Proceedings International Seminar of Aerospace Science and Technology 17th SIPTEKGAN -2013, 32: 228-238

DESIGN AND INTEGRATION TEST OF PILOT SCALE PRODUCTION OF HTPB BY CONTINUOUS PROCESS*

Heri Budi Wibowo[1)], Lee Suuk[2)]
[1)]Rocket Technology Center, National Aeronautics and Space Institute - LAPAN
[2)]Reaction Eng. Co. Ltd, Korea
heribw@gmail..com

Abstract

This paper is adesignof a reactor HTPB pilot scale manufacturing process. HTPB designed products have the characteristics of an average molecular weight of 2500-5000 g/mol, the dominant structure of 1,4 -HTPB, with a production capacity of 2 tons per year. Process HTPB production mechanism using free radical polymerization method with hydrogen peroxide catalyst and solvent alcohol.

Design is calculated base on production capacity of 2 tons per year and 40 % conversion. The process principle is:raw materials butadiene is fed into the reactor at a temperature of 180 °C and a pressure of 300 psi. H_2O_2 catalyst material introduced into the reactor with a flow rate of 0-100 mL per minute at a temperature of 170 °C. Technical ethanol solvent fed to the reactor at a flowrate 0-100 mL per minute at a temperature of 180 °C and a pressure of 300 psi. The reactor type is a reactor pipe flow reactor. Reaction products from the reactor is then cooled and separated from other solvents by solvent extraction. Butadiene reresidue and ethanol is separated from the products by distillation, and then fed back into the reactor.

Design has acquired production equipment systems that support continuous HTPB. Simulation results indicate that the program HYSIS fluid flow every pipe in accordance with the desired and demonstrate appropriate products. Results of testing equipment that has been developed and integrated show that HTPB can be produced with a capacity of 2 tons per year and it worked fine. HTPB test results showed that the average molecular weight of 2500-5000 g/mol with the dominant structure is 1,4-HTPB (60%). Catalyst reacts completely exhausted.

Key Words: *HTPB, polybutadiene`, butadiene, propellant*

1. Introduction

Space agency in accordance with the strategic plan, that mastery of rocket technology is intended to develop the ability to launch the rocket in accordance charge of the mission, both civilian mission and defense security missions. Rocket technology needed to master a great independency both in structure, electronics, as well as providing for the transfer of technology booster rocket motor areas are very difficult to obtain from developed countries.

Based on the mission, the rocket carrying the satellite can be used for various purposes, Sonda payload to study the characteristics of the air, and took charge of the defense and security interests. Rocket development began to get a place for the benefit of the launching of satellites orbiting satellite based development of rocket RX-550 rocket motor to deliver nano satellites into low orbit. RX-550 rocket was developed with a target altitude of 100 km using a diameter 550 mm, length 6000 mm,and HTPB composite solid propellant types. Self-sufficiency in the supply of propellant is important because it can overcome the propellant material procurement difficulties that cannot be continuous from the overseas manufacturers. As a result of propellant raw materials obtained from different manufacturers, the quality and characteristics of different propellant rocket complicate the design with the same characteristics (standard).

Composite solid propellant is shaped solid propellant consisting of granular oxidizer and additives are dispersed in a polymer matrix. Composite propellant base HTPB is being developed with the use of propellant oxidizer ammonium perchlorate (AP), HTPB binder material (*Hydroxy Terminated polybutadiene*) and the additive primary aluminum (Al). To get a good propellant formulations, the composition of which can be used is 70-75 % AP, HTPB 10-20 %, Al 5-15 %, and 0-5 % other additives.

Based on map material needs for research and development propellant rocket LAPAN, where it takes 10 tons of propellant per year, then the purpose of raw materials Ap is 10 tons per year, HTPB 2 tons per year, and aluminum is 1 ton per year. Ap and HTPB materials are strategic material because it is only used for rocket propellant. Aluminum materials are readily available as it is also widely used materials industry. The expected result is the availability of HTPB production capacity of 2 tons per year (PILOT scale). HTPB desired is the specifications of fuel binder HTPB propellant and lasts continuously for HTPB guarantee results every time the same process and quality standards.

Materials binder HTPB propellant fuel specifications have requirements average molecular weight of 2000-5000 gr/mol, the viscosity of 500cp, the main structure of cis 1, 4-HTPB (minimum 30 %). Based on existing publications, HTPB materials with the main structure of cis 1, 4 polymerization of butadiene can be made by using a metal catalyst buthyl lithium or lithium (Wibowo, 2004). Buthyl lithium materials are chemicals that require considerable handling complex that is not the top choice. The main difficulty in making HTPB research is that the reaction must be free of air and very high purity butadiene. To get HTPB with the dominant structure of cis - 1, 4-HTPB and the average molecular weight of 2800, it is necessary to study the manufacture of HTPB with variable catalyst concentration, butadiene concentration, operation temperature and pressure. If the structure and molecular weight HTPB as a function of catalyst, butadiene gas concentration, operating temperature and pressure is obtained, by planning HTPB pilot scale manufacturing. The final results in the form of pilot scale equipment manufacturing HTPB (200 kg/year) to meet the needs of LAPAN.

HTPB material is a material that is not commercially available, so the acquisition is difficult, especially associated with the military industry. Therefore it is necessary to be able to make yourself so HTPB propellant composite primary purposes of solid materials can be satisfied yourself.The propellant composition is tailored based on the reference of the mechanical properties of solid propellant as seen in Table 1.

Table 1 . Mechanical properties of polyurethane for solid propellant ever used

Composition	TS ($kgcm^{-1}$)	E (%)	hardness	Reference
HTPB/TDI/TMP R=0,8	1,2-8,9	129-30		Manjari et.al.(1994)
HTPB:TDI, R=1	4-16	90-1080	4-16	Jain et.al. (1993)
Polisiloksan	2,4-9	65-100		Agrawal et.al.(1998)
HTPB: TDI	5,3-13	83-74,4	25-50	Gupta et.al. (1997)
MDI	6,6-15,3	71,9-56,8	30-58,4	
HMDI	3,2-8,8	147-51,9	27-55,2	
IPDI	3,6-9,4	62-93	26-43,7	
HTPB:TDI	15,3	123	62	Gupta et.al. (1995)
MDI	16,3	100,5	70	
HMDI	14,5	74,3	68	
IPDI	**14,6**	**153,0**	**54,7**	
Glisidil asida	4-10	78-90		Duncan (1995)
HTPB-TDI	4 – 10	85–400		LAPAN (2000)
HTPB-IPDI	4 – 7	100-300		
Solithane	6–15	75-350		

2. Theory

2.1. Need of HTPB

HTPB - making technology in the lab can be done by using a batch reactor capacity of 1 L using radical methods with hydrogen peroxide catalyst. Once the process is obtained HTPB 100 mL. To meet the needs of larger HTPB can be upgraded to the PILOT scale (scale above 1 tonne per year). Data covering the design and type of raw material composition, operating conditions, aspect reaski kinetics, and analysis of all the results have been obtained.

Because the process of HTPB has high sensitivity results in the presence of a catalyst composition, operating conditions and reaction time, the results of each does not have the same standard characteristics. For further processing, it is necessary the systems with continuous system, to guarantee standardization product obtained. The research base has a production capacity of 1 ton per year. Types of reactors that can be used is the pipe flow reactor (Plug Flow Reactor, PFR) or flow stirred tank reactor (Continuous Stirrer Tank Reactor, CSTR).

The reactor can produce the desired fuel quality binder HTPB propellant with a maximum production capacity of 1 ton, effective products 60 % , using a continuous system. HTPB has produced specification : the requirements of the average molecular weight of 2000-5000 , the viscosity of 500 cp , the main structure of cis-1,4-HTPB (minimum 40 %), good shape polyurethane with toluene diisocyanate (TDI).

2.2 . Electoral Process

To ensure a good HTPB obtained, then the selected free radical polymerization reaction system. The raw materials used are butadiene premises of at least 98 % purity. Free radical reaction system according to the method of (Wibowo, 2009), namely polymerization catalyst with 32 % hydrogen peroxide, 80-95 % solvent ethanol. Catalyst concentration is 5 -10 % , solvent 50-60 % , with the minimum conversion of butadiene is 40 %.

HTPB is usually made in industrial scale by radically mechanism using raw material butadiene, hydrogen peroxide catalyst, and alcohol as solvent (Flory, J., 1979). 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^oC (Wibowo, 2001). To get HTPB with an average molecular weight of 2500-5000 g/mole, it will take 1 hour process time. Theoretically, the formation of HTPB reaction begins with the formation of hydrogen peroxide from the radicals to form a radical butadiene monomer (M*) as shown in equation (1). Furthermore radicals will react with other monomers to form a radical containing butadiene monomer or the lengthier as shown in equation (2) to (4). Polymer growth will stop if the radical iscolliding as shown in equation (5).

$$H_2O_2 + M \dashrightarrow 2MOH^* \quad (1)$$

$$MOH^* + M \dashrightarrow M_2OH^* \quad (2)$$

$$M_2OH^* + M \dashrightarrow M_3OH^* \quad (3)$$

$$M_nOH^* + M \dashrightarrow M_{n+1}OH^* \quad (4)$$

$$M_nOH^* + M_mOH^* \dashrightarrow HOM_{n+m}OH \quad (5)$$

3 . Simulation and Result

Simulation conducted to determine the fluid flow in each pipe flow and to prove that the flow results according to the desired design. Simulation is designed base on the flow diagram of reactor as seen in figure 1.

Any fluid flow pipes are as follows as seen in figure2.

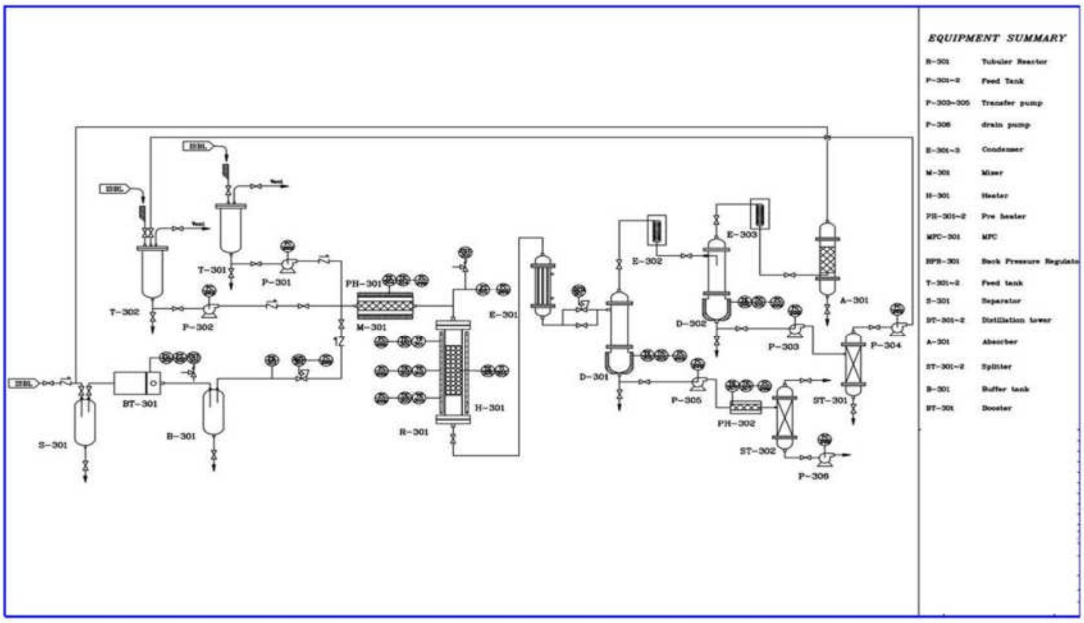
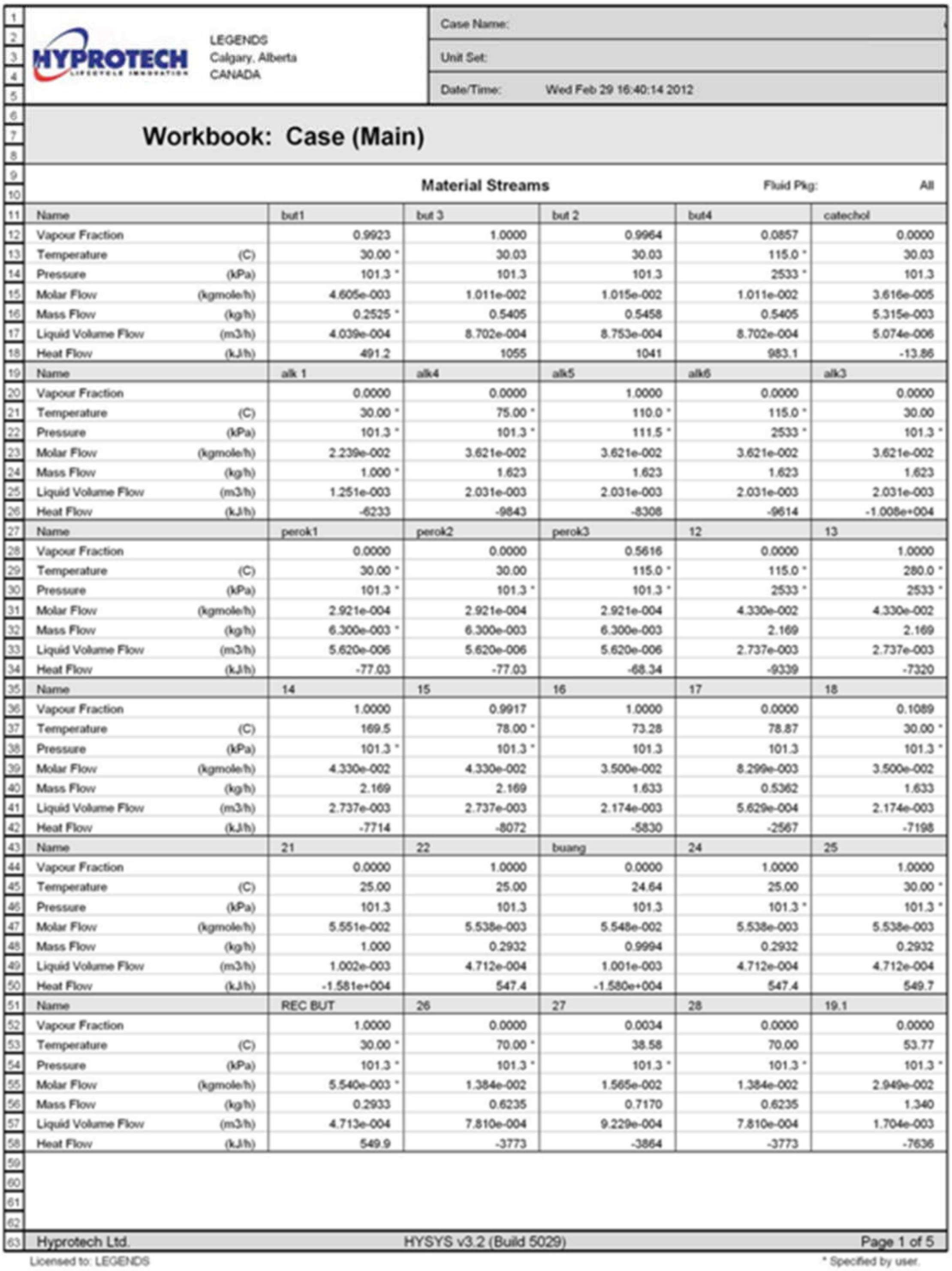


Fig 1. The design of Pilot Scale Reactor System HTPB



HYPROTECH

LEGENDS
Calgary, Alberta
CANADA

Case Name:

Unit Set:

Date/Time: Wed Feb 29 16:40:14 2012

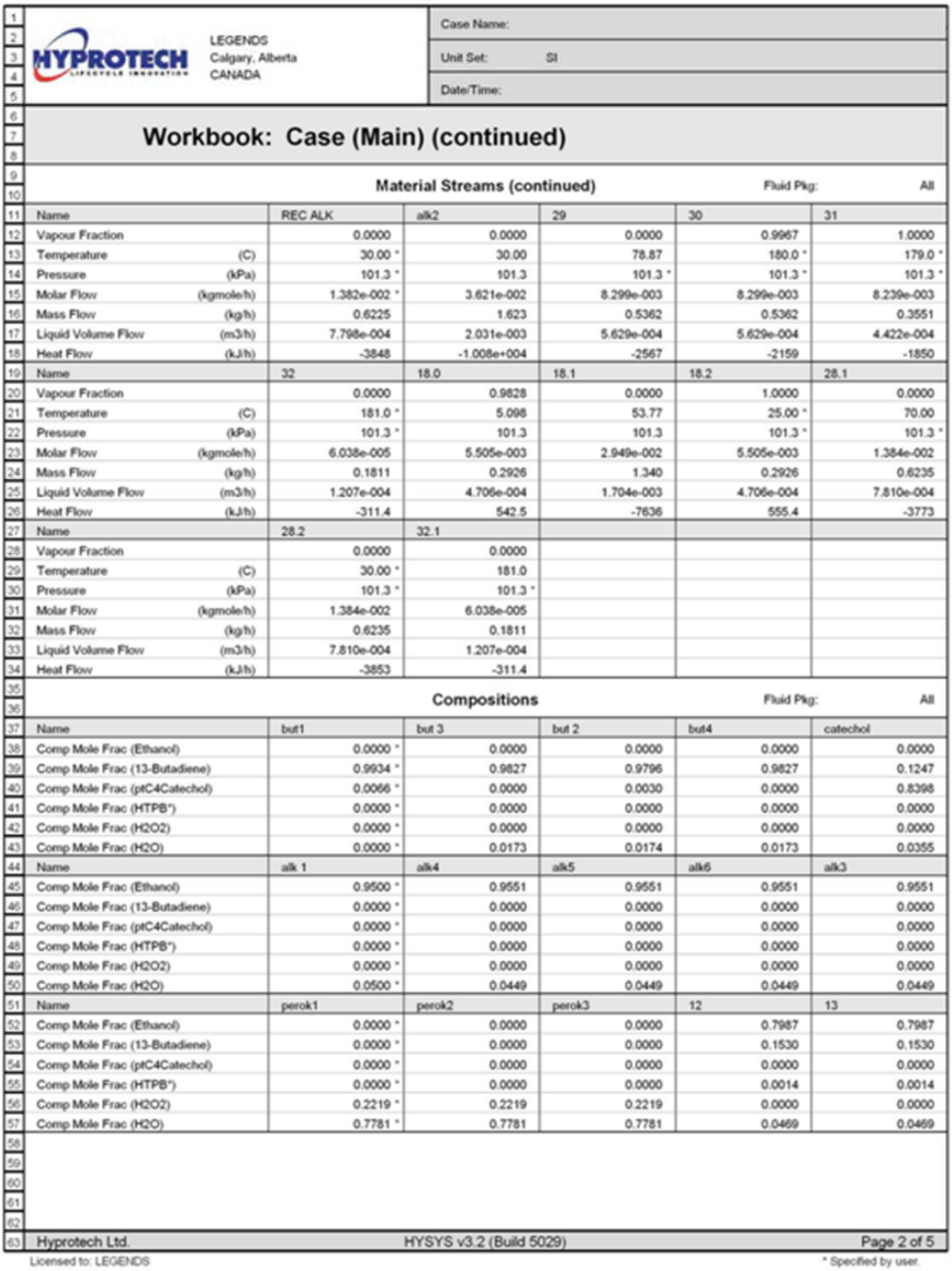
Workbook: Case (Main)

Material Streams Fluid Pkg: All

Name		but1	but 3	but 2	but4	catechol
Vapour Fraction		0.9923	1.0000	0.9964	0.0857	0.0000
Temperature	(C)	30.00 *	30.03	30.03	115.0 *	30.03
Pressure	(kPa)	101.3 *	101.3	101.3	2533 *	101.3
Molar Flow	(kgmole/h)	4.605e-003	1.011e-002	1.015e-002	1.011e-002	3.616e-005
Mass Flow	(kg/h)	0.2525 *	0.5405	0.5458	0.5405	5.315e-003
Liquid Volume Flow	(m3/h)	4.039e-004	8.702e-004	8.753e-004	8.702e-004	5.074e-006
Heat Flow	(kJ/h)	491.2	1055	1041	983.1	-13.86
Name		alk 1	alk4	alk5	alk6	alk3
Vapour Fraction		0.0000	0.0000	1.0000	0.0000	0.0000
Temperature	(C)	30.00 *	75.00 *	110.0 *	115.0 *	30.00
Pressure	(kPa)	101.3 *	101.3 *	111.5 *	2533 *	101.3 *
Molar Flow	(kgmole/h)	2.239e-002	3.621e-002	3.621e-002	3.621e-002	3.621e-002
Mass Flow	(kg/h)	1.000 *	1.623	1.623	1.623	1.623
Liquid Volume Flow	(m3/h)	1.251e-003	2.031e-003	2.031e-003	2.031e-003	2.031e-003
Heat Flow	(kJ/h)	-6233	-9843	-8308	-9614	-1.008e+004
Name		perok1	perok2	perok3	12	13
Vapour Fraction		0.0000	0.0000	0.5616	0.0000	1.0000
Temperature	(C)	30.00 *	30.00	115.0 *	115.0 *	280.0 *
Pressure	(kPa)	101.3 *	101.3 *	101.3 *	2533 *	2533 *
Molar Flow	(kgmole/h)	2.921e-004	2.921e-004	2.921e-004	4.330e-002	4.330e-002
Mass Flow	(kg/h)	6.300e-003 *	6.300e-003	6.300e-003	2.169	2.169
Liquid Volume Flow	(m3/h)	5.620e-006	5.620e-006	5.620e-006	2.737e-003	2.737e-003
Heat Flow	(kJ/h)	-77.03	-77.03	-68.34	-9339	-7320
Name		14	15	16	17	18
Vapour Fraction		1.0000	0.9917	1.0000	0.0000	0.1089
Temperature	(C)	169.5	78.00 *	73.28	78.87	30.00 *
Pressure	(kPa)	101.3 *	101.3 *	101.3	101.3	101.3 *
Molar Flow	(kgmole/h)	4.330e-002	4.330e-002	3.500e-002	8.299e-003	3.500e-002
Mass Flow	(kg/h)	2.169	2.169	1.633	0.5362	1.633
Liquid Volume Flow	(m3/h)	2.737e-003	2.737e-003	2.174e-003	5.629e-004	2.174e-003
Heat Flow	(kJ/h)	-7714	-8072	-5830	-2567	-7198
Name		21	22	buang	24	25
Vapour Fraction		0.0000	1.0000	0.0000	1.0000	1.0000
Temperature	(C)	25.00	25.00	24.64	25.00	30.00 *
Pressure	(kPa)	101.3	101.3	101.3	101.3 *	101.3 *
Molar Flow	(kgmole/h)	5.551e-002	5.538e-003	5.548e-002	5.538e-003	5.538e-003
Mass Flow	(kg/h)	1.000	0.2932	0.9994	0.2932	0.2932
Liquid Volume Flow	(m3/h)	1.002e-003	4.712e-004	1.001e-003	4.712e-004	4.712e-004
Heat Flow	(kJ/h)	-1.581e+004	547.4	-1.580e+004	547.4	549.7
Name		REC BUT	26	27	28	19.1
Vapour Fraction		1.0000	0.0000	0.0034	0.0000	0.0000
Temperature	(C)	30.00 *	70.00 *	38.58	70.00	53.77
Pressure	(kPa)	101.3 *	101.3 *	101.3 *	101.3 *	101.3 *
Molar Flow	(kgmole/h)	5.540e-003 *	1.384e-002	1.565e-002	1.384e-002	2.949e-002
Mass Flow	(kg/h)	0.2933	0.6235	0.7170	0.6235	1.340
Liquid Volume Flow	(m3/h)	4.713e-004	7.810e-004	9.229e-004	7.810e-004	1.704e-003
Heat Flow	(kJ/h)	549.9	-3773	-3864	-3773	-7636

Hyprotech Ltd. HYSYS v3.2 (Build 5029) Page 1 of 5

Licensed to: LEGENDS * Specified by user.



LEGENDS
Calgary, Alberta
CANADA

Case Name:
Unit Set: SI
Date/Time:

Workbook: Case (Main) (continued)

Material Streams (continued)

Fluid Pkg: All

Name	REC ALK	alk2	29	30	31
Vapour Fraction	0.0000	0.0000	0.0000	0.9967	1.0000
Temperature (C)	30.00 *	30.00	78.87	180.0 *	179.0 *
Pressure (kPa)	101.3 *	101.3	101.3 *	101.3 *	101.3 *
Molar Flow (kgmole/h)	1.382e-002 *	3.621e-002	8.299e-003	8.299e-003	8.239e-003
Mass Flow (kg/h)	0.6225	1.623	0.5362	0.5362	0.3551
Liquid Volume Flow (m3/h)	7.798e-004	2.031e-003	5.629e-004	5.629e-004	4.422e-004
Heat Flow (kJ/h)	-3848	-1.008e+004	-2567	-2159	-1850
Name	32	18.0	18.1	18.2	28.1
Vapour Fraction	0.0000	0.9828	0.0000	1.0000	0.0000
Temperature (C)	181.0 *	5.098	53.77	25.00 *	70.00
Pressure (kPa)	101.3 *	101.3	101.3	101.3 *	101.3 *
Molar Flow (kgmole/h)	6.038e-005	5.505e-003	2.949e-002	5.505e-003	1.384e-002
Mass Flow (kg/h)	0.1811	0.2926	1.340	0.2926	0.6235
Liquid Volume Flow (m3/h)	1.207e-004	4.706e-004	1.704e-003	4.706e-004	7.810e-004
Heat Flow (kJ/h)	-311.4	542.5	-7636	555.4	-3773
Name	28.2	32.1			
Vapour Fraction	0.0000	0.0000			
Temperature (C)	30.00 *	181.0			
Pressure (kPa)	101.3 *	101.3 *			
Molar Flow (kgmole/h)	1.384e-002	6.038e-005			
Mass Flow (kg/h)	0.6235	0.1811			
Liquid Volume Flow (m3/h)	7.810e-004	1.207e-004			
Heat Flow (kJ/h)	-3853	-311.4			

Compositions

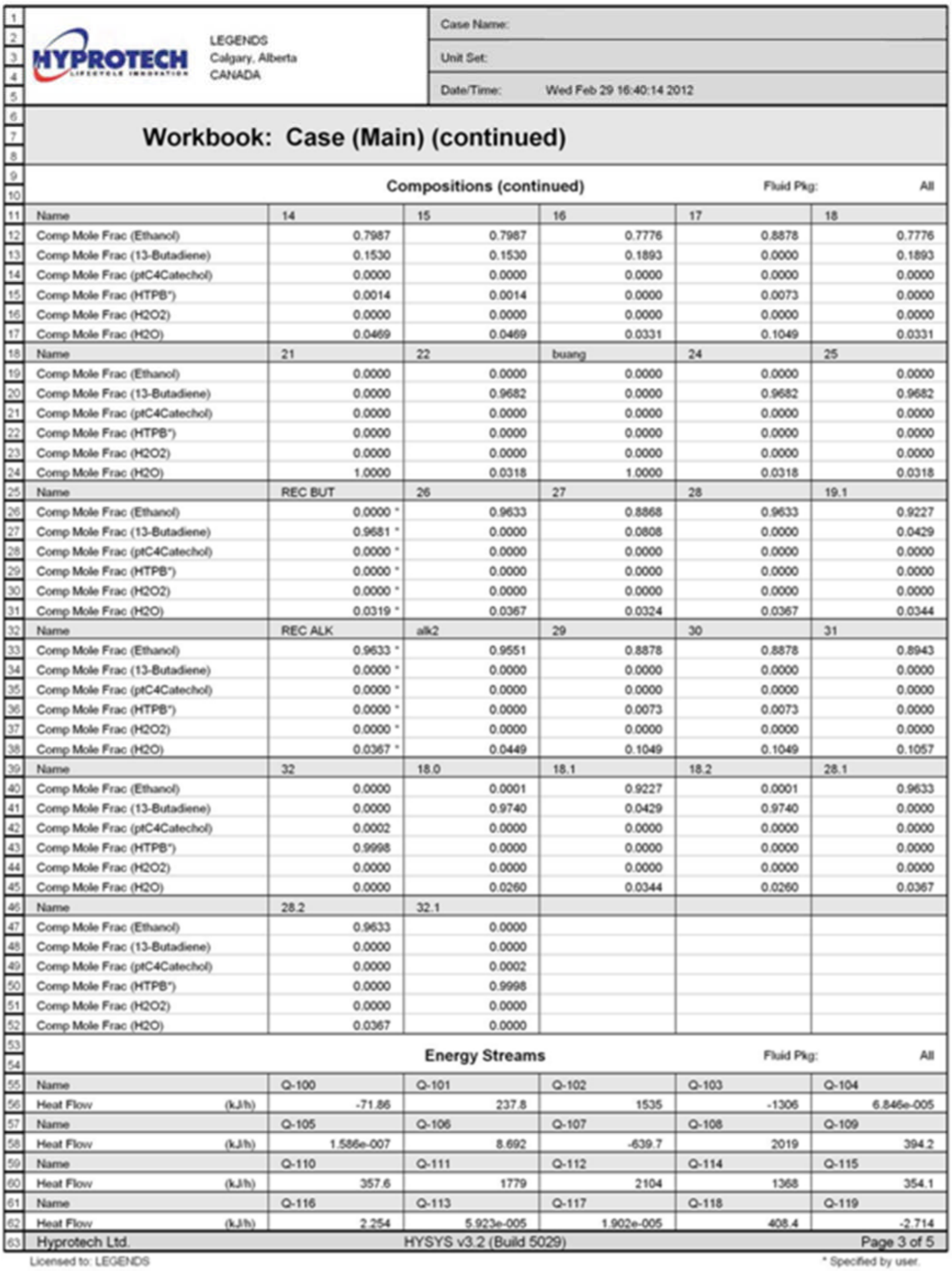
Fluid Pkg: All

Name	but1	but 3	but 2	but4	catechol
Comp Mole Frac (Ethanol)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (13-Butadiene)	0.9934 *	0.9827	0.9796	0.9827	0.1247
Comp Mole Frac (ptC4Catechol)	0.0066 *	0.0000	0.0030	0.0000	0.8398
Comp Mole Frac (HTPB*)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O2)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0000 *	0.0173	0.0174	0.0173	0.0355
Name	alk 1	alk4	alk5	alk6	alk3
Comp Mole Frac (Ethanol)	0.9500 *	0.9551	0.9551	0.9551	0.9551
Comp Mole Frac (13-Butadiene)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (ptC4Catechol)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (HTPB*)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O2)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0500 *	0.0449	0.0449	0.0449	0.0449
Name	perok1	perok2	perok3	12	13
Comp Mole Frac (Ethanol)	0.0000 *	0.0000	0.0000	0.7987	0.7987
Comp Mole Frac (13-Butadiene)	0.0000 *	0.0000	0.0000	0.1530	0.1530
Comp Mole Frac (ptC4Catechol)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (HTPB*)	0.0000 *	0.0000	0.0000	0.0014	0.0014
Comp Mole Frac (H2O2)	0.2219 *	0.2219	0.2219	0.0000	0.0000
Comp Mole Frac (H2O)	0.7781 *	0.7781	0.7781	0.0469	0.0469

Hyprotech Ltd. HYSYS v3.2 (Build 5029) Page 2 of 5

Licensed to: LEGENDS

* Specified by user.



HYPROTECH
LEGENDS
Calgary, Alberta
CANADA

Case Name:
Unit Set:
Date/Time: Wed Feb 29 16:40:14 2012

Workbook: Case (Main) (continued)

Compositions (continued) Fluid Pkg: All

Name	14	15	16	17	18
Comp Mole Frac (Ethanol)	0.7987	0.7987	0.7776	0.8878	0.7776
Comp Mole Frac (13-Butadiene)	0.1530	0.1530	0.1893	0.0000	0.1893
Comp Mole Frac (ptC4Catechol)	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (HTPB*)	0.0014	0.0014	0.0000	0.0073	0.0000
Comp Mole Frac (H2O2)	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0469	0.0469	0.0331	0.1049	0.0331
Name	21	22	buang	24	25
Comp Mole Frac (Ethanol)	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (13-Butadiene)	0.0000	0.9682	0.0000	0.9682	0.9682
Comp Mole Frac (ptC4Catechol)	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (HTPB*)	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O2)	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	1.0000	0.0318	1.0000	0.0318	0.0318
Name	REC BUT	26	27	28	19.1
Comp Mole Frac (Ethanol)	0.0000 *	0.9633	0.8868	0.9633	0.9227
Comp Mole Frac (13-Butadiene)	0.9681 *	0.0000	0.0808	0.0000	0.0429
Comp Mole Frac (ptC4Catechol)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (HTPB*)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O2)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0319 *	0.0367	0.0324	0.0367	0.0344
Name	REC ALK	alk2	29	30	31
Comp Mole Frac (Ethanol)	0.9633 *	0.9551	0.8878	0.8878	0.8943
Comp Mole Frac (13-Butadiene)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (ptC4Catechol)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (HTPB*)	0.0000 *	0.0000	0.0073	0.0073	0.0000
Comp Mole Frac (H2O2)	0.0000 *	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0367 *	0.0449	0.1049	0.1049	0.1057
Name	32	18.0	18.1	18.2	28.1
Comp Mole Frac (Ethanol)	0.0000	0.0001	0.9227	0.0001	0.9633
Comp Mole Frac (13-Butadiene)	0.0000	0.9740	0.0429	0.9740	0.0000
Comp Mole Frac (ptC4Catechol)	0.0002	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (HTPB*)	0.9998	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O2)	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0000	0.0260	0.0344	0.0260	0.0367
Name	28.2	32.1			
Comp Mole Frac (Ethanol)	0.9633	0.0000			
Comp Mole Frac (13-Butadiene)	0.0000	0.0000			
Comp Mole Frac (ptC4Catechol)	0.0000	0.0002			
Comp Mole Frac (HTPB*)	0.0000	0.9998			
Comp Mole Frac (H2O2)	0.0000	0.0000			
Comp Mole Frac (H2O)	0.0367	0.0000			

Energy Streams Fluid Pkg: All

Name	Q-100	Q-101	Q-102	Q-103	Q-104
Heat Flow (kJ/h)	-71.86	237.8	1535	-1306	6.846e-005
Name	Q-105	Q-106	Q-107	Q-108	Q-109
Heat Flow (kJ/h)	1.586e-007	8.692	-639.7	2019	394.2
Name	Q-110	Q-111	Q-112	Q-114	Q-115
Heat Flow (kJ/h)	357.6	1779	2104	1368	354.1
Name	Q-116	Q-113	Q-117	Q-118	Q-119
Heat Flow (kJ/h)	2.254	5.923e-005	1.902e-005	408.4	-2.714

Hyprotech Ltd. HYSYS v3.2 (Build 5029) Page 3 of 5

Licensed to: LEGENDS

* Specified by user.

Fig. 2. The massflow each of pipe in simulation of flowdiagram process HTPB production

Equipment called reactor scale manufacture of HTPB PILOT continuously after analysis equipment availability on the market, it is modified as follows.

1. Gas Feed Module (MFC - 301) : P1 : 30 atm , P2 : 25 atm , Flow Range : 0 ~ 30ml/min , 316SS material , Brand : Coriflow , Input Signal : 0 - 5VDC , Output Signal : 0 - 5VDC .

2. Module Liquid Feed Pump (P - 301) , for H_2O_2 : High pressure Digital Metering Pump , P1 : 4000 psig , Flow Range : 0.002 ~ 2.5ml/min , Materials : PEEK .
3. Module Liquid Feed Pump (P - 302) , High Pressure Digital Metering Pump (P301) : P1 : 1500 psig , Flow Range : 12:02 ~ 40ml/min , Materials : 316SS
4. Transfer Module pump (P - 303 ~ 4) , for EtOH , Digital diaphragm Pump (P301) : P1 : 60 psig , Flow Range : 12:02 ~ 40ml/min , Materials : PVDF .
5. Transfer Module pump (P - 305) , Mixer , Digital diaphragm Pump (P301) : P1 : 3000 psig , Flow Range : 0.01 ~ 20ml/min , Materials : 316SS
6. Drain Pump Module (P - 306) , for HTPB , Digital diaphragm Pump (P301) : P1 : 3000 psig , Flow Range : 0.002 ~ 5ml/min , Materials : 316SS
7. Module Reactor (R - 301) , Type : PFR , Volume : 200 ml , Materials : 316SS , Design Max . Pressure : 30 atm , Design Max . Temp . : 300C , Dimension : ID : 1 " x IL : 600mm
8. Electric Heater Module (H - 301) : Furnace : 3 Zone , 0.5 Kw x 3 , Temperature : 300C , Materials : Ceramic Fiber , " K " Type Thermocouple .
9. Feed Module Tank (T - 301) for H_2O_2 , Capacity : 300 ml , Materials : PTFE or PVC , Design Pressure : atmospheric , Design Temp . : 100C , Dimensions : ID : 55mm x IL : 130mm .
10. Feed Module Tank (T - 302) for EtOH , Capacity : 10Liter , Materials : 304SS , Design Pressure : 1 atm , Design Temp . : 100C , Dimensions : ID : 210mm x IL : 360mm
11. Mixer Module (M - 301) , Capacity : 150 ml , Materials : 316SS , Design Pressure : 30 atm , Design Temp . : 200C , Dimensions : ID : 55mm x IL : 75mm .
12. Module preheater (PH - 301 ~ 2) , Electric Band Heater , Design Temperature : 150C .
13. Separator Module (S - 301) , Capacity : 2 Liter , Materials : 316SS , Design Pressure : 3 atm , Design Temp . : 100C , Dimensions : ID : 107mm x IL : 220mm .
14. Condenser Module (E - 301) (= Heat Exchanger) , Type : Shell & Tube Type , Materials : 316SS , Capacity : 300 ml , Design Pressure : 30 atm , Design Temp . : 80C .
15. Condenser Module (E - 302) (= Heat Exchanger) , Materials : 316SS , Capacity : 150 ml , Design Pressure : 3 atm , Design Temp . : 30C .
16. Condenser Module (E - 303) (= Heat Exchanger) , Type : Shell & Tube Type , Materials : 316SS , Capacity : 150 ml , Design Pressure : 3 atm , Design Temp . : 250C .
17. Distillation tower Module (DT - 301) : Capacity : 2 Liter , Materials : 316SS , Design Pressure : 3 atm , Design Temp . : 150C .
18. Distillation tower Module (DT - 302) , Capacity : 2 Liter , Materials : 316SS , Design Pressure : 3 atm , Design Temp . : 150C .
19. Absorber Module (A - 301) , Capacity : 2 Liter , Materials : 316SS , Design Pressure : 3 atm , Design Temp . : 250C , Absorbent excluded .
20. Absorber Module (A - 301) ; Capacity : 2 Liter , Materials : 316SS , Design Pressure : 3 atm , Design Temp . : 250C , Absorbent excluded .
21. Splitter Module (ST - 302) : Capacity : 2 Liter , Materials : 316SS , Design Pressure : 3 atm , Design Temp . : 100C .
22. Buffer Module (B - 301) , Capacity : 2 Liter , Materials : 316SS , Design Pressure : 30 atm , Design Temp . : 100C , Pressure Gauge (0 ~ 30 atm) , Pressure Transmitter (0 ~ 30 atm) , Pressure Relief Valve (225 ~ 750 psig) .
23. Gas Booster (BT - 301) ; Materials : 304SS , Air operated type , P1 : atm , P2 : 30 atm .

4. Testing Results and Discussion

Results from the integration of production equipment HTPB PILOT scale is shown in the following figure, following the process flow diagram of the design. In the integration of the equipment, the equipment can be operated manually or by a computer program. Equipment reorganized to make it more compact and concise, so that the overall dimensions of the equipment are 2x2x1 m. For a PILOT scale production process , then the dimension can be said to be very compact because of all the equipment arranged very close together, and cultivated cables or pipes as possible so that the fluid flow very smoothly .

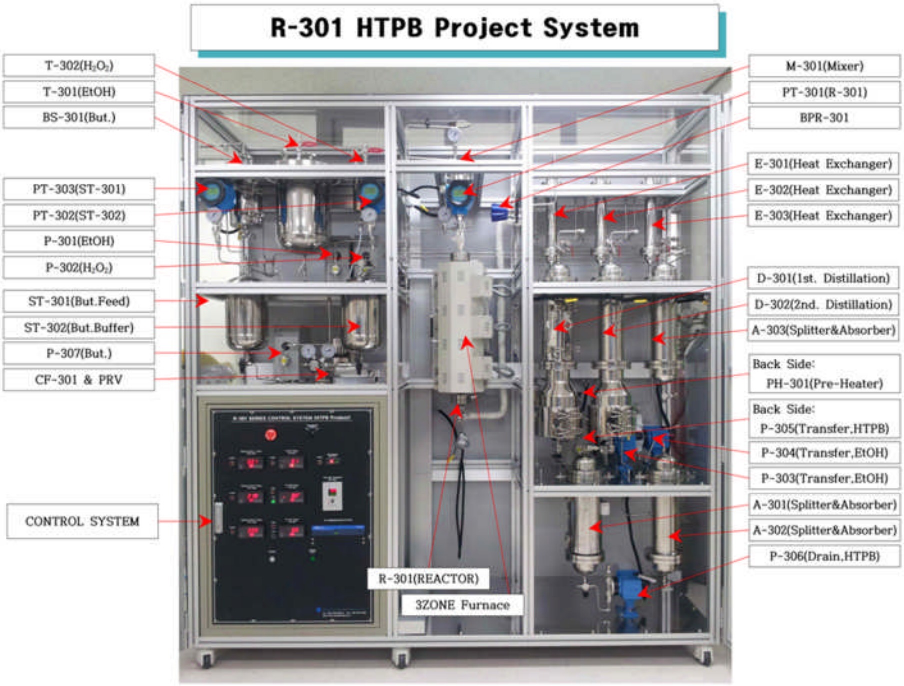
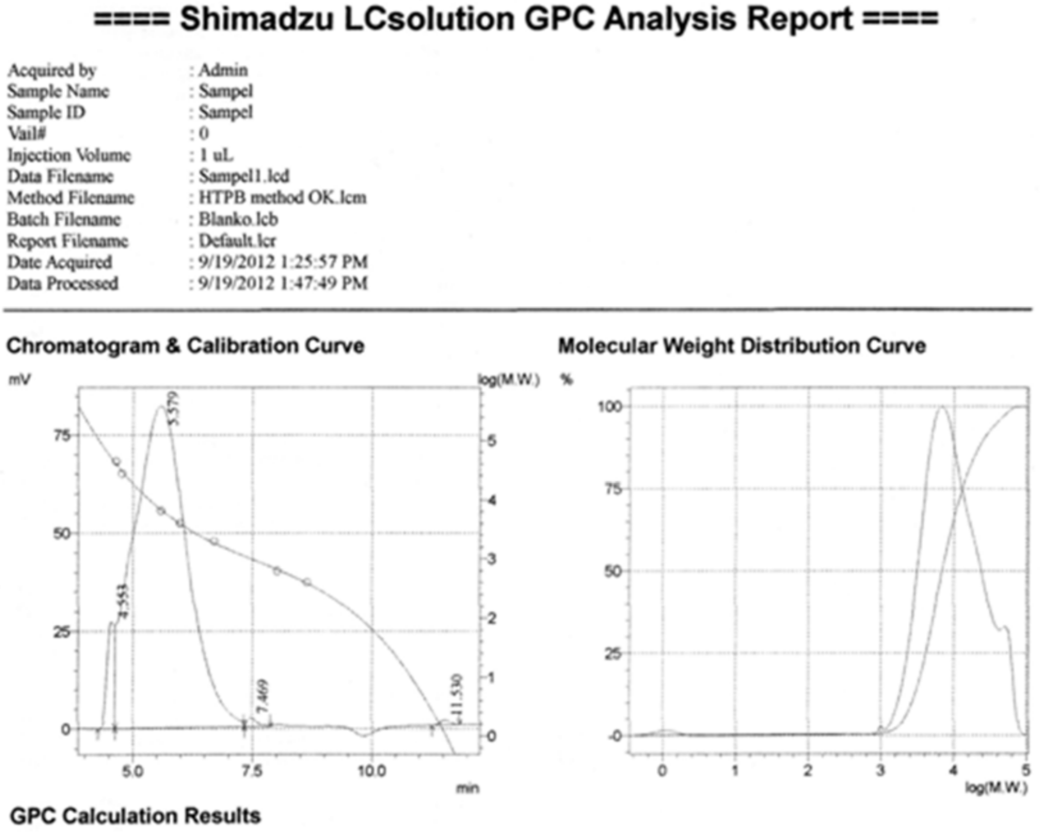


Fig. 3. Integrated System Pilot Scale Production of HTPB

Equipment tested during 1 hour operation, the results obtained HTPB with average molecular weight test by gel chromatography (GPC), identify structure of polymer with an infrared spectrometer (FTIR), and viscosity testing with digital viscometer. Results of testing the average molecular weight can be shown in the figure 4.1 and it turns out that average molecular weight polymer obtained was 3500 g/mole. The value entered in the range of requirements for fuel binder propellant. If desired HTPB with smaller molecular weight, it can done by regulating the amount of catalyst. It is conformed to Flory theory (1979) that the radical addition polymerization reaction, then the length of the polymer is strongly influenced by the number of radicals formed by the catalyst. The more the amount of catalyst in the same time it will produce polymer with an average molecular weight of the shorter. This is due to the number of radicals more so termination time at the same time will produce polymer with a number of much more radical, so that the same monomer chain length becomes shorter than the original polymer.



==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by : Admin
Sample Name : Sampel
Sample ID : Sampel
Vail# : 0
Injection Volume : 1 uL
Data Filename : Sampel1.lcd
Method Filename : HTPB method OK.lcm
Batch Filename : Blanko.lcb
Report Filename : Default.lcr
Date Acquired : 9/19/2012 1:25:57 PM
Data Processed : 9/19/2012 1:47:49 PM

Chromatogram & Calibration Curve

Molecular Weight Distribution Curve

GPC Calculation Results

Fig 5. GPC test of HTPB

FTIR analysis results are used to determine the composition of the dominant structure of HTPB generated. This test indicates that the obtained polymer quite homogeneous. When it is compared with the reaction process HTPB in batch process, where the rate of variation of the results is high enough, then the continuous polymerization better than batch process.

Further analysis of the structure of HTPB obtained show that the dominant polymer is trans 1,4-HTPB (60 %), cis 1,4-HTPB (10 %), and 1,2 - HTPB (30 %). The result shows that the HTPB obtained in accordance with the dominant structure qualify as a propellant fuel binder, which is the dominant structure requires 1.4 - HTPB. The desired result is high cis-1, 4 but polymer obtained is low. It can be caused by conditions of the operations performed, the reaction temperature and pressure. In accordances with the results of the study (Wibowo, 2002), that which affects the dominant structure in the formation of a polymerization reaction of HTPB is temperature and type of catalyst. Reaction rate constants for the formation of cis, Trans, and vinyl structure will be a function of temperature. This fact can be used as an agenda for further research in order to obtain operating condition manipulate levels of cis-1, 4 HTPB be higher.

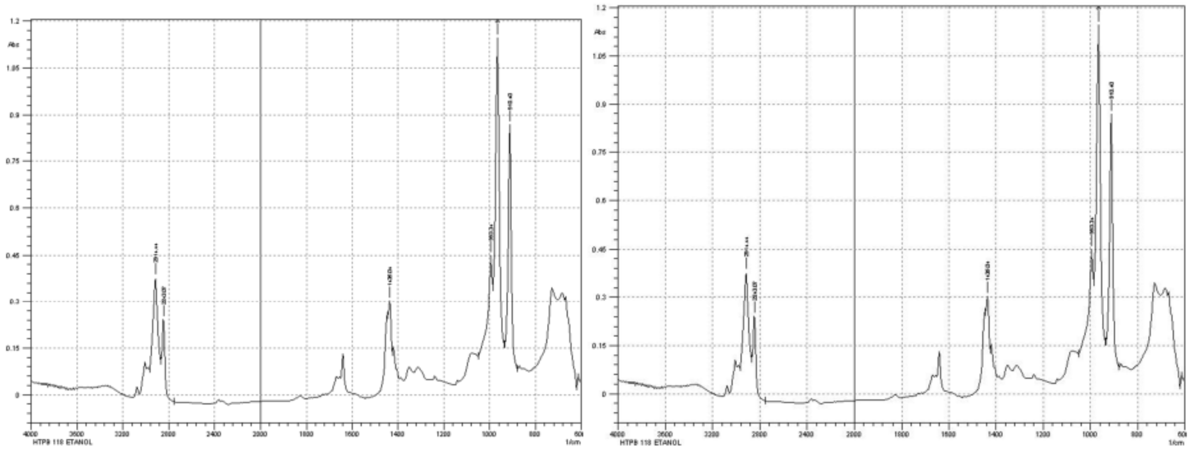


Fig. 6. FTIR spectra of HTPB at 60 minute operation and 70 minute operation time

Analysis of the test results can be shown following table. It turns out that in each interval time 10 minute for 1 hour, HTPB results have the same structure, and the same viscosity and molecular weight are almost the same. This suggests that the production process results in continuous process are more than in batch process. Wibowo (2004) state that HTPB result of procedural differences batch to vary molecular weight 2500-7000 gr/mole, the structure cis 0-12 % for 10 times the process is done.

Table 2. Spectra FTIR at interval time reaction

No	IR Spectra wavelength	Absorbance at Interval of reaction				
		60 minute	70 minute	80 minute	90 minute	100 minute
1	910 cm^{-1}	2,001	2,023	2,021	2,010	2,091
2	790 cm^{-1}	12,020	12,070	12,056	12,011	12,090
3	970 cm^{-1}	34,001	33,901	34,022	34,012	34,061

5. Conclusion

Based on the simulation results and test reactors that have been created and integrated, it can be concluded that the process of HTPB -scale reactors can be designed with PILOT 2 ton per year results. By using basic production 2 ton per year of production calculation, 40 % conversion of the reaction, all of catalyst completely reacted, as well as all the rest of the reactants are fed back into the reactor the production system has been designed HTPB PILOT scale. Results reactor integration can be carried out in accordance with the results. HTPB continuous process gives more homogeneous results compared with the batch process. The results of testing for 1 hour operation shown that HTPB have same characteristics during the 10 minute interval results along one hour's operation. HTPB obtained have average molecule weight of 3500 g/mole, the structure cis1, 4-HTPB 10%. To get a better HTPB can done by adjusting operating conditions (temperature and pressure) and the catalyst used.

References

1) Avery , HE *: Basic Reaction Kinetics and Mechanisms* , The MacMillan Press Ltd. . , Hong Kong (1982), pp . 355-370.
2) Bahl , B.S. *: Advanced Organic Chemistry*, New Delhi, S. Chand and Co. . Ltd. (2001).
3) Flory , J. : *Polymer Chemistry* , London, Cornell University Press (1979)
4) Dubois, C., Desilets, S., Ait-kadi, A., and Tanguy, P., 1995, *Bulk Polymerization of HTPB with TDI : a Kinetics Study Using ^{13}C-NMR Spectroscopy*., **J. Appl. Polym. Sci**., **58**, 827-834.
5) Gupta, D.C., Deo, S.S., Wast, D.V., Raomore, S.S., and Gholap, Dd.H. :*HTPB-Based Polyurethanes for Inhibition of Composite Propellants***., J. Appl. Polym. Sci., 55**, 1151-1155. (1995)
6) Gupta, D.C., Divekar, P.K., and Phadke, V.K. :*HTPB-Based Polyuretanes for Inhibition of Composite-Modified Double Base (CMDB) Propellants***., J. Appl. Polym. Sci., 65**, 355-363. (1997)
7) Hepburn, C. :*Polyurethane Elastomers*, Applied Science Publishers, pp. 355-359, New York. (1982)
8) Jain, D.R., Sekar, V., Krishnamurti, V.N. : *Mechanical and Swelling Properties of HTPB-based Copolyurethane Networks*., **J. Appl. Polym. Sci., 48**, 1515-1523. (1994)

9) Manjari, R., Pandureng, L.P., Somasundaran, U.I., and Sriram, T. :*Structure-Property Relationship of HTPB-Based Propellants. I. Effect of Hydroxyl Value of HTPB Resin*.,**J. Appl. Polym. Sci**, **48**, 2711-278. (1994)

10) Sarner, S.F. : *Propellant Chemistry*, Reinhold Publishing Company, New York. (1996)
11) Stevens , R.M. : *Polymer Chemistry*, PradnyaParamita, Jakarta (2001)
12) Timnat , J. : *Advanced Rocket Propulsion* . Interscience Publishers, London (1992)
13) Wibowo , H.B. : *Effects of Particle Size In Reaction Polymerization Catalysts Catalysts butadiene with lithium*, National Seminar on Chemistry UGM (2004)
14) Wibowo , H.B. : *As a catalyst in the activation Lithium Reaction Formation HTPB* . Aerospace Science and Technology Seminar, Jakarta (2004).
15) Wibowo , H.B. : *Applications Infrared Spectrometer (IR) for Studying Reaction Kinetics butadiene emulsion polymerization*. Proceedings of National Seminar JASAKIAI IV(2001)
16) Wibowo , H.B. : *In Emulsion Polymerization Kinetics of butadiene with H2O2/Fe Initiator (II)*. National Seminar Proceeding JNK, Jakarta (2000)
17) Wibowo , H.B. : *In emulsion polymerization of butadiene* , LAPAN Magazine Vol 2 No 3 (2000).
18) Wibowo , H.B. : *Polybutadiene Polymer Structure And Control Engineering Production* , GAMATECH Magazine Vol 2 No 3 (2012)