sources in inert water-immiscible organic solvent successfully. On the basis of analyzes (FT-IR, SEM, TGA/DSC) obtained, it was seen that phenol acted as a support to borate structure framework and thermal characterisation of the amorphous solid under determined conditions suggested that usage of different boron sources had effects for glass transition temperature in TPB production. The exergy analysis was performed to the TPB production to determine efficiency. The exergy analysis showed that the highest exergy efficiency was obtained by using boron oxide as a boron source. Consequently, all analyses results showed that TPB was produced successfully. Accordingly, characterization and exergy analysis supported each other.

Key words: Triphenyl Borate, Borate, Borax, Exergy.

Introductıon

Boron is a unique and precious element in rocks, soil, water and various sources. Economically sized deposits of boron minerals are generally found in arid areas with a history of volcanism. Such deposits are being exploited in Turkey, the United States, and several other countries [1]. Turkey is ranked top with its share of almost 73% in the global boron reserve with 5 distinct areas (Bigadiç, Sultançayir, Kestelek, Emet and Kirka) standing [2] and since a very long time the presence of boron deposits for general applications. Turkey is the largest producer for boron mineral in the world. The analysis of energy and exergy analyses have importance with regards to the evaluation of boron resources, economically. The most important boron minerals of Turkey's are tincal, colemanite and ulexite. Turkey, utilizing reserves, has transformed the picture entirely with a number of measures taken in recent years [3]. Over 150 minerals are known to contain the element boron. They may be seperated into three broad groups by comparing their origin and geological environments [4]. The recent evoluations show that the problems in the continental borate and other salts formations have been solved along with the development of the laboratory studies about volcanic arc and the related springs [5].

There are differences between consumption of borates in the United States and in Western Europe. In Europe, a major application of borates is the detergent industry [6]. Boron compounds needed to make it suitable for industrial use different degree of processing varies enormously. Some industries use mineral concentrates while others make use of refined boron products [7].

The location is the main use of borates glass industry. All over the world use 42% of boron in the glass industry. Boron oxide, borosilicate glass, textile glass fibers and glass fiber insulation is an important compound. These three products of boron compounds in the glass industry is the main place of consumption [8].

Boron compound in the manufacture of glass fiber insulation is widely used as borax pentahydrate. Fiberglass insulation, construction industry, in building insulation, using the rolls is applied to the wall or ceiling. In addition, pipes, boiler and tank coatings, insulation panels, automobiles and sound insulation are applied as applications [8, 9].

There are a lot of flame retardant substances. In industry sectors, halogen-free zinc borates as flame retardants are interested. For instance, zinc borate is worked with PVA as flame retardant [10]. Borates are used as fire retardant. Flame retardants are used to reduce the level of flame. Flammable is being able to be with the addition of flame retardant material reduction [11, 12].

Borax is also used to protect from insect attack. Boron compounds are toxic to insects, especially beetles. Boric acid and borax pentahydrate or similar formulations are boron-containing compounds [8, 11]. The grains or powders of boron

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carbide are used as the abrasive. Commercial abrasive grains are 1-1000 μm in size [12]. Borate mineral structure, the corners of the hydroxyl groups which have incorporated oxygen or boron-based three-sided BO_3 or four-sided BO_4 groups constitute [13]. Borates could not precipitate from sea water under dynamic, crystallizing conditions until the concentration was 2500-4000 ppm B because of extreme super saturation [14].

Antifouling paints (in marine industry) are used to prevent biofouling on ships and fishing nets. Triphenylborane-pyridine (TPBP) is one of the alternative biocides. It is used for ship antifouling paint in some Asian countries, including Japan [15]. A commercial organic borane compound, pyridine-triphenylborane (PTPB) is often applied to ship hulls as an antifouling agent [16].

TPB [17] is used as a weak Lewis acid and complexing agent toward nitrogen-containing compounds. It also attracts interest as model compound for the preparation of poly(methylenetriphenyl borates). Lenskii et al. (2009) [18] examined polycondensation of triphenyl borate with 1,3,5-trioxane using boron trifluoride-ether complex as catalyst and xylene as solvent.

The reaction of TPB was carried out with the phenol and boric acid preferably mixed together in an inert water-immiscible organic solvent and the reaction was carried out at the boiling temperature of the reaction mixture. Although the reaction was carried out at temperatures between about 90-150^{o}C, the higher or lower temperatures may be employed depending upon the particular solvent and phenol present in the reaction mixture [19].

In a process, performance indexes have great importance to evaluate the thermodynamic efficiencies. In addition, energy quality is related to the capacity of energy in processes [20].

Exergy analysis has been worked during the past decades to improve the energy efficiencies. For example, the investigators studied a detailed exergy analysis for a distillation system to obtain the exergy destruction distribution [21].

In this study, the reactions of TPB were carried out by using both phenol and various boron sources in inert water-immiscible organic solvent (CCl_4) successfully. Unlike from the literature, TPB productions by using different boron sources were compared and the energy, exergy analyses were investigated in detail. The novelty of this paper is to synthesize TPB as original, unique material for anti-fouling applications. It was needed mass, energy and exergy balances for efficiency calculations to produce TPB. This paper also represents the feasibility of TPB productions from different boron sources. The analysis results (FT-IR, SEM, TGA/DSC) and exergy efficiency calculations have importance economically in terms of evaluation of this material in various applications as flame retardants, marine industry etc. Because, exergy means available energy and it is defined as the difference in amount between energy and anergy. It can be explained as the maximum amount of useful work. In addition, exergy analysis provides a better concept of the effect of thermodynamic phenomena on the process effectiveness, comparison of the precedency of various thermodynamic factors, and the determination of the most effective ways of developing the process. As a result, the energy and exergy analyses were performed to all TPB productions by using different boron sources and the exergy efficiency values were figured out. It was seen that the highest exergy efficiency was calculated with boron oxide as a boron source. By extension, characterization and exergy analysis promoted each other.

Experimental

Materials

The boric acid used was supplied from Eti Mine Works General Management. Also, boron oxide, borax decahydrate and borax pentahydrate were supplied from Eti Mine Works General Management. The phenol and CCl_4 used throughout the experiments were supplied from Merck.

Methods

The reaction of TPB was carried out with the phenol and boric acid preferably mixed together in an inert water-immiscible organic solvent (CCl_4) and the reaction was carried out at the boiling temperature of the reaction mixture. In addition to usage of boric acid, unlike from the literature, boron oxide, borax decahydrate and borax pentahydrate as boron sources were used to synthesize TPB. In a similar manner phenol (25.08-27.23%, w/w), boron sources (4.16-4.47%, w/w) and CCl_4 (63.43-70.75%, w/w) were mixed together and heated to approximately the boiling temperature of the solvent (76.8°C) for a period of 1 hours.

Solution of the crude borate was fractionally distilled until reaction completed (Fig. 1). In a similar

manner, phenol was reacted with CCl_4 and the presence of such as boric acid, borax decahydrate, borax pentahydrate, boron oxide. The reactions were given as Eq. 1-4:

$$3C_6H_5OH+H_3BO_3 \longrightarrow (C_6H_5O)_3B+3H_2O \quad (1)$$

$$12\ C_6H_5OH + Na_2B_4O_7.10H_2O \longrightarrow 4\ (C_6H_5O)_3B + 2\ NaOH + 15\ H_2O \quad (2)$$

$$12\ C_6H_5OH + Na_2B_4O_7.5H_2O \longrightarrow 4(C_6H_5O)_3B + 2\ NaOH + 10\ H_2O \quad (3)$$

$$6C_6H_5OH+B_2O_3 \longrightarrow 2(C_6H_5O)_3B+3\ H_2O \quad (4)$$

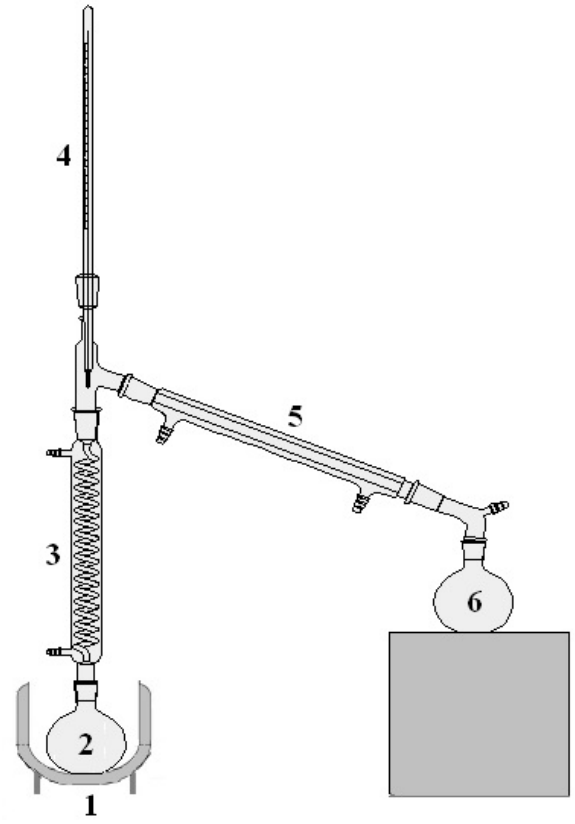

Fig. 1: Experimental set up: (1) Heater with jacket, (2) Reaction vessel, (3) Condenser, (4) Thermometer, (5) Distillation Column, (6) Sample vessel.

Characterization

The TPB products were characterized by using FT-IR (Bruker-Opus, Alpha-P) (Resolution for the normal setting is 4 cm^{-1}). FT-IR identified the functional groups present in TPB products. SEM analysis (Jeol – Model: 5410 LV) obtained the physical morphology and TGA/DSC (SDT Q600) showed the thermal behaviour of the products.

Results and Discussion

FT-IR Analysis

TPB products were characterized under determined conditions by FT-IR. Two vibrations (BO) were symmetric-antisymmetric B-O stretching modes. The absorption band associated with the latter was identified at 1350 cm^{-1} and it was the strongest band for TPB. The borate ion spectrum was seen at 910 cm^{-1}. The symmetric-antisymmetric stretching vibrations of the B-O were compared in TPB [22, 23] with similar vibrations of the BO_3. A strong peak at 505 cm^{-1} was obtained due to the symmetric deformation with the spectra of the alkyl borates at 544 and 525 cm^{-1}, respectively. It was expected to determine the corresponding band in the spectrum of TPB at a lower band (598 cm^{-1}). C-O stretching vibration in TPB was seen at 1214 cm^{-1}. Although this band was in range of the C-H deformation vibrations of the benzene ring, it was the substantial band in that region.

As a result, the C-H stretching vibrations in TPB showed weak absorption. The ring deformation was found at 635 cm^{-1} as previous study [24] (Fig. 2).

SEM Analysis

Morphological structures of products were determined by using SEM. Particle sizes of boric acid, boron oxide, borax decahydrate, borax pentahydrate were 59-109 μm, 21-67 μm, 7-14 μm and 3-20 μm, respectively. The particle sizes of TPBs [22, 23] by using boric acid, boron oxide, borax decahydrate, borax pentahydrate were changed in range of 14-20 μm, 17-39 μm, 8-17 μm and 8-20 μm, respectively. Therefore, the particle sizes of products boric acid were more undersize than reference boric acid (Fig. 3).

TGA/DSC Analysis

TGA measurements were carried out using SDT Q600. The TPB samples were put into a silisium pan. They were heated from 20 to 900°C under N_2 flow at 10°C/min. DSC scans of TPB samples were obtained in a SDT Q600 DSC connected to a SDT Q600 computer. Thermal profiles of TPB were determined under isothermal conditions in Fig. 4. TG analysis of as-prepared powder gave 80-97% a sharp weight loss between 20-900°C for TPB (Fig. 4). The peak temperature values in

TGA/DSC are also consistent with the literature [25-28]. The DSC scans were typical of TPB in the amorphous state. The scans displayed a glass transition, small exothermic peaks (at about 60°C) and large exothermic peaks (at 150°C). Curve differences in DSC were apparent depending on boron sources. The amorphous state of the product was obtained by the presence of a heat capacity changed with the boron sources changed.

Thermal characterization of the amorphous solid under determined conditions suggested that usage of different boron sources to stabilise the amorphous state had effects in TPB production.

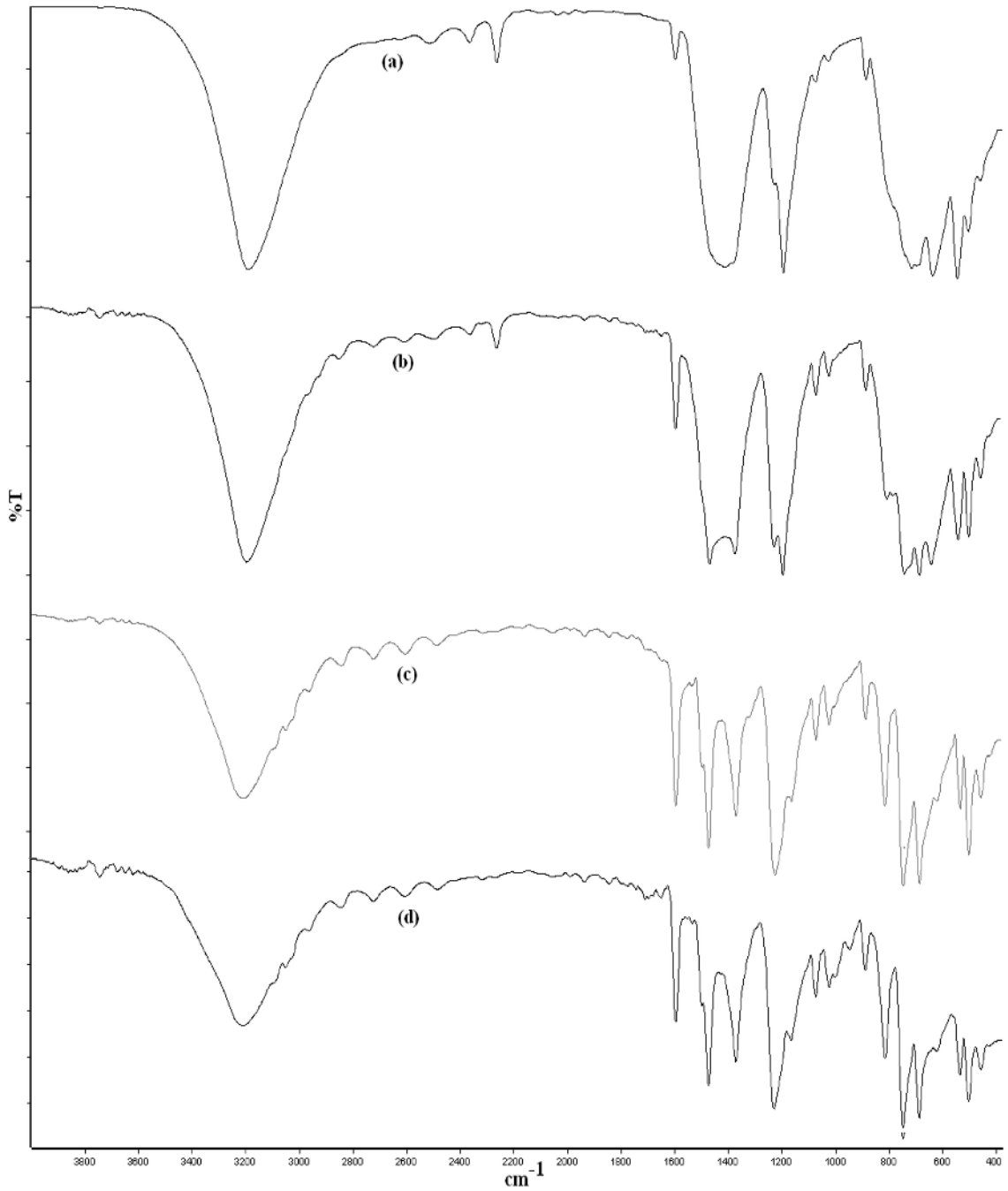

Fig. 2: FT-IR spectra of TPB by using (a) Boric acid , (b) Boron oxide, (c) Borax decahydrate, (d) Borax pentahydrate.

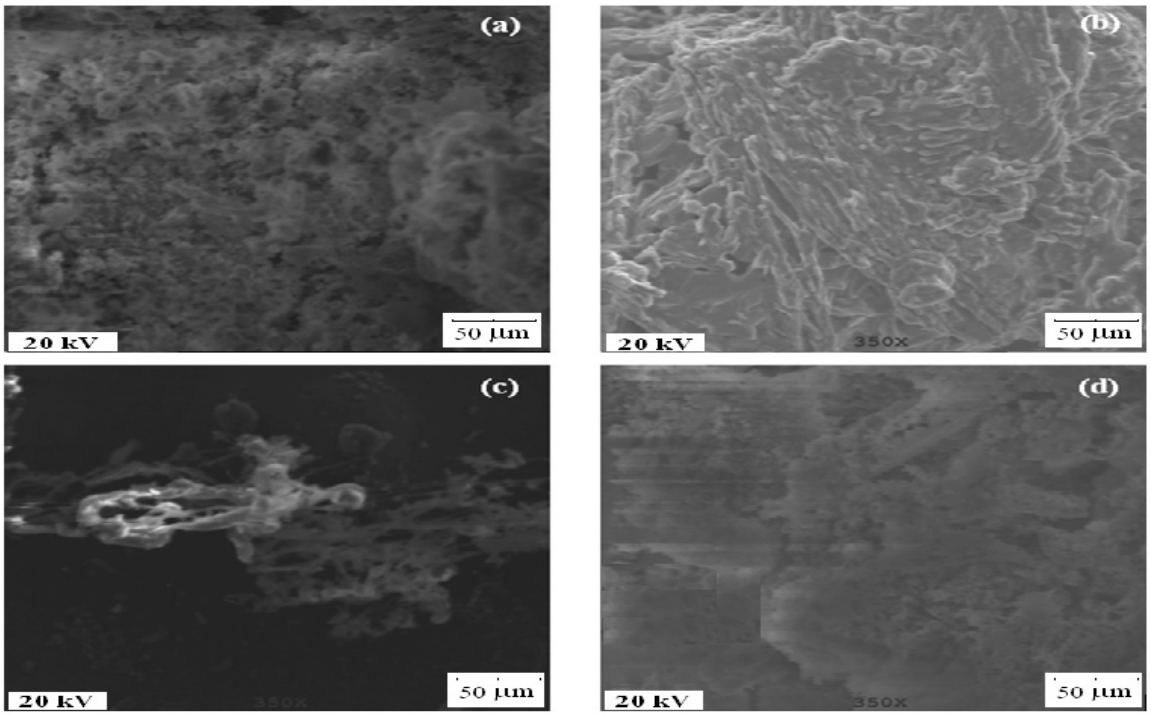

Fig. 3: SEM images of TPB by using: (a) Boric acid (x350), (b) Boron oxide (x350), (c) Borax decahydrate (x350), (d) Borax pentahydrate (x350).

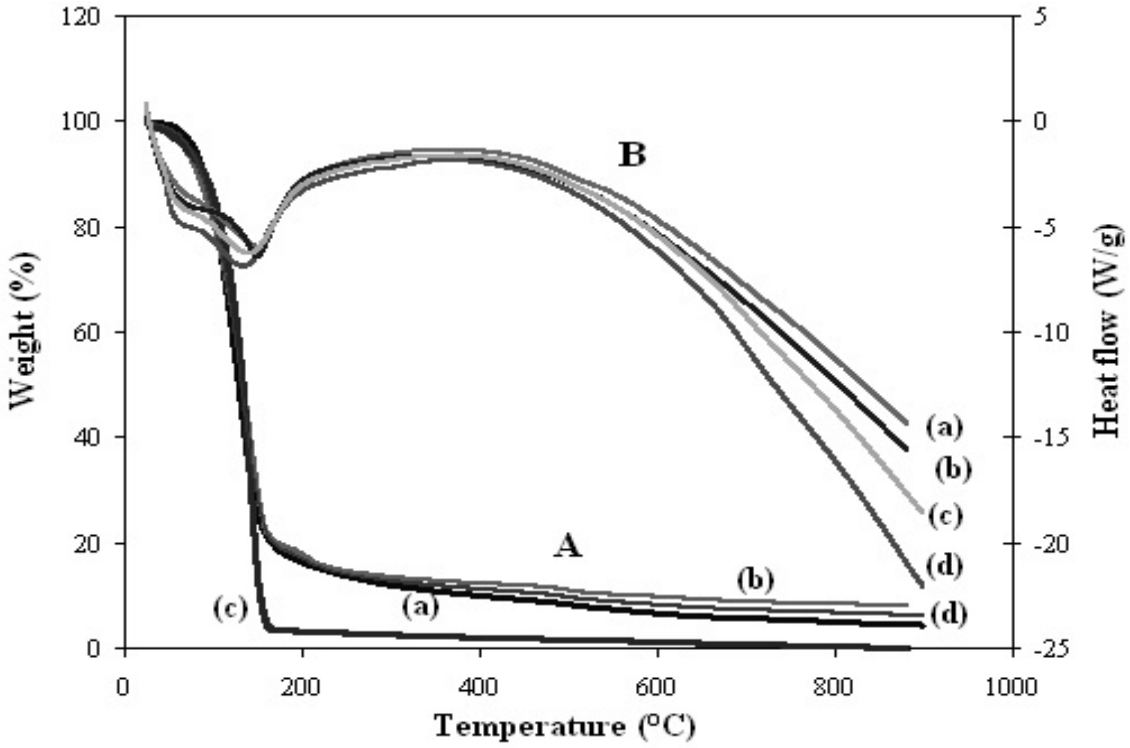

Fig. 4: TGA/DSC analysis: A – all TGA; B – all DSC: a - TPB by using boric acid; b - TPB by using boron oxide; c - TPB by using borax decahydrate: d - TPB by using borax pentahydrate.

Energy and Exergy Analyses

Exergy means the maximum amount of useful work when the system is brought to equilibrium with the surroundings through reversible processes [29]. Three points have significance for energy and exergy terms. First, exergy is useful part of energy, notwithstanding energy counts all energy flows regardless of their working potential [30]. Second, exergy is not preserved, however energy is preserved. Third, energy forms are accounted for thermodynamically and contain all possible forms such as chemical, mechanical, potential energy etc. This means that exergy equally clarifies materials, movements, currents or heat and the transformations between each other [31].

The main equations involving mass, energy and exergy [32, 33] are given for the individual components of the system. This components are used as control volume at steady state.
Mass balance is written as Eq. (5):

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \qquad (5)$$

where "i" indis shows input and "e" indis output.

Energy balance is applied as Eq. (6):

$$\sum_i \dot{m}_i .h_i + \dot{Q}_{cv} = \sum_e \dot{m}_e .h_e + \dot{W}_{cv} \qquad (6)$$

Exergy balance is expressed as Eq. (7):

$$\sum_i \dot{m}_i .\Psi_i - \sum_e \dot{m}_e .\Psi_e = \dot{W}_{cv} + \dot{I} \qquad (7)$$

where Ψ shows exergy flow and $\dot{I}$ is irreversibility

Exergy shows the measure of energy quality in a given environment. Exergetic balance indicates how much exergy will be lost in process. This exergetic losses display a measure of degradation for energy quality. The total exergy (Ex) can be stated as Eq. 8 [20, 34]:

$$Ex = Ex_K + Ex_P + Ex_{PH} + Ex_{CH} \qquad (8)$$

The kinetic (Ex_K) and potential (Ex_P) exergy components can be displayed with ordinary kinetic and potential energy equations. The physical exergy (Ex_{PH}) is explained as the maximum amount of work obtained by physical processes as Eq. 9-13 [20]:

$$\Delta H = \dot{m}.(h - h_0) = \dot{m}.\int_{T_0}^{T} C_p.dT \qquad (9)$$

$$\Delta S = S_s - S_0 \quad \text{(kJ/kg.K)} \qquad (10)$$

$$\Delta S = m.C_p.\ln(\frac{T_s}{T_0}) \qquad (11)$$

$$\Delta S = \dot{m}\int_{T_0}^{T} C_p.\ln(\frac{T}{T_0}) \qquad (12)$$

$$E_{PH} = \Delta H - (T_0.\Delta S) \quad \text{(kJ/h)} \qquad (13)$$

where S shows entropy; T_0 environment temperature; H enthalpy.

The total chemical exergy (Ex_{CH}) is stated as maximum work amount obtained by a reversible process containing only mass, heat and compression-expansion work transfer. The specific chemical term of mixture is showed as Eq. 14:

$$\sum Ex_{CH} = \dot{m}.\sum x_i(Ex_{CH,i} + R.T_0.\ln(x_i)) \qquad (14)$$

where $Ex_{CH,i}$ represents specific exergy; x_i is mass fraction. The exergies of TPB productions with different boron sources were calculated by using Eq. 9-13 as Tables 1-4.

Efficiency ratio is a performance criteria and the exergy relations between flowing out of process (Ex_e) and into the process (Ex_i) can be explained with the ratio [20]. The exergy efficiency (Table 5) is defined as Eq. 15:

$$\psi = \frac{\sum \Delta Ex_e}{\sum \Delta Ex_i} \qquad (15)$$

The exergy values calculated from Tables 1-4 were used to Figure out the exergy efficiency by using Eq. 15. As a result, the exergy analysis calculations have importance in terms of industrial applications, economically. This study revealed that the usage of various boron sources effected the exergy efficieny and the maximum exergy efficiency was obtained as 37.57% by using boron oxide source in TPB production. This result showed that the usage of boron oxide was more proper to produce TPB.

Table-1: Exergy analysis of TPB production by using boric acid.

INPUT	Mass Flow (kg/h)	Physical Exergy (J/h)	Standard Chemical Exergy (J/mol)	Chemical Exergy (J/h)	Total Exergy (J/h)
Boric acid	0,000412	0,00	29000	193,23	102630,75
Phenol	0,0025	0,00	3126200	83046,44	
CCl_4	0,00631	0,00	472700	19391,09	
	TOTAL	0,00	TOTAL	102630,75	
OUTPUT					
TPB	0,0024	30,38	2172980	17975,84	37474,90
Water	0,001024	11,61	900	51,20	
CCl_4	0,00631	14,77	472700	19391,09	
	TOTAL	56,77	TOTAL	37418,13	

Table-2: Exergy analysis of TPB production by using boron oxide.

INPUT	Mass Flow (kg/h)	Physical Exergy (J/h)	Standard Chemical Exergy (J/mol)	Chemical Exergy (J/h)	Total Exergy (J/h)
Boron oxide	0,000415	0,00	69400	413,69	105079,19
Phenol	0,0025	0,00	3126200	83046,44	
CCl_4	0,007035	0,00	472700	21619,06	
	TOTAL	0,00	TOTAL	105079,19	
OUTPUT					
TPB	0,002374	30,06	2172980	17781,11	39479,88
Water	0,000541	6,13	900	27,05	
CCl_4	0,007035	16,47	472700	21619,06	
	TOTAL	52,66	TOTAL	39427,22	

Table-3: Exergy analysis of TPB production by using borax decahydrate.

INPUT	Mass Flow (kg/h)	Physical Exergy (J/h)	Standard Chemical Exergy (J/mol)	Chemical Exergy (J/h)	Total Exergy (J/h)
Borax decahydrate	0,00041	0,00	1686850	1813,44	104220,23
Phenol	0,0025	0,00	3126200	83046,44	
CCl_4	0,0063	0,00	472700	19360,36	
	TOTAL	0,00	TOTAL	104220,23	
OUTPUT					
TPB	0,002475	31,33	2172980	18537,59	37971,02
Water	0,00044	4,99	900	22,00	
CCl_4	0,0063	14,75	472700	19360,36	
	TOTAL	51,07	TOTAL	37919,95	

Table-4: Exergy analysis of TPB production by using borax pentahydrate.

INPUT	Mass Flow (kg/h)	Physical Exergy (J/h)	Standard Chemical Exergy (J/mol)	Chemical Exergy (J/h)	Total Exergy (J/h)
Borax pentahydrate	0,00041	0,00	1219760	1716,50	104031,10
Phenol	0,0025	0,00	3126200	83046,44	
CCl_4	0,00627	0,00	472700	19268,16	
	TOTAL	0,00	TOTAL	104031,10	
OUTPUT					
TPB	0,00245	31,02	2172980	18350,34	37692,42
Water	0,00046	5,21	900	23,00	
CCl_4	0,00627	14,68	472700	19268,16	
	TOTAL	50,91	TOTAL	37641,51	

Table-5: Exergy efficiency of TPB production by using different boron sources.

Experiment No	Boron sources	Exergy efficiency (%)
1	Boric acid	36.51
2	Boron oxide	37.57
3	Borax decahydrate	36.43
4	Borax pentahydrate	36.23

Conclusion

Turkey is an abundant country in terms of boron sources. By this means, boron sources could be evaluated for various applications with consist of this study. In conclusion, FT-IR, SEM and TGA/DSC analyses displayed that TPB was successfully produced with determined conditions and the TPB produced had different glass transmission temperatures by using different boron sources for various applications. The usage of different boron sources effected the exergy efficieny and boron oxide was selected the most efficient boron source for TPB production due to the highest exergy efficiency (37.57%). As a result, it was seen that characterization and exergy analysis promoted each other.

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