TREATMENT METHODS OF BUTADIENE ON HTPB (*HYDROXY TERMINATED POLYBUTADIENE*) PRODUCTION TO MEET THE PURITY REQUIREMENTS OF FRESH BUTADIENE*

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Abstract

HTPB was the important propellant binder material of solid rockets. In order HTPB production process efficiency , it is necessary to process improvement method that equipment cost , energy , and raw material efficiency. During this time , the process of making raw material butadiene HTPB using pure grade (99.8 %) . The research aims to obtain the optimal processing method utilizing technical grade butadiene that available in producent of butadiene.

The study was conducted in two stages . The first stage is to find the minimum conditions necessary for the quality of butadiene can be used as fresh feed to the reactor HTPB . HTPB is made by by the radical polymerization of butadiene using catalyst 32 % hydrogen peroxide. Butadiene is fed into the reactor of HTPB with capacity 1 L , the reactor is run for 1 hour. The results of HTPB is separated by extraction using hot water , weighed and tested structure by FTIR and tested an average molecular weight by GPC (Gel Permeation Chromatography) . The research variables are stabilizers and butadiene concentrations . The second stage is to start treatment on technical butadiene with butadiene technical laundering in order to be processed into HTPB reactor. Technical butadiene before entry into the reactor were washed in water , and then boil up at a temperature of 40 ° C , and then fed into the reactor HTPB 1 L with the same operating conditions . HTPB results observed weight , structure , and average molecular weight .

The results showed that the minimum terms that HTPB is formed when butadiene purity of 98 % and a maximum of 0.1 % stabilizers concentration . Technical butadiene has a purity of between 86-98 %. Efforts to utilize technical butadiene using washing method can improve the purity butadiene from 86-98 % to 98 % so it can be fed into the reactor HTPB fresh .Therefore , to take advantage of technical butadiene as fresh bait needs to be added butadiene laundering.

Key Words: *HTPB, butadiene, propellant, rocket*

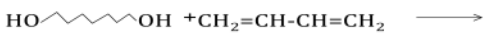
1. Introduction

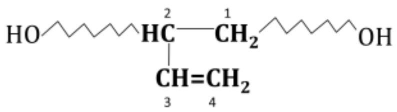
HTPB is a polybutadiene resin premises hydroxyl end groups . HTPB is used as a material for the manufacturing of composite resin , elastomer or synthetic rubber , foam , adhesives , and coating materials . HTPB is a good elastomer mechanical properties and have a good combustion energy to be used as a binder composite propellants . HTPB is the main ingredient of modern composite propellant(5). It is serve as fuel binder HTPB composite propellant . HTPB use in production is largely used to meet the requirements of composite propellants . HTPB has the structure and molecular weight vary and the resulting polyurethane elastomer will be different characteristics. Therefore , HTPB manufactured in accordance with the desired characteristics .

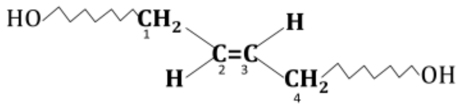
HTPB in the industry are usually made by radical polymerization of butadiene using hydrogen peroxide catalyst(3) . Results of previous studies showed that the HTPB successfully made using radical polymerization system , using 32 % hydrogen peroxide catalyst and solvent ethanol or n-butanol . HTPB production reactor system design has been made for a capacity of 1 L with HTPB result was produced with a yield of 40% by using a butadiene content of 99 %(11) . In order to get to industrialization , it is necessary to measure the efficiency that can be used cost of equipment , raw materials , energy , and human resources are cheap but still produce high productivity . One effort to do is to use local raw material butadiene are usually in the technical grade . If able to be produced , then the cost of making both operational HTPB be cheap . For comparison is pure butadiene gas price is Rp . 400.000, - per liter , while the price of technical butadiene is Rp. 80.000 , - per liter . Thus , the effort to replace butadiene gasfrom pure grade to technical grade must be done in order to achieve efficiency in raw material prices .Technically , technical butadiene has a purity of 86-98 % , pure butadiene has a purity of 99.8 % (10) . Technical butadiene has stabilizers and impurities like butane and butene that can interfere on the formation of HTPB . Technical butadiene should be treated earlyin order to remove stabilizers and to minimized imputities. Butadiene can be purified by washing or distillation . If the minimum requirements necessary purity butadiene production as fresh material obtained , then there is a pretreatment technology that butadiene purity can be increased up to the minimum standard required , then the efficiency of the raw material can be obtained .This paper will present treatment method of butadiene in order to meet the purity requirements of fresh butadiene.

2. Theory

HTPB is a polymer base on butadiene monomer with hydroxyl end groups (HO - (C4H6) n - OH). The polymerization of butadiene by addition mechanism to the butadiene chain that made possible isomer 1.2 and 1.4 [(3)].The1.2 isomer refers to the bonding of the atoms C bond polymerization No. 1 and 2 (a) , while the 1,4 bond is a bond refers to the polymerization of the C atom No. 1 and No. 4 on the C atom butadiene monomer . The 1,4-isomer can be distinguished whether the bonding configuration of cis or trans. Cis bond is a bond where there is the same group in a position to line one side of the double bond (b) , trans bond is a bond where there is the same group in the opposite position (c) .

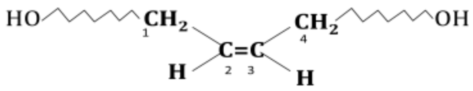






(1)

(a) (b)



(c)

Theoretically, there are two ways of making HTPB, ionic polymerization and radical polymerization . Ionic polymerization catalyst performed using alkaline earth metal ion (LI , Na , K) or alkaline earth metal organic (Buthyl lithium, Buthylnatrium, etc.)[(3)]. Polymerization takes place with the growth of one by one method. Ionic polymerization is very difficult and is not applied in the industry because it requires a high vacuum conditions so that the process is very expensive [(10)] .

HTPB is usually made in industrial scale by radically mechanism using raw material butadiene, hydrogen peroxide catalyst , and alcohol as solvent[(3)]. The results showed that the HTPB can be produced from the polymerization of butadiene with a catalyst 32 % hydrogen peroxide in ethanol solvent at a temperature of 178^{o}C[(9)]. To get HTPB with an average molecular weight of 2500-5000 gr/mole, it will take 1 hour process time. Theoretically, the formation of HTPB reaction begins with the formation of radicals from hydrogen peroxide to form a radical butadiene monomer (M *) as shown in equation (2) . Furthermore radicals will react with other monomers to form a radical butadiene containing monomer or the more lengthy as shown in equation (3) to (5) . Polymer growth will stop if the radicals is collide as shown in equation (6) .

$$H_2O_2 + M \rightarrow 2MOH^* \quad (2)$$
$$MOH^* + M \rightarrow M_2OH^* \quad (3)$$
$$M_2OH^* + M \rightarrow M_3OH^* \quad (4)$$
$$M_nOH^* + M \rightarrow M_{n+1}OH^* \quad (5)$$
$$M_nOH^* + M_mOH^* \rightarrow HOM_{n+m}OH \quad (6)$$

2.2 . Factors Affecting Production

Based on the reaction kinetics of the formation of HTPB , the general factors that affect HTPB products is monomer concentration , catalyst concentration, the operating conditions such as reaction temperature, pressure and stirring [(1)] .

(1) Based on Le Cathelier principle , then to get the results that many chemical reactions should be shifted to the right . To shift to the right the concentration of raw materials (butadiene) should be increased , so that the reaction equilibrium shifts to the right .

(2) The speed of stirring will increase the surface area of contact between the molecules, so that the frequency of collisions between the particles more and a greater possibility of reactions occur . Thus the higher the complaint , then the reaction will be faster.

(3) Based on the Arrhenius theory , that the rate constant of the reaction kinetics depends on the speed of the collision. The increase in reaction temperature will increase the kinetic energy of the collision , so the reaction will be greater.
(4) The function of a catalyst is necessary: lowering the activation energy for the reaction . The more catalyst is used, the activation energy will become increasingly fall , so it will be a common reaction , the reaction will be increased.

2.3 . Requirements of The Polymerization Reaction

Based on the reaction mechanism as shown in equation (1) to the equation (6) , then there are requirements that must be met before running the polymerization reaction. The hydrogen peroxide must maintain at high concentration that all of them react to form hydroxyl radicals as shown in equation (2). If the hydrogen peroxide is dilute, the hydroxyl radical is not produced, so the reaction stops.

The reaction of hydroxyl free radical formation in equation (2) can occur at high temperatures and high concentrations of catalyst[2,6] . If the concentration of catalyst is low, the resulting decomposition reaction are hydroxyl ions (OH-). The simultaneous equations decomposition of hydrogen peroxide at high temperatures is shown in equation (7) in which the reaction rate constants k_1 shows the decomposition of hydrogen peroxide .

$$H_2O_2 \rightarrow OH^* + OH^- + H_2O + O_2 \quad (7)$$

Hydroxyl radicals to be generated by increasing the reaction rate constant (k_1) or by shifting the reaction to the right. Raise the reaction rate can be done by raising the reaction temperature. Reaction shifts to the right can be done by taking each outcome (oxygen and water) are formed . The amount of water vapor is allowed in the decomposition reaction can be determined by experiment variation of water content of hydrogen peroxide , butadiene water content , and water content of the solvent (alcohol) .

Butadiene materials typically be in the mix with other ingredients such as 1-buthane and 1-buthene. Ingredients 1-buthane and 1-buthene reacts with hydrogen peroxide to form a buthanol and buthaldehyde so the butadiene is not polymerize.

Butadiene materials have low stability , easily polymerized to form dimers or trimers that are stable, so it can not be polymerized by hydrogen peroxide. For storage purposes, the butadiene was added stabilizers that are not oxidized or polymerized, such as hydroquinone , tertbuthylcatecol , and others [4] .

2.4 . Purification of Butadiene

Butadiene is produced from the cracking of petroleum materials. Butadiene in the technical grade will consist of a stabilizer material tertbuthylcatecol , dimer , trimer , water , buthanol , and other carbon materials such as ethane, buthene, etc.

Purification of butadiene in the industry is usually performed by washing in water, so that all material that soluble in water, and the resulting gas is fed directly into the HTPB production system. Distillation butadiene will remove all material that soluble in water, solids , and insoluble in water . Selection of purification methods are usually tailored to the character or quality of the desired polymer, as well as the cost of production [4,5].

3. Methode

The study was conducted by using a autoclave reactors for butadiene polymerization reaction 1 L capacity that come with a cooling fluid, heating up to temperatures of 200^{o}C, regulator of stirring up to 200 rpm.

Early stage of research is to obtain butadiene moisture content allowed in order to produce HTPB. The butadiene is polymerize using technical grade materials varies from 68-98 % , then testing the structure of HTPB with FTIR.

The second research is to design an pretreatment of butadiene technical grade to get the minimum levels requirement. The technical grade butadiene attempted purified by passing into the water absorber, then boil up at a temperature of 40 ^{o}C, then butadiene proceeds are used as feed on the the HTPB production. HTPB generated is charaterized by FTIR (Fourier Transform Infra Red) spectroscopy to ensure that the polymer formed. HTPB also tested for molecule weight characterization by GPC (Gel Permeation Chromatography). HTPB structure is indicated absorbtionInfra red at specific wave length 2270 cm^{-1}, 710 cm^{-1}, 910 cm^{-1} , or 790 cm^{-1}[7,8].

Fig. 1.Reactor HTPB

4. Result and Discussion

To get the minimum requirement butadiene purity that fed into HTPB reactor, some of butadiene with varied levels of 68-99 % is fed into the HTPB reactor. Concentration limits are made to follow butadiene available in the market, where technical butadiene levels varied from 68-98 %. Butadiene is polyerized in HTPB reactor. The test results are shown in table 4-1. At the butadiene purity is 68 up to 97 %, apparently HTPB not formed. It is characterized by the absence of polymer extracts obtained after the solution was washed with water and benzene. This suggests that there is a minimum limit of butadiene for the reaction to run. Butadiene purity that can be used is at least 98%. Interesting to butadiene gas treatment can be designed to have a minimum level of 98 % butadiene .

Table 1.Polymer results in a variation of butadiene purify

No.	**butadien purify (%)**	**HTPB (gr)**	**FTIR identification**
1	68	0	-
2	75	0	-
3	80	0	-
4	90	0	-
5	96	0	-
6	98	100	+
7	99	100	+

Treatment of butadiene is done by passing into washing column of water where the water soluble impurities such as trimers and dimers can be removed. Subsequent treatment of butadiene pass a absorber tube heater temperature 40 °C to remove most of buthene-1 and stabilizers catecol. Washing is done by using a factor of 1:10 laundering , meaning that the total butadiene flowing is 1/10 of the total volume of water needed. Gas distillation carried out at 40^oC so that all are in the gas butadiene , buthene-1 can be left partially and buthylcatecol in the solids form can be left behind and sequestered absorber of silica.

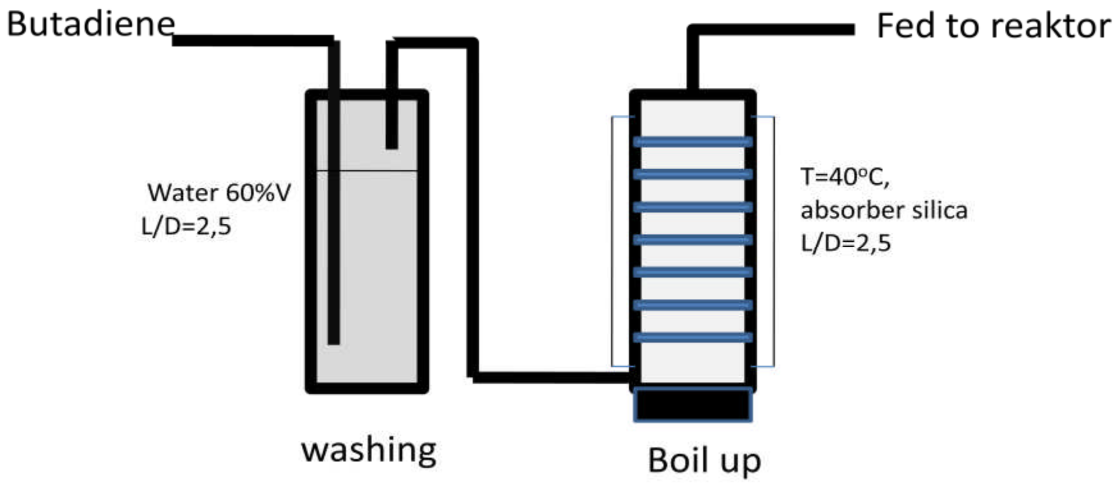


Fig. 2 . Technical butadiene treatment proccess

The test results of gas content of butadiene shown in Table 2. Butadiene gas assays performed with gas chromatography. Removed catecol is measure the difference in weight of butadiene gas in the bottle before and after vaporized. Based on the test results , it turns on all the technical butadiene gas after passing through treatment will have catecol levels of 0.1% and a butadiene purify increased 98.5 % . Thus, the initial treatment is needed for technical butadiene gas in order to meet the requirement as fed material into the reactor. Catecol is a solid compounds while butadiene at room temperature in a state of gas-liquid equilibrium, although the amount of gas over a lot of the liquid . Catecol can be separated if all of butadiene in the gas phase. It is evident that almost all catecol be drawn from butadiene gas is distilled at 40^{o}C.

Table 2 . Butadiene concentration analysis results after initial treatment

No.	**Before treatment**		**After treatment**	
	butadien purify (%)	**catecol (%)**	**butadien purify (%)**	**catecol (%)**
1	68	4,1	98,5	0,1
2	75	2,1	98,5	0,1
3	80	2,1	98,5	0,1
4	90	1,3	98,5	0,1
5	98	1,3	98,5	0,1

Furthermore, to prove that the butadiene after initial treatment can be fed into the HTPB reactor, then all samples that had been given technical grade butadiene pretreatment later incorporated into the polymerization reactor. The results shown in Table 3. It turns out all the technical grade butadiene can be generated HTPB. The analysis showed that HTPB formed with the formation of a viscous liquid after extracted with hot water. Test results with FTIR showed an absorption at wave length 2273cm^{-1} as the long form of the CO bond specifically for HTPB structure, the 910cm^{-1} absorption as a form of the double bond and 710cm^{-1} as the form of the cis double bond configuration.

Table 3 . HTPB analysis results with butadiene feed after pretreatment

No.	**butadiene purify (%)**	**HTPB (gr)**	**FTIR identification**	**Molecule weight**
1	68	100	+	3000-5000
2	75	102	+	3000-6000
3	80	103	+	3000-5000
4	90	100	+	3000-5000
5	98	100	+	3000-5000

The test results with GPC can be shown that the average molecular weight of the polymer is 3000-5000 grams per mole . These results indicate that butadiene is used as fresh material has the same specification especially butadiene purify. Thus , HTPB can be produced from fresh feed with low purify of butadiene at least 98 % and the maximum content of stabilizers is 0.1 %. To be able to use the technical butadiene , it would require pretreatment such as washing and distillation at 40 °C to obtain a yield of 98.5 % purify butadiene with catecol content below 0.1 %.

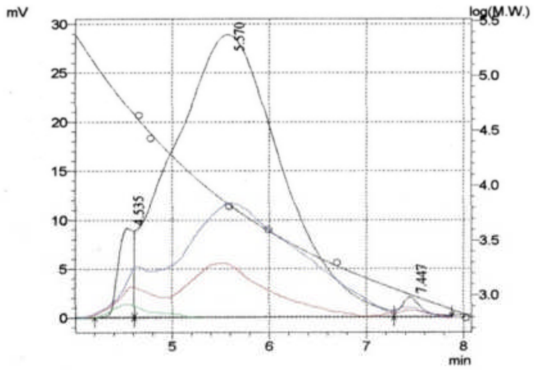


Fig. 3. GPC identification of HTPB

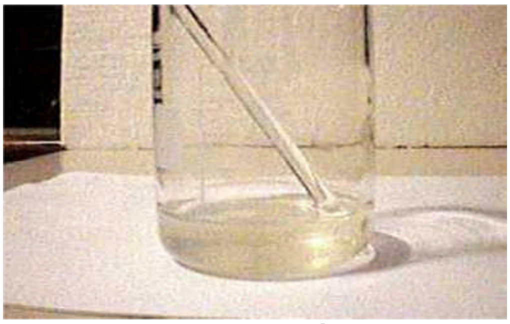


Fig. 4. HTPB product

5. Conclusion

Based on the analysis and testing, it can be generatedthat there is a minimum order butadiene purify requirement can be used as fresh feed in the HTPB reactor. Minimum requirement butadiene gas can be used as bait fresh is to have 98 % and the content of buthylcatecol levels less than 0.1 % . Pretreatment of the technical grade butadiene who coined levels may increase from 86-98 % purityto 98.5 % and 0.1 % levels of maximum catecol. Technical grade butadiene after going through treatment can be fed fresh start at making reactor HTPB with good results .

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