

# Reactivity of Unsaturated Hydrocarbons Via Adiabatic Calorimetry

by

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## ABSTRACT

Selected olefins, diolefins, and alkynes have been examined via adiabatic calorimetry to understand the behavior of these species as a function of temperature. APTAC (Automatic Pressure Tracking Adiabatic Calorimeter) and Vent Sizing Package (VSP) testing has revealed the uncatalyzed reactivity of these compounds. Conjugated diolefins such as cyclopentadiene, 1,3-butadiene, and isoprene show trends consistent with Diers-Alders condensation to form dimers, trimers, etc. At elevated temperatures, the oligomers/polymers formed from these species apparently decompose exothermically. Several of the alkynes react at temperatures above 200°C and ultimately approach temperatures of 900°C. A conjugated alkene-yne, on the other hand, shows reactivity comparable to butadiene (i.e., onset temperature of 80-90°C). In contrast to these results, straight-chain olefins exhibit no exothermic behavior for temperatures up to 340°C.

## INTRODUCTION

### Background

Unsaturated hydrocarbons can comprise the most significant portion of the diet of olefins, solvents, and polymer plants. Species with carbon-carbon double and/or triple bonds have the potential to release considerable energy when undergoing saturation or condensation reactions. The reactivity of some of these species has been studied extensively, as in the case of the behavior of 1,3-butadiene in the presence of oxygen or free radical sources [1,2] or when subjected only to external heating [3,4]. The *catalyzed* dimerization and oligomerization/polymerization of olefins are often characterized as part of the development and optimization of dedicated commercial processes. In addition, uncatalyzed reactions of unsaturates sometimes become the focus of intensive investigations pertaining to safety-related incidents [5].

While the reaction kinetics for many unsaturated species may be available within a narrow-temperature range, these kinetics may not shed understanding of the full dynamics of runaway reactions involving these species. Dimerization that takes place at relatively low temperatures can drive temperatures upward, causing the process to evolve toward polymerization. Moreover, some polymers of unsaturated species can themselves decompose exothermically at high temperatures and generate significant pressures [6,7].

In this study, the reaction behavior of selected olefins, diolefins, and alkynes has been examined through use of adiabatic calorimetry. Through measurement of heat release and pressure generation, this approach provides the opportunity to observe and characterize in a laboratory the accelerating reaction environment setting that might be experienced in a commercial-scale incident.

## EXPERIMENTAL

### Equipment

Most of the testing for this study was carried out in the Automatic Pressure Tracking Adiabatic Calorimeter (APTAC™) available from Arthur D. Little, Inc. Several experiments were also conducted in the Vent Sizing Package (VSP) from Fauske & Associates, Inc. The two instruments operate on the same basic principle; that is to minimize the heat loss from the sample and sample bomb by heating the gas space surrounding the bomb to match the sample temperature. This allows the sample undergoing an exothermic reaction to self-heat at a rate and extent comparable to that in a large-scale, adiabatic environment. The sample bomb resides in a containment vessel equipped with heaters and thermocouples for this purpose. A thermocouple is also placed inside the sample bomb. The internals of the APTAC are depicted in Figure 1.

The instruments also adjust the pressure in the containment vessel to match the pressure in the bomb allowing for a relatively thin-wall sample container. Sample pressures reaching nearly 2000 psia can be accommodated. For the APTAC, a thin-wall 2-12" titanium sample bomb is employed to limit the amount of heat absorbed from the sample. The VSP employs a thin-wall 2" x 2-1/2" stainless steel can. The relative thermal capacitance of the bomb/can plus sample to the sample alone is expressed by the thermal inertia factor,  $\phi$ ,

$$\phi = 1 + \frac{m_b C_{p_b}}{m_s C_{p_s}}$$

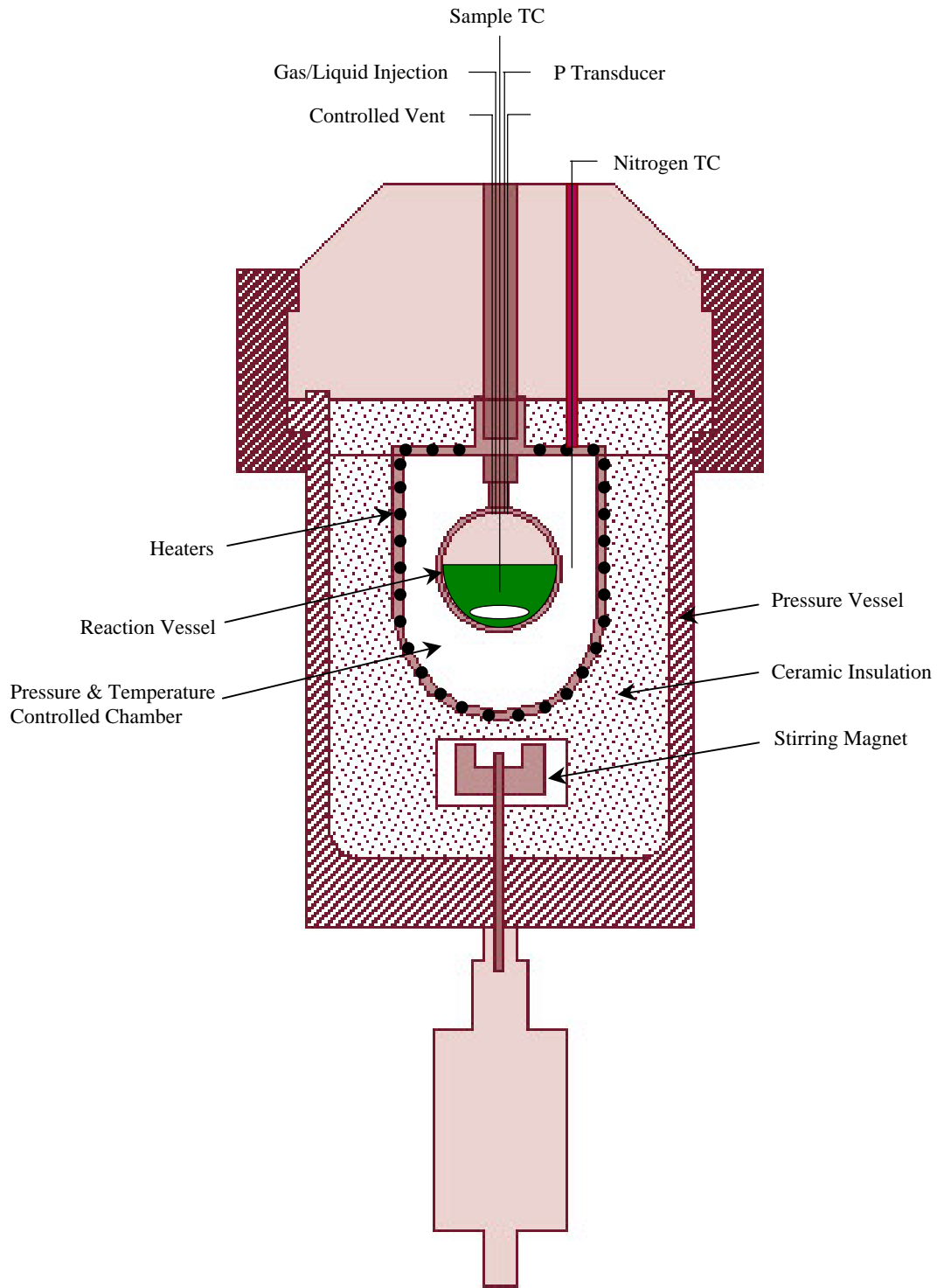
where  $m$  denotes the mass,  $C_p$  the heat capacity, subscript  $b$  the bomb+stir bar, and  $s$  the sample. The  $\phi$  factor of commercial equipment approaches a value of unity; a value of 1.15 – 1.30 is typical of APTAC tests and 1.05 – 1.15 for VSP tests.

Stirring is accomplished via a teflon-coated magnetic stir bar inserted in the sample bomb/can. In the APTAC, three-zone heating is provided in the containment vessel along with an additional heater for the tubing bundle connected to the sample bomb. The APTAC can match temperature and pressure rise rates of up to 400°C/min and 10,000 psi/min, respectively.

Operation is typically in the heat-wait-search mode. That is, the sample is heated to a pre-selected temperature and upon reaching this temperature, the instrument waits for a period of time (usually 25 minutes) for the bomb and containment vessel temperatures to stabilize. After the wait period, the instrument continues at that temperature (for another 25 minutes) to determine if there is any exothermic activity. During this time, the temperature of the containment vessel gas space is adjusted to match that of the sample thermocouple. If no heat-up activity exceeding a pre-set self-heating rate threshold is observed, it is concluded that there is no exotherm. The sample is then heated to the next temperature and the process repeated. If an exotherm is detected, the APTAC tracks the sample conditions and adjusts the temperature and pressure of the containment vessel accordingly (adiabatic or exotherm mode).

In this study, APTAC exotherm thresholds of 0.05 – 0.06°C/min (vs. the quoted 0.04°C/min detection limit of the APTAC) were employed to reduce the likelihood of the occurrence of "drift" (in which a slight thermocouple calibration imbalance yields a slow temperature rise rate and is interpreted as an exotherm). In the VSP tests, the exotherm threshold was 0.1-0.2°C/min.

Figure 1: Depiction of the Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)



## Samples

The following species were analyzed in this study:

<u>Olefins</u>	<u>Conjugated Diolefins</u>	<u>Alkynes</u>
1-Butene	1,3-Cyclopentadiene	2-Butyne
Trans-2-Butene	1,3-Butadiene	1-Pentyne
2-Pentene (cis/trans mix)	Isoprene (Methyl-1,3-butadiene)	2-Pentyne
Dicyclopentadiene	Piperylene (1,3-Pentadiene)	2-Methyl-1-Buten-3-yne
Limonene		

Most of these species were obtained from commercially-available sources (primarily Aldrich and Avocado), as indicated in Tables 1 and 2. Shell commercial butadiene was also employed in one test. Finally, cyclopentadiene is not easily procured as it has a relatively short shelf life—even if stored in a standard freezer. Instead, samples were prepared by taking advantage of the equilibrium at elevated temperatures between dicyclopentadiene and cyclopentadiene. Prior to each CPD test, dicyclopentadiene was distilled at 210-220°C and CPD collected in the overhead in a dry ice trap. Some of the samples prepared in this manner were spot-checked by GC-MS to ensure CPD purity.

## Procedures

To preclude reaction of the unsaturated hydrocarbon species with oxygen, steps were taken in all experiments to purge air from the system. A summary of test characteristics may be found in Table 1. No gas samples for compositional analysis were taken at the end of any of the tests.

### *VSP tests*

Butadiene was withdrawn from a compressed gas sample can via hand-operated pressure syringe and then injected into a evacuated VSP test can. Piperylene was injected into an evacuated test can by allowing the vacuum to transfer piperylene through tubing from a syringe; the VSP test can was then evacuated again via house vacuum afterwards.

Total sample weights ranged from 38.4 to 53.6 g while the total weight of stainless steel can and stir bar ranged between 37.9 and 40.8 g.

### *APTAC Tests*

Low boiling point hydrocarbons (such as the C4 olefins) and most conjugated diolefins (such as CPD and 1,3-butadiene) were charged into an APTAC sample bomb by attaching each compressed gas sample can to a dry ice/acetone-cooled condenser. Once sufficient material collected in the condenser's graduated trap, the material was transferred by cannula under nitrogen pressure into a dry ice/acetone-cooled APTAC sample bomb (fitted with a septum and purged with nitrogen). The sample bomb and its ice bath were then placed in a glove bag. After attaching the glove bag to the APTAC containment vessel head and purging with five vacuum/nitrogen cycles, the sample bomb was then attached to the vessel head.

In the case of isoprene, the sample was injected by gas-tight syringe into an APTAC sample bomb equipped with a septum and purged with nitrogen. The aforementioned glove bag procedure was then followed for attaching the bomb to the APTAC vessel head.

For the remaining higher boiling point unsaturates, material was poured into the APTAC sample bomb in air. Upon attaching the sample bomb to the APTAC containment vessel head, the

sample bomb was evacuated via house vacuum and re-pressurized to around atmospheric pressure with nitrogen. The vacuum/nitrogen steps were then repeated four more times.

Total sample weights ranged from 25.0 to 43.6 g while the total weight of titanium bomb and stir bar ranged between 34.3 and 38.7 g.

Table 1: Summary of APTAC Test Conditions and Results for Olefins and Alkynes

Run ID	A00311a	A00318	A00332	A00319b	A00230	A0231	A00232	A00320
Material	t-2-Butene	1-Butene	2-Pentene (cis/trans mix)	2-Butyne	1-Pentyne	2-Pentyne	2-Methyl-1-Buten-3-yne	2-Methyl-1-Buten-3-yne
Source	Aldrich #29,508-6	Aldrich #29505-1	Aldrich #14,377-4	Avocado #503-17-3	Aldrich #25,656-0	Aldrich #27,135-7	Aldrich #M3,280-1	Aldrich #M3,280-1
Instrument	APTAC	APTAC	APTAC	APTAC	APTAC	APTAC	APTAC	APTAC
Sample Mass [g]	32.19	31.58	36.87	25.95	24.99	25.67	28.80	26.29
Sample Pad Gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen
Sample Bomb Mass [g]	31.10	31.01	31.06	31.40	31.13	31.02	31.07	30.85
Stir Bar Mass [g]	3.36	3.38	3.57	3.34	3.38	3.47	3.45	3.42
Stirring Rate (magnetic) [rpm]	300	300	300	300	300	300	300	300
Expt (Search) Start Temp [°C]	40	40	40	40	40	40	40	40
Expt Final or Max Temp [°C]	420	420	420	400	400	400	400	400
Heat-Wait-Search Increment [°C]	20	20	20	10	20	20	20	10
Expt Duration (before S/D) [min]	940	856	1528	2093	782	1263	322	542
Expt Shutdown Cause	Press Limit	Press Limit	Press Limit		Press Rate	Temp Limit	Press Rate	
Expt Exotherm Limit (N <sub>2</sub> ) [°C]	430	430	430	420	420	420	420	420
Expt Temperature Shutdown [°C]	460	460	460	450	450	450	450	450
Expt Pressure Shutdown [psia]	1800	1700	2000	1800	1800	1800	1800	1800
Expt Heat Rate Shutdown [°C/min]	2000	2000	2000	2000	2000	2000	2000	2000
Expt Press Rate Shutdown [psi/min]	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000
Exotherm Threshold [°C/min]	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Number of Exotherms	0	0	0	1	1	1	1	1
Observed Onset Temp (0.06°C/min) [°C]	---	---	---	(210)	(234)	(280)	(89)	81
Max Observed Temp [°C]	286	270	362	901 <sup>3</sup>	805	806	899 <sup>3</sup>	901 <sup>3</sup>
Max Observed Pressure [psi]	1803	1701	2001	2154	1653	2067	2043	1556
Max Obs'd Self-Heat Rate [°C/min]	---	---	---	11,000	21,400	22,000	13,800	18,100
Max Obs'd Press. Rate [psi/min]	---	---	---	23,200	26,900	38,700	26,900	23,800
Temp at Max Self-Heat Rate [°C]	---	---	---	893 <sup>1</sup>	782 <sup>1</sup>	782 <sup>1</sup>	897 <sup>1</sup>	901 <sup>2</sup>
Temp at Max Press. Rate [°C]	---	---	---	900 <sup>1</sup>	635 <sup>1</sup>	733 <sup>1</sup>	340 <sup>1</sup>	553 <sup>1</sup>
Thermal Inertia, $\phi$	1.24	1.24	1.22	1.26	1.24	1.25	1.27	1.25
Comments					Formed black, fluffy powder	Formed black, fluffy powder	Formed black, fluffy powder	

<sup>1</sup>Self-heat and pressurization rates sufficiently high to cause possible temperature, pressure reading lags

<sup>2</sup>Reached equipment maximum reading

Parentheses ( ) denote extrapolation to lower temperature



Table 2: Summary of APTAC Test Conditions and Results for Diolefins

Run ID	A00142	A00143a	A044-29	A00287	A00129	A00130	B01-02	B01-03	A00146	A00145
Material	CPD	CPD	1,3-Butadiene	1,3-Butadiene	Isoprene	Isoprene	Piperylene	Piperylene	DCPD	Limonene
Source	Distilled DCPD	Distilled DCPD	Matheson CP	Shell Chemical	Aldrich #I-1,955-1	Aldrich #I-1,955-1			Avocado #13643	Aldrich #21,836-7
Instrument	APTAC	APTAC	VSP	APTAC	APTAC	APTAC	VSP	VSP	APTAC	APTAC
Sample Mass [g]	43.56	40.86	53.6	34.86	33.06	33.95	40.86	38.43	39.90	39.60
Sample Pad Gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen
Sample Bomb Mass [g]	34.51	34.67	40.76	31.01	35.28	35.07	37.89	37.95	34.60	35.06
Stir Bar Mass [g]	3.53	3.53		3.47	3.46	3.63			3.52	3.55
Stirring Rate (magnetic) [rpm]	300	300		300	300	300			300	300
Expt (Search) Start Temp [°C]	20	20	50	40	80	80	120	140	80	80
Expt Final or Max Temp [°C]	380	380	---	460	380	380	---	---	420	420
Heat-Wait-Search Increment [°C]	10	10	10	10	10	10	10	10	10	10
Expt Duration (before S/D) [min]	170	174	410	734	510	535	415	174	862	2048
Expt Shutdown Cause	Temp Limit	Temp Limit	Press Limit	Press Rate	Temp Limit	Temp Limit	Temp Limit	Temp Limit	Temp Limit	Temp Limit
Expt Exotherm Limit (N <sub>2</sub> ) [°C]	410	410	---	430	410	410	---	---	430	430
Expt Temperature Shutdown [°C]	430	430	---	460	430	430	492	---	450	450
Expt Pressure Shutdown [psia]	1750	1750	---	1800	1750	1750	1130	---	1750	1750
Expt Heat Rate Shutdown [°C/min]	2000	2000	---	2000	2000	2000	---	---	2000	2000
Expt Press Rate Shutdown [psi/min]	10,000	10,000	---	10,000	10,000	10,000	---	---	10,000	10,000
Exotherm Threshold [°C/min]	0.05	0.05	0.05	0.05	0.05	0.05	0.1	0.1	0.05	0.05
Number of Exotherms	3+	3+	1+	1+	2+	2+	2+	1+	2+	1+
Observed Onset Temp (0.06°C/min) [°C]	(26)	31	(96)	84	101	102	(137)	(131)	152	245/285
Max Observed Temp [°C]	589	620	474	894	527	527	524	545	565	434
Max Observed Pressure [psia]	1941	2018	1965	2089	1604	1520	1142	1310	2216	485
Max Obs'd Self-Heat Rate <sup>1</sup> [°C/min]	a) 120 b) 35 c) 1140	a) 175 b) 39 c) 1470	2500	6100	a) 300 b) 645	a) 205 b) 245	a) 69 b) 273	a) 400 b) 484	a) 6.3 b) 385	11.5
Max Obs'd Press. Rate <sup>1</sup> [psi/min]	a) 33 b) 100 c) 31,500	a) 52 b) 110 c) 38,000	6440	19800	a) 200 b) 20,000	a) 205 b) 3550	a) 52 b) 2700	a) 32 b) 3310	a) 20 b) 3010	140+
Temp at Max Self-Heat Rate <sup>1</sup> [°C]	a) 172 b) 279 c) 546	a) 183 b) 275 c) 460	336	893	a) 345 b) 431	a) 331 b) 500	a) 336 b) 481	a) 197 b) 510	a) 257 b) 489	427
Temp at Max Press. Rate <sup>1</sup> [°C]	a) 190 b) 371 c) 565	a) 187 b) 372 c) 586	304	367	a) 323 b) 411	a) 331 b) 419	a) 281 b) 488	a) 256 b) 536	a) 332 b) 542	---
Thermal Inertia, $\phi$	1.19	1.20	1.13	1.17	1.19	1.19	1.14	1.15	1.20	1.16
Comments	Premature test end		2.5% w Hexane VSP can failed				Black liq & solid formed	Bomb ruptured; black solid		

<sup>1</sup> a), b), and c) refer to the primary exotherms observed in the tests in order of appearance

<sup>2</sup>Self-heat and pressurization rates sufficiently high to cause possible temperature, pressure reading lags

<sup>3</sup>Reached equipment maximum reading

Parentheses ( ) denote extrapolation to lower temperature

## RESULTS AND DISCUSSION

### Olefins

Application of adiabatic calorimetry to some four- and five-carbon olefins, 1-butene, trans-2-butene, and a cis/trans mixture of 2-pentene, revealed no evidence of exothermic activity up to temperatures of 260-340°C. This is illustrated in the temperature-time profiles of Figure 2 where only the stair-step features of the heat-wait-search mode are observed. (In the case of 2-pentene, instrument drift seems to be present between 200 and 240°C.) Similar behavior appears in the pressure-time plot of Figure 3. The exerted pressure of the butenes, reaching 1700-1800 psia, bounds the upper temperature of those experiments. A considerably higher temperature was attained in the 2-pentene test due to its lower vapor pressure and to relaxation on the instrument pressure shutdown. Minor exothermic activity involving the C4 olefins could have, in principle, been present, but may have been masked by some loss of sample (note the slight loss of pressure during the wait-search portions of the steps). Pressure loss is absent for the 2-pentene run.

Corresponding to the absence of exothermic activity in the temperature-time profiles, there is an absence of any exotherms in the self-heat rate vs. reciprocal temperature plot of Figure 4; only the H-W-S steps (and apparent drift for the 2-pentene) appear. Likewise, no peaks are found in Figure 5, the analogous pressurization rate plot. Thus, not only are there no exotherms, there are no reactions generating non-condensable gas or light vapor species. This is confirmed in Figure 6, where total pressure is plotted vs. reciprocal temperature. The cool-down pressure profiles superimpose upon the heat-up pressure profiles while also matching the combined vapor pressure/pad gas pressure. A summary of results is included in Table 1.

Since no exotherms are found for these species, a time-to-maximum rate plot is not appropriate.

In the presence of a suitable catalyst, olefin oligomerization/polymerization readily takes place and liberates considerable heat. It is apparent from these tests that such behavior is absent in a non-catalytic system--at least to temperatures up to 340°C.

Figure 2: Temperature History of Olefins Samples in the APTAC

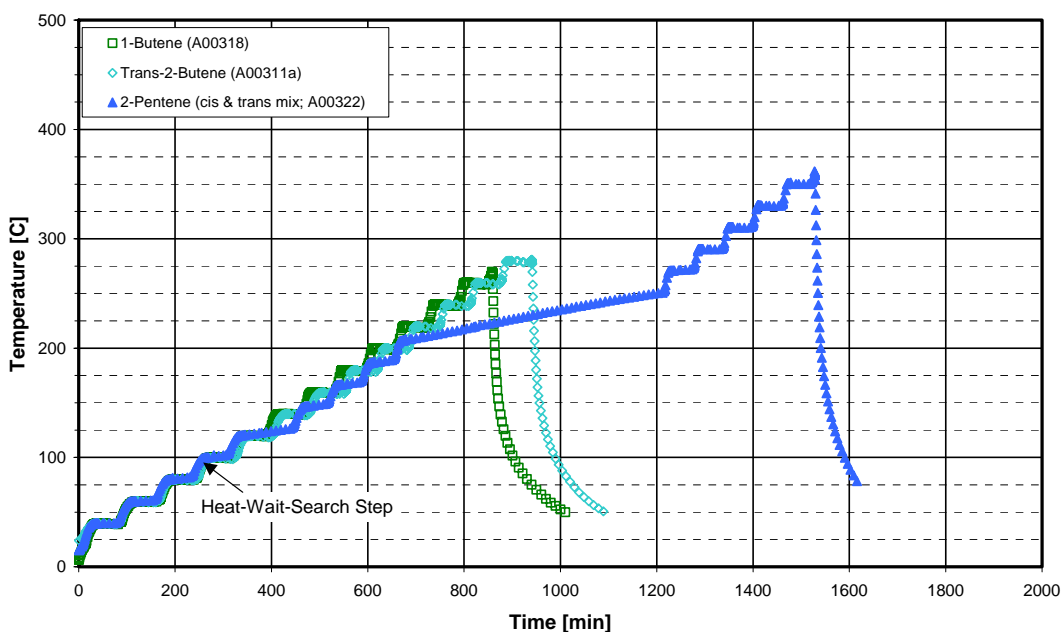




Figure 3: Pressure History of Olefins Samples in the APTAC

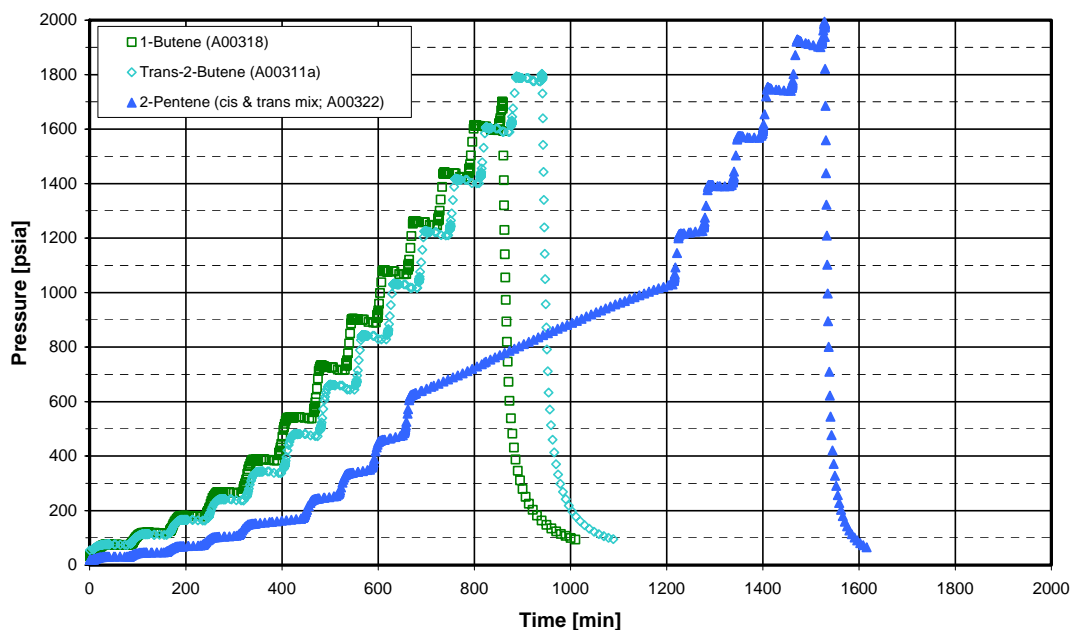


Figure 4: Self-Heat Rate-Temperature Profiles of Olefins Samples in the APTAC

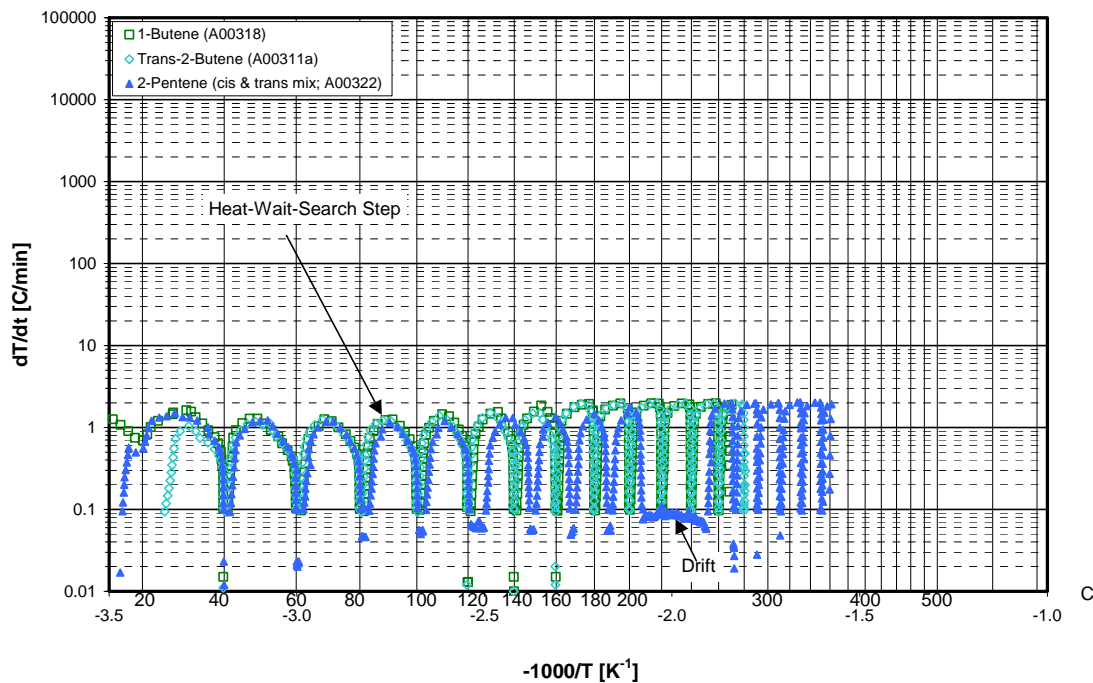


Figure 5: Pressurization Rate-Temperature Profiles of Olefins Samples in the APTAC

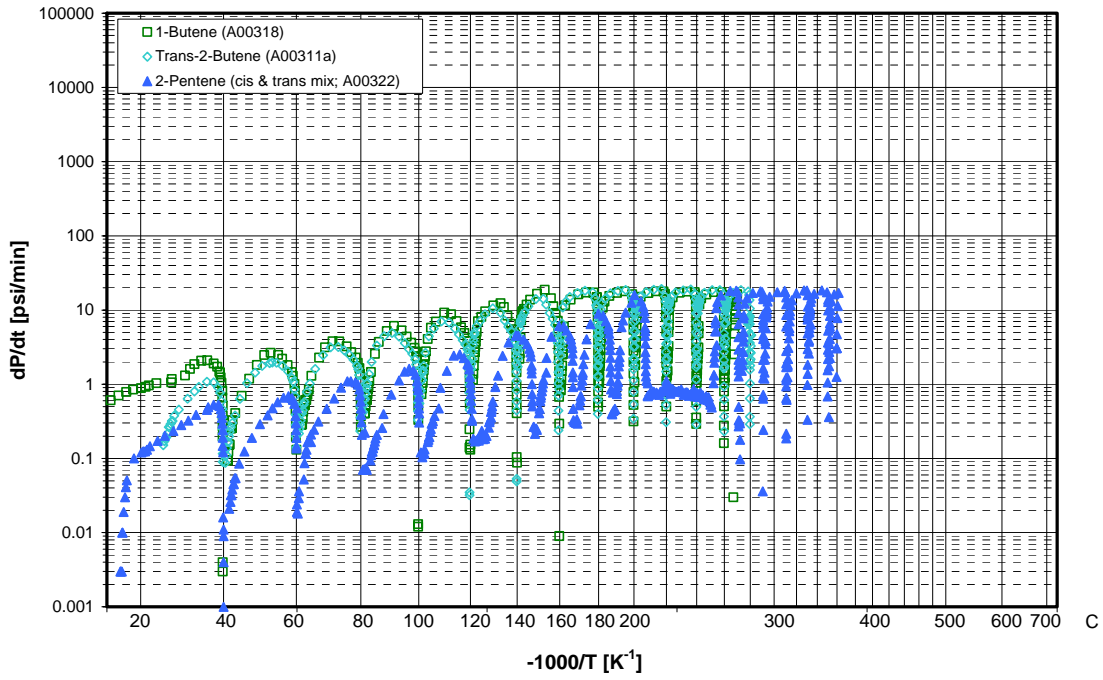
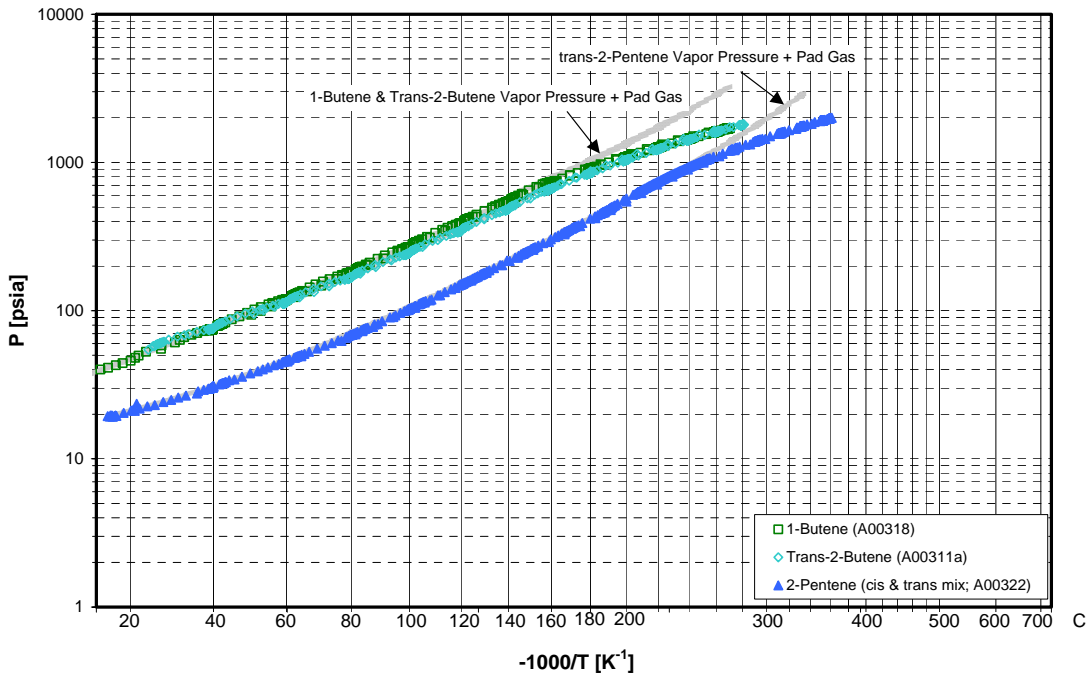


Figure 6: Pressure-Temperature Profiles of Olefins Samples in the APTAC



## Diolefins

### Conjugated Diolefins

In contrast to the mono-olefins, the *conjugated* diolefins tested exhibit considerable exothermic activity. A summary of results for these species is found in Table 2. Temperature profiles for 1,3-cyclopentadiene (CPD), 1-3-butadiene, isoprene, and piperylene are shown in Figure 7. Despite the programmed heater shutdown for 430-460°C for most of these tests, temperatures in excess of 500°C were achieved in all cases. In particular, the CPD samples generated temperatures of near or above 600°C. Cyclopentadiene begins reacting around room temperature. At least two distinct regions of reaction can be discerned, where the second reaction appears just above 200°C, while temperatures approaching 100°C are needed for butadiene and isoprene. The piperylene does not show exothermic activity until 120°C.

Significant increases in sample pressure accompany the temperature excursions (Figure 8). Pressures exceeding 1100 psia and as high as 2200 psia were generated. In most cases, the pressure balancing in the containment vessel was sufficiently rapid to match the sample bomb pressure. In two cases, a butadiene test and a CPD test, the test cell failed. For the butadiene experiment, this was likely due to hydrostatic pressure arising from too much liquid charged to the cell initially [3].

The qualitative kinetic behavior of the sample is more directly illustrated in the self-heat rate plot in Figure 9. This graph displays temperature rise rate vs. negative reciprocal temperature (with the corresponding temperatures in degrees Celsius shown). The direct link to an Arrhenius plot can be obtained by multiplying the self-heat rate by the sample heat capacity and dividing by the heat of reaction to yield the observed reaction rate. Figure 10 displays the same information as Figure 9, except that the initial heat-wait-search steps have been removed for clarity.

One of the prominent features of Figure 10 is the pair of curves reflecting cyclopentadiene dimerization, initiating at about room temperature, peaking at 180-190°C, and decaying to a low

Figure 7: Temperature History of Diolefins Samples in the APTAC

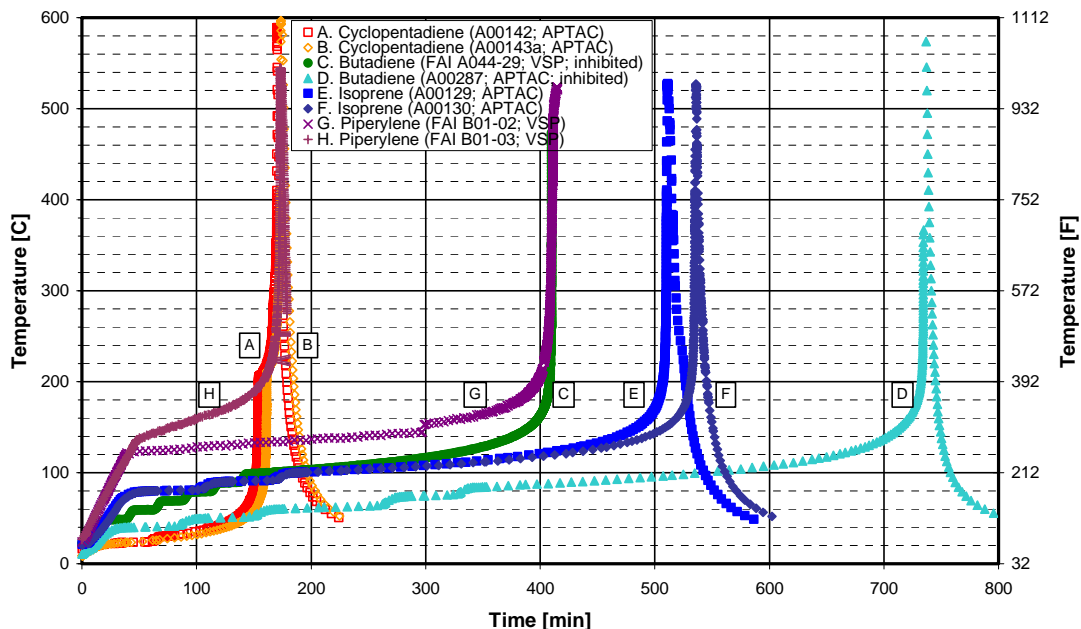
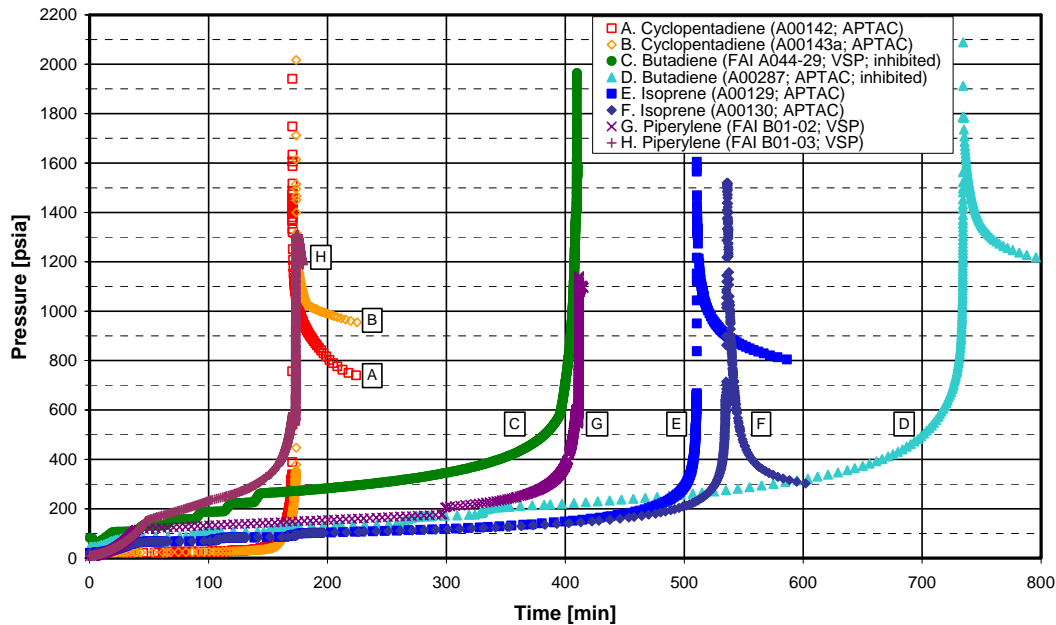


Figure 8: Pressure History of Diolefins Samples in the APTAC



self-heat rate at about 210°C. This peak is followed immediately by a second exotherm initiating at 210°C and progressing to 300°C. At 300°C, a third exotherm continuing beyond 500°C becomes dominant. It also appears that the second exotherm is “riding” on a leading extension of the third exotherm, giving rise to the significant temperature rise rates at the transition points between exotherms. Rates approaching 200°C/min for the first exotherm and exceeding 1000 °C/min for the last exotherm are observed. Cyclopentadiene can evidently self-heat from room temperature to over 600°C in a continuous manner in the course of only a couple of hours!

The next most reactive pair of curves corresponds to t-butyl catechol-inhibited 1,3-butadiene. The thermal dimerization of 1,3-butadiene has been discussed elsewhere [3,4]. Curiously, the self-heat rate profiles in these tests show a break in the slope near the species’ critical temperature (152°C). In addition, the slope of the self-heat rate for the APTAC test is somewhat lower than that for the VSP test. The upper temperature of the VSP test was limited by the apparent failure of the test can at about 350°C. Thermal expansion of the butadiene was not taken into account in the design of that experiment. In the APTAC test that followed much later, the butadiene charge was reduced to preclude the sample bomb rupture from hydrostatic pressure. The maximum temperature reached was nearly 900°C—considerably higher than in the earlier test.

Isoprene displays a reactivity that is comparable, but a bit slower than that of 1,3-butadiene. It is also apparent that the isoprene is unable to achieve the elevated temperatures of butadiene. The presence of the methyl group seems to limit the extent of polymerization/decomposition at high temperature.

Piperylene, a 1,3-pentadiene, reacts at a rate that is about 5-10 times slower than butadiene. The extension of the butadiene molecule by a methyl group appears to cause a significant lowering of the reactivity. The maximum temperature reached is comparable to that for isoprene.

Figure 9: Self-Heat Rate-Temperature Profiles of Diolefins Samples in the APTAC

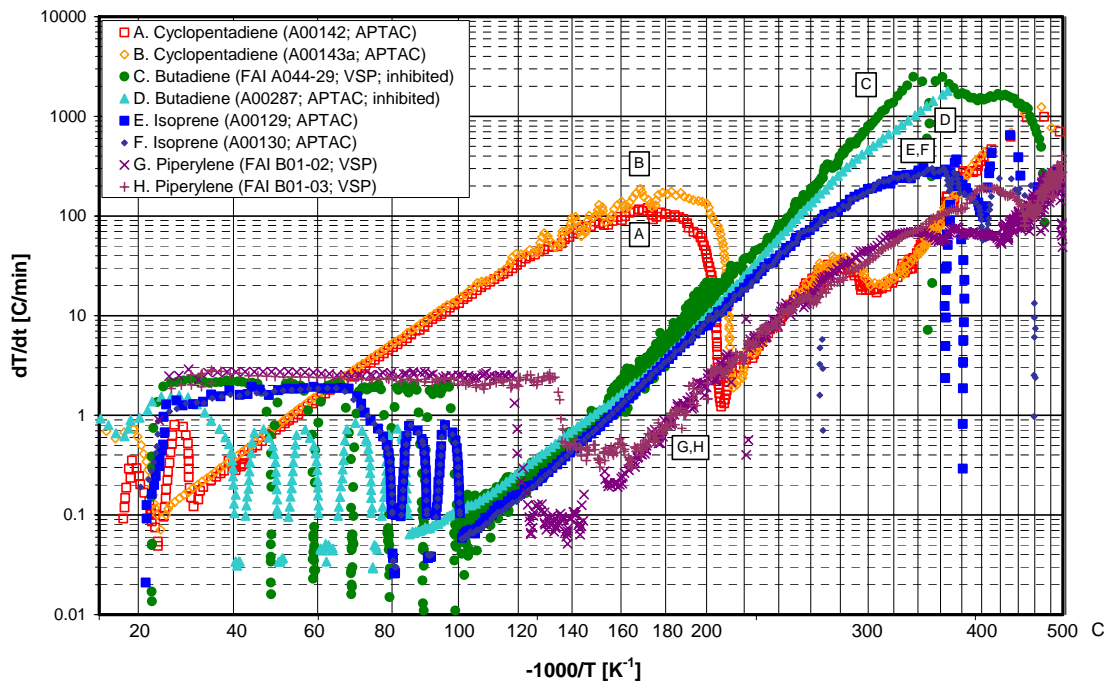
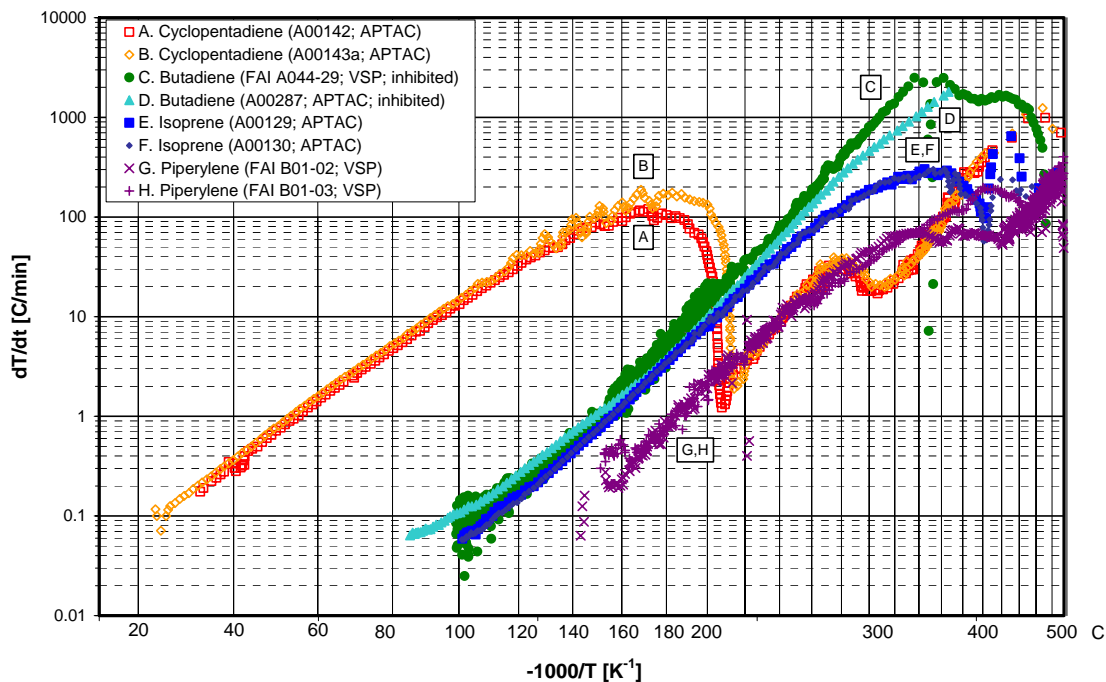


Figure 10: Self-Heat Rate-Temperature Profiles of Diolefins Samples in the APTAC Heat-Wait-Search Steps Removed



The pressurization rate vs. temperature profiles corresponding to the self-heat rate curves are shown in Figure 11. Pressurization *rates* significantly in excess of 10,000 psi/min were experienced in several cases (see Table 2). The reactions generating these pressurization rates and leading to the high pressures in the tests are most likely associated with decomposition of the oligomer/polymer formed from the diolefins [7]. Evidence for this is found in Figure 12 by the increase in pressure at the end of the tests, reflecting generation of non-condensable species.

The differences in reactivity between species are more clearly illustrated in the time-to-maximum rate plot of Figure 13. Cyclopentadiene, the most active of the conjugated diolefins tested, would reach its maximum self-heat rate starting from room temperature in about two hours. 1,3-Butadiene and isoprene, on the other hand, would have to be heated to over 110°C to achieve their maximum rates in this timeframe. At a lower temperature of 80°C, the time-to-maximum rate is about 5 hours. Piperylene would require a temperature of 140°C to reach its maximum rate in two hours.

#### *Dimers of Conjugated Diolefins*

The reactivity of two additional diolefins have also been investigated as part of this study. Specifically, dicyclopentadiene (the dimer of CPD) and d-limonene (one of the possible dimers of isoprene) were tested. A significant difference between these compounds and their originating monomers is that the double bonds are not conjugated. The two double bonds in each compound reside in remote sections of the molecules. This change in electronic characteristic substantially alters the behavior of the species when heated.

Figure 11: Pressurization Rate-Temperature Profiles of Diolefins Samples in the APTAC

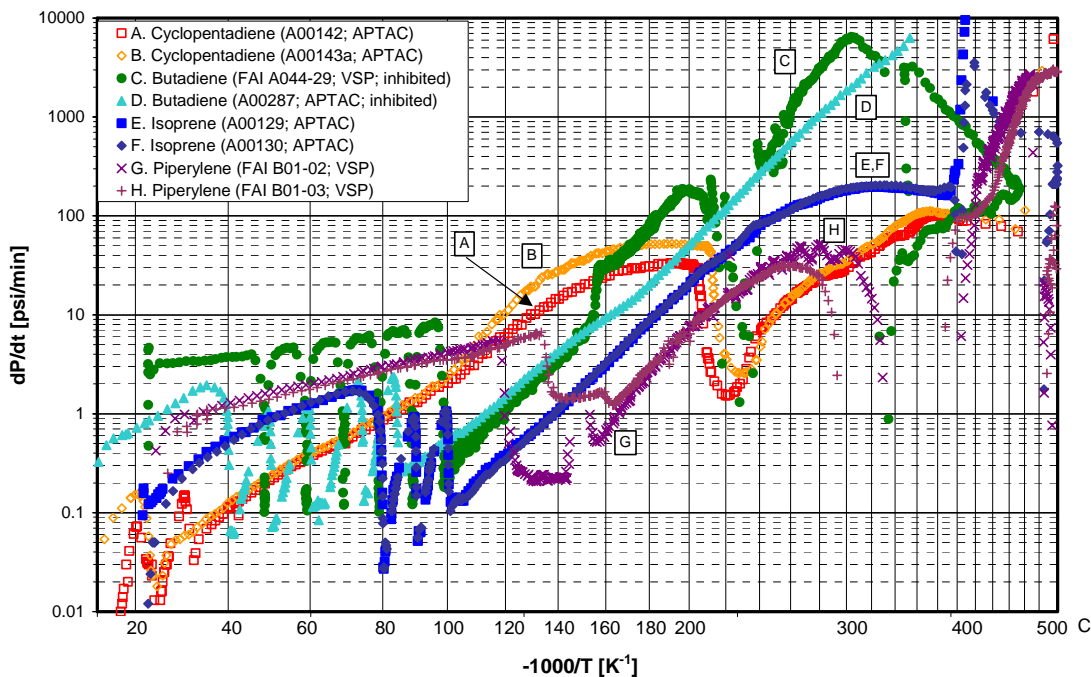


Figure 12: Pressure-Temperature Profiles of Diolefins Samples in the APTAC

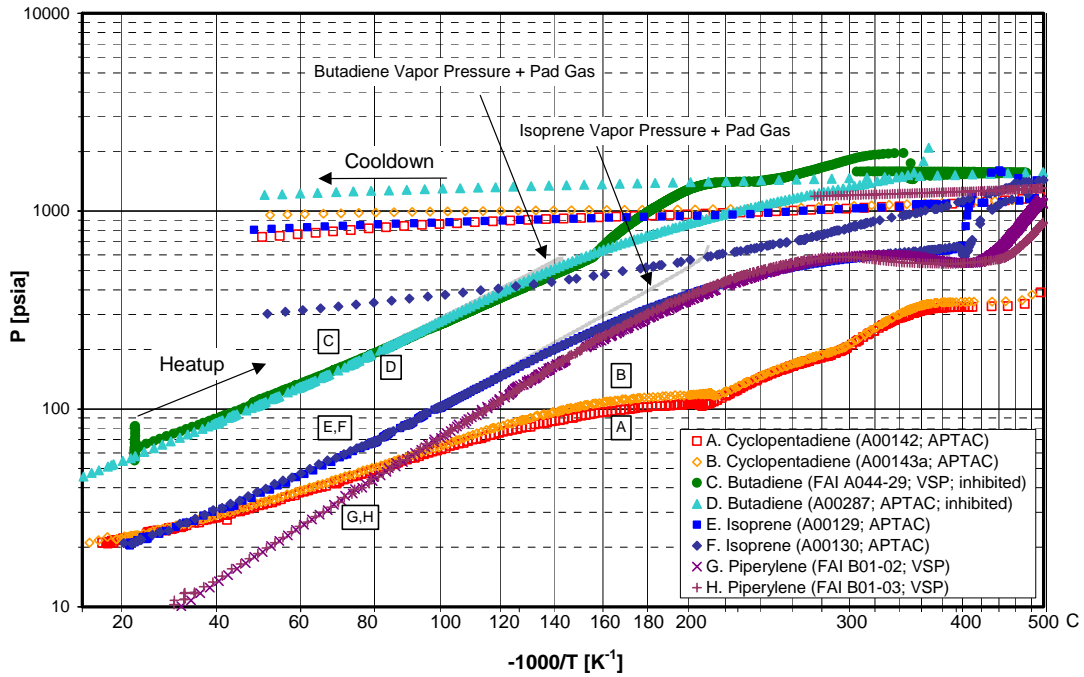
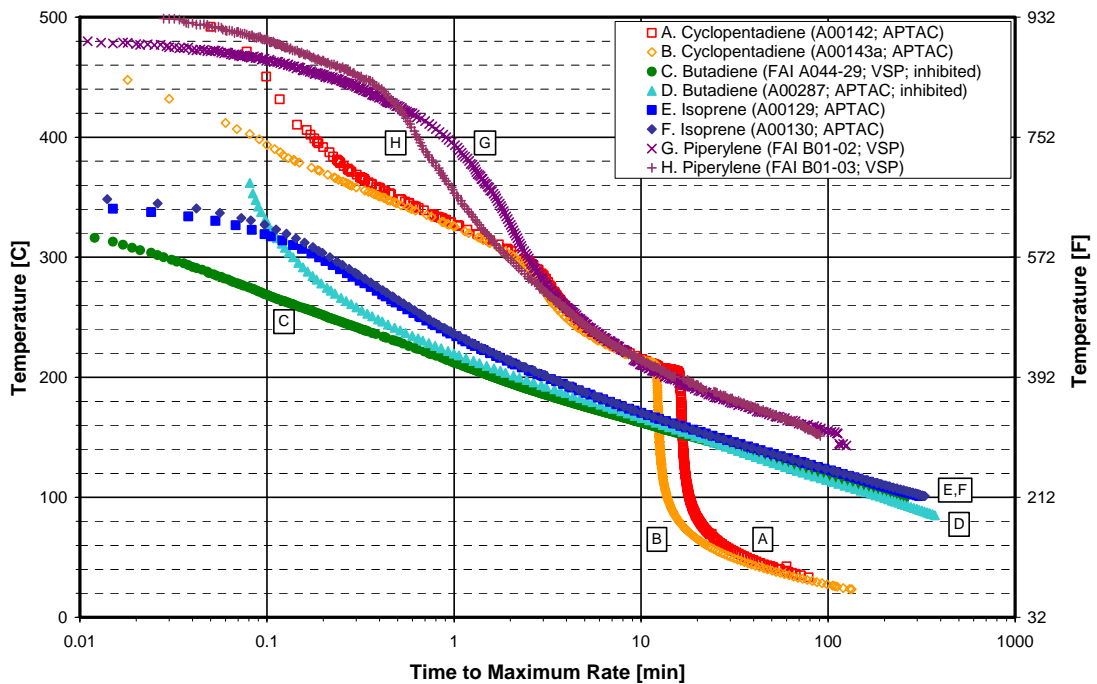


Figure 13: Time-to-Maximum Rate Profiles of Diolefins Samples in the APTAC



Inspection of Figure 14, a self-heat rate vs. reciprocal temperature plot for dicyclopentadiene combined with the previous results for cyclopentadiene, reveals that DCPD does not exhibit any exothermic activity until about 150°C. Moreover, the shape of the exotherm, including the distinct peak and the increasing rate at higher temperatures, bears a strong resemblance to the high temperature portion of the CPD exotherm. The primary differences between the DCPD behavior and the corresponding trends in the CPD traces are a displacement to about 30°C lower temperature for DCPD and an overall lower rate of reactivity (by a factor of about six or seven). This latter observation is again suggestive of some background reactivity occurring with the CPD at the higher temperatures. The observed onset temperature for DCPD along with the qualitative appearance of the reaction peaks are consistent with results of an Accelerating Rate Calorimetry/APTAC study published by Ahmed and Lavin [8].

The same qualitative similarities hold for comparison of the pressurization rates of DCPD and CPD (Figure 15). Again, the DCPD results resemble the high temperature portion of the CPD curve except for the displacement to lower temperature and the reduced activity. Similar results appear in the time-to-maximum rate plot of Figure 16.

Analogous to the DCPD-CPD comparison, Figure 17 illustrates the behavior of limonene and isoprene. In this case, the reactivity of limonene is offset by about 180-220°C from that of isoprene itself. The limonene peak rate is more than two orders-of-magnitude lower than that for isoprene in the same temperature range. The pressurization rate for limonene is virtually non-existent up to about 300°C and above that temperature, exhibits a substantial rise in rate (Figure 18). Nevertheless, the pressurization rate never attains the magnitude of isoprene. Consistent with the self-heat rate plot, the time-to-maximum rate curve of limonene parallels those of isoprene, but is displaced to much higher temperatures—indicative of the lower reactivity of limonene.

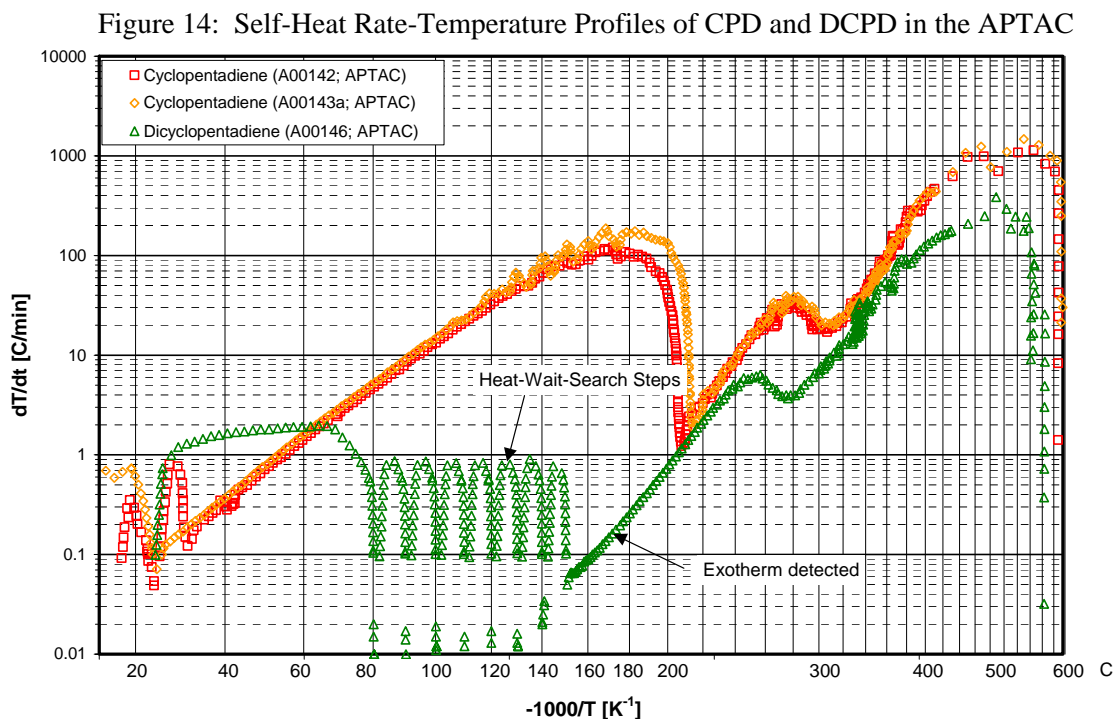




Figure 15: Pressurization Rate-Temperature Profiles of CPD and DCPD in the APTAC

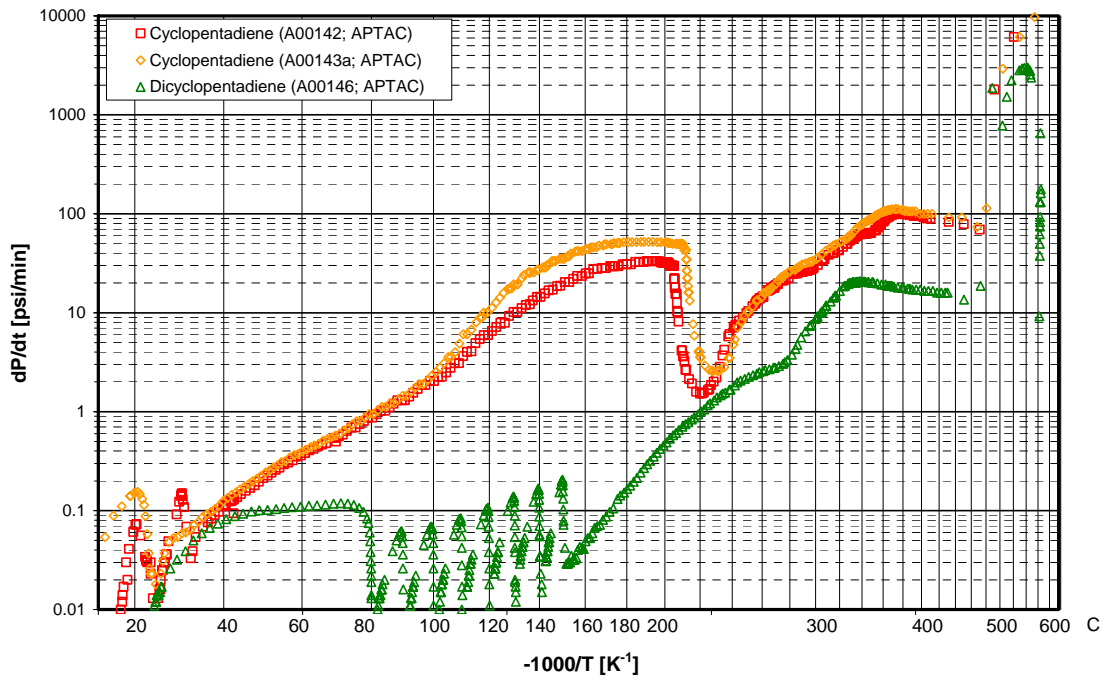


Figure 16: Time-to-Maximum Rate Profiles of CPD and DCPD in the APTAC

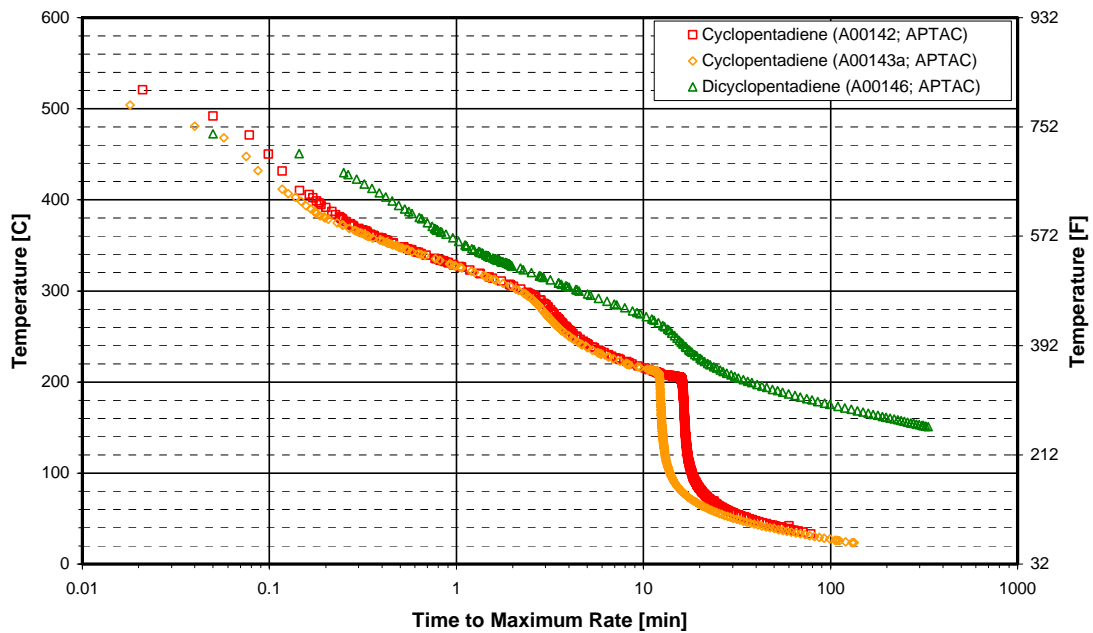


Figure 17: Self-Heat Rate-Temperature Profiles of Isoprene and Limonene in the APTAC

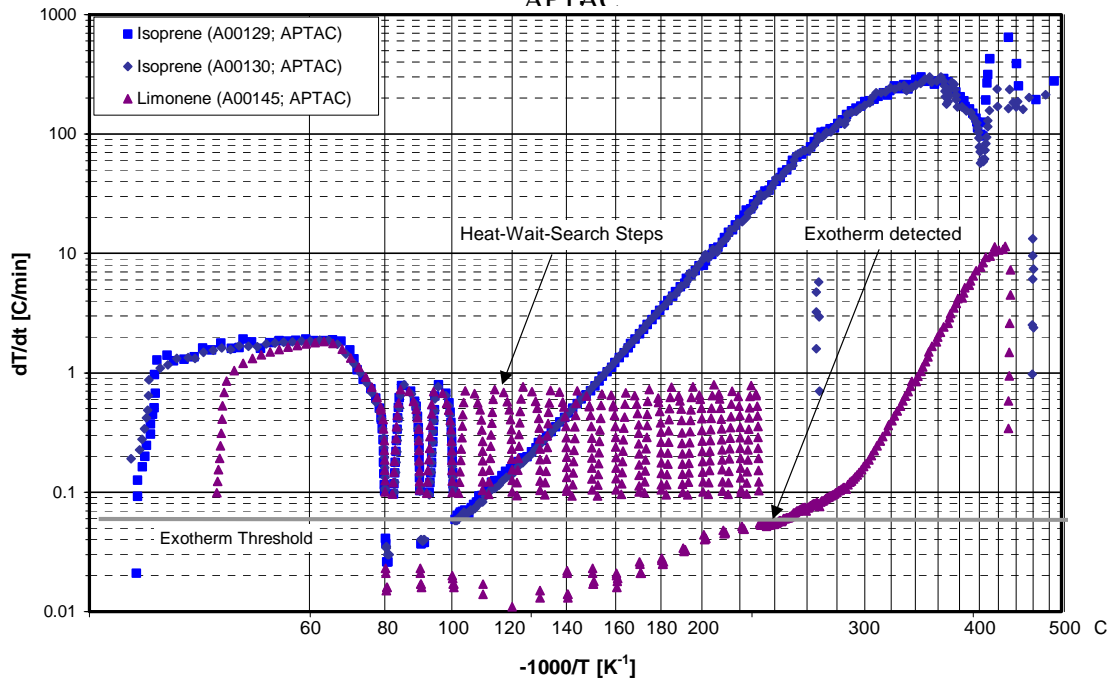


Figure 18: Pressurization Rate-Temperature Profiles of Isoprene and Limonene in the APTAC

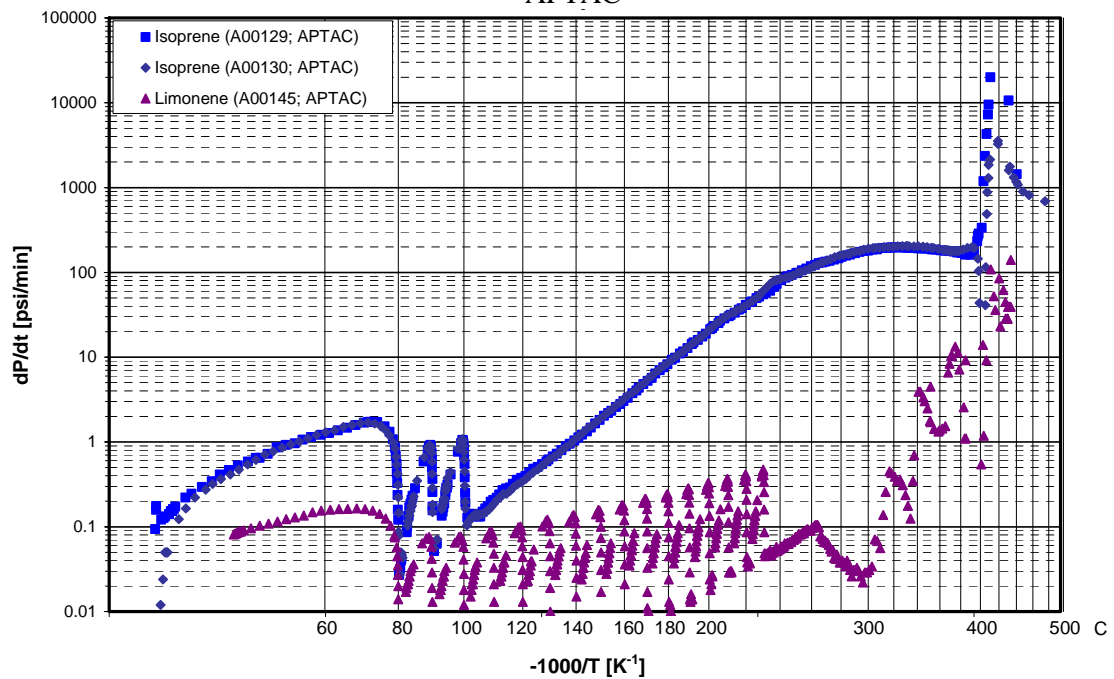
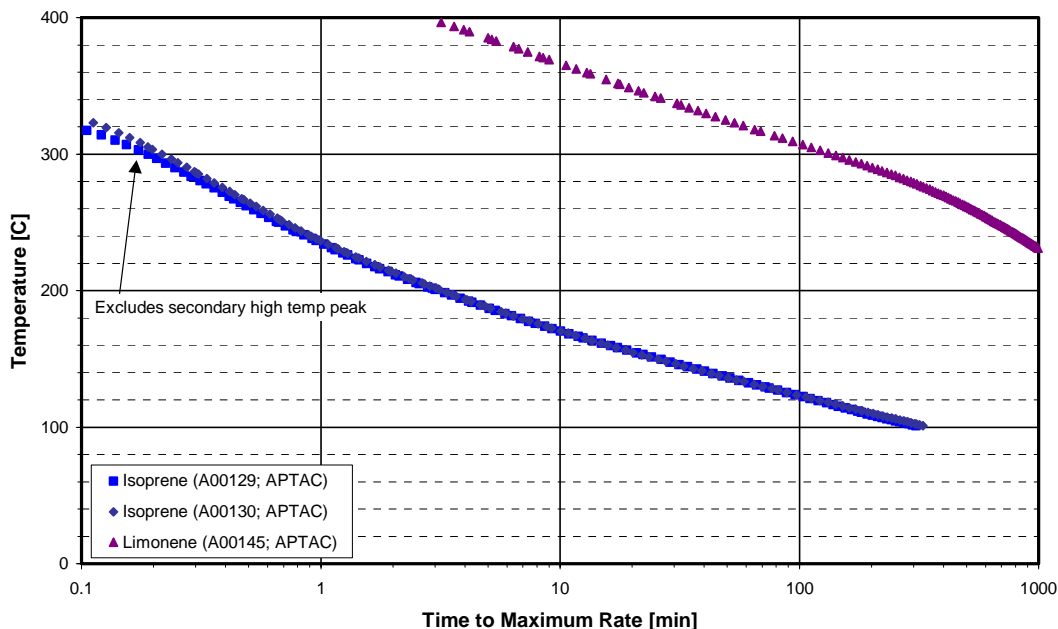
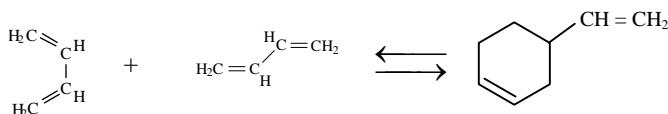
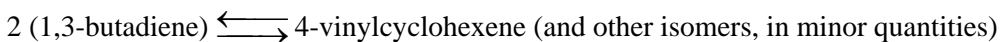
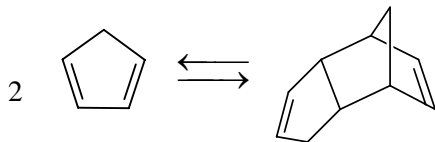
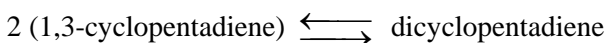


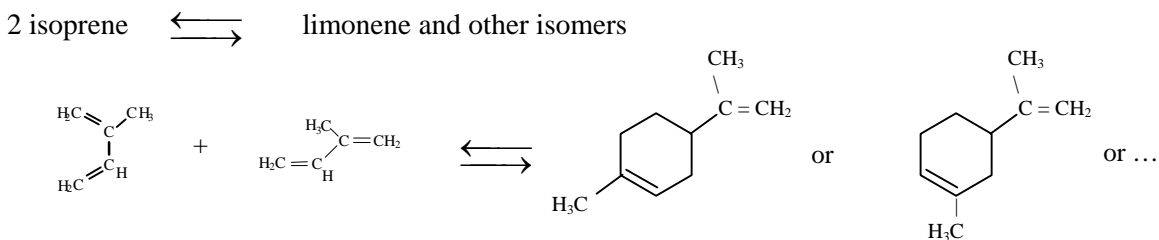
Figure 19: Time-to-Maximum Rate Profiles of Isoprene and Limonene in the APTAC



#### Reaction Path of Conjugated Diolefins

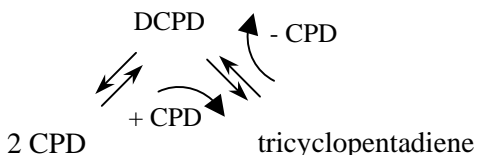
It is well-known that conjugated diolefins, in the absence of catalyst or free radical promoters (including oxygen), will undergo “thermal” reaction via a Diels-Alder reaction pathway [9,10]. To accomplish this, the conjugated double bonds of at least one of the reacting molecules must be in a *cis* conformation when approaching a double bond of the second reacting molecule. This is the case automatically for cyclopentadiene. For butadiene, isoprene, and piperylene, this conformation is less-favored than the *trans* conformation; however, interchange between these conformations does take place. The dimerization may be depicted as follows





Note that the dimers of CPD, butadiene, and isoprene do not have conjugated double bonds. This means that further Diels-Alder addition involving only the dimers cannot take place. Any more reaction requires a different pathway or reaction with additional conjugated molecules.

The conjugated diolefin reactions are equilibrium-limited and, at elevated temperatures, the reverse reaction becomes significant. (Reliance on this equilibrium allowed for production of cyclopentadiene from dicyclopentadiene via distillation for this study.) As the conjugated diolefins react *exothermically* in the adiabatic environment of the APTAC, increased temperatures are experienced, leading to the equilibrium limitation on conversion of monomer to dimer. However, at the point equilibrium has been established, dimer has been produced in sufficient concentration to allow for Diels-Alder reaction between the *dimer* and monomer. Since reaction to form the trimer is also exothermic, the temperature is thus driven higher yet. This increasing temperature, in conjunction with the dimer-monomer equilibrium, will ultimately deplete the dimer in favor of monomer and trimer. For cyclopentadiene, this can be depicted as



with analogous representations for 1,3-butadiene and isoprene. The process can then be repeated to convert trimer into tetramer. Through this sequence of reactions, the neat conjugated diolefins are ultimately converted to oligomers. At high enough temperatures, thermal cracking of the oligomer can take place, generating light hydrocarbon species and a carbon-rich solid phase. Such decomposition can appear exothermic given the abundance of double bonds in the system.

For mixtures of conjugated diolefins and other olefins, the same considerations are expected to hold. The process may be slowed somewhat due to the reduced initial concentration of diolefin and to the generation of only a single diolefin monomer from reversion of an olefin-diolefin co-dimer. Nevertheless, the energetics and thermodynamics should drive the mixture toward higher temperatures, oligomerization, and decomposition.

The preceding discussion clearly pertains to reactions involving only one particular conjugated diolefin. Though no tests have been performed in this study on mixtures of various conjugated diolefins, it is easy to imagine that the reaction pathways will become significantly more complicated as the number of co-dimers, co-trimers, etc. and the associated equilibrium considerations are taken into account.

## Alkynes

The temperature histories of selected C4 and C5 triple bonded hydrocarbons are shown in Figure 20. The most reactive species is the 2-methyl-1-buten-3-yne (an alkyne analog of isoprene) which begins reacting at about 80-90°C. For all of these species, temperatures exceed 800°C and, in some cases, reach the maximum instrument limit of 900°C. The corresponding pressure-time relationships appear in Figure 21. By the end of the tests, pressures above 1550 psia and as high as 2150 psia were achieved before shutdown of the calorimeter eventually limited further reaction. A lightweight, black powder was usually generated, most likely forming during the high temperature stage of the experiments.

The self-heat rate behavior of these species appears in Figures 22 and 23 (again, with and without the heat-wait-search steps, respectively). Three of the four alkynes exhibit exothermic activity beginning in the 210+°C range. It appears that some instrument drift is accompanying the trace for 2-butyne between 210 and 260°C. Drift may also be playing a role for the small “peak” appearing at about 125°C.

Other than the regions of apparent drift, the reactivity of 2-butyne is similar to that of 2-pentyne. These internal unsaturates both react at higher temperature, and are thus less reactive, than 1-pentyne. This is consistent with the concept that the acidity of the alpha hydrogen of the *primary* triple bond gives the 1-pentyne more reactivity. In addition, there is less steric hindrance in 1-pentyne allowing greater access to the triple bond.

One of the more prominent features of the self-heat rate plot is the low temperature exotherm of the methyl buten-yne. Exotherm onset (0.06°C/min) begins at about 80-90°C, which indicates that this species is as reactive as 1,3-butadiene and isoprene. A replicate of this test confirms this activity.

Figure 20: Temperature Histories of Alkynes in the APTAC

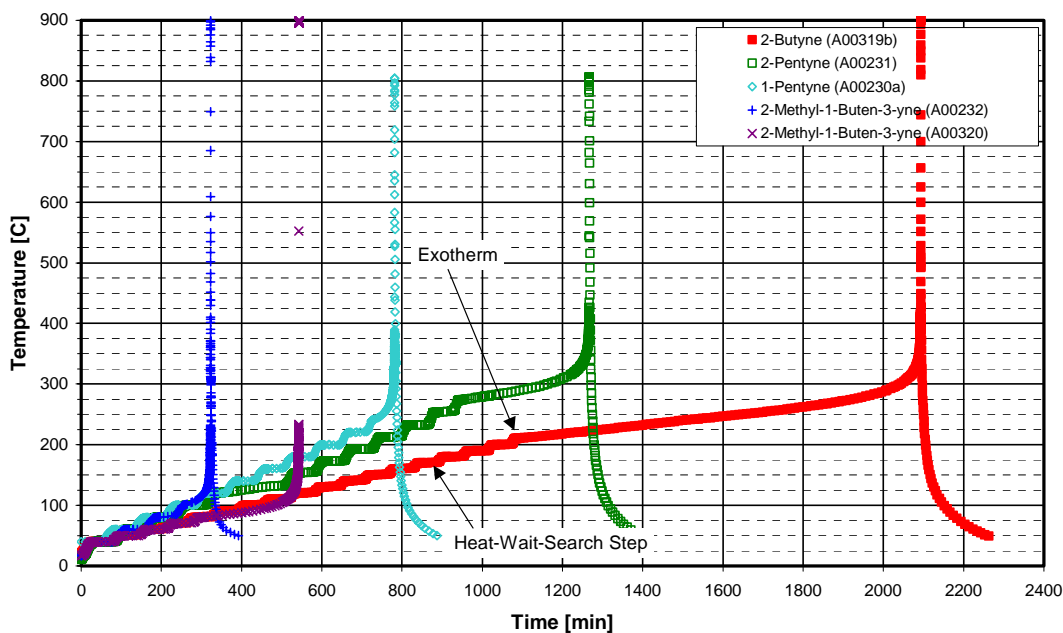


Figure 21: Pressure Histories of Alkynes in the APTAC

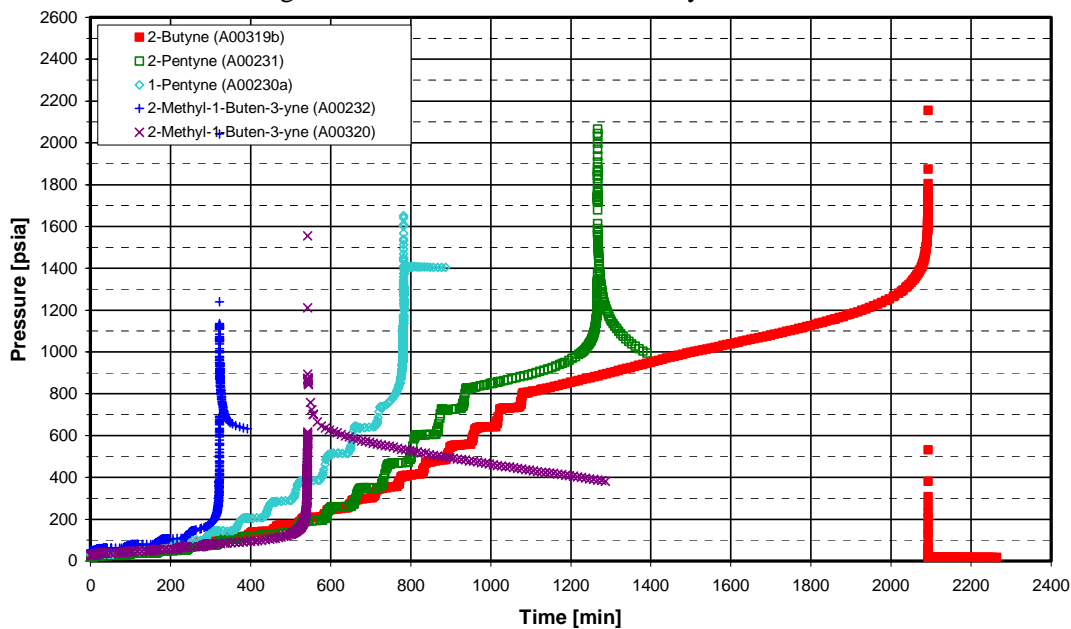
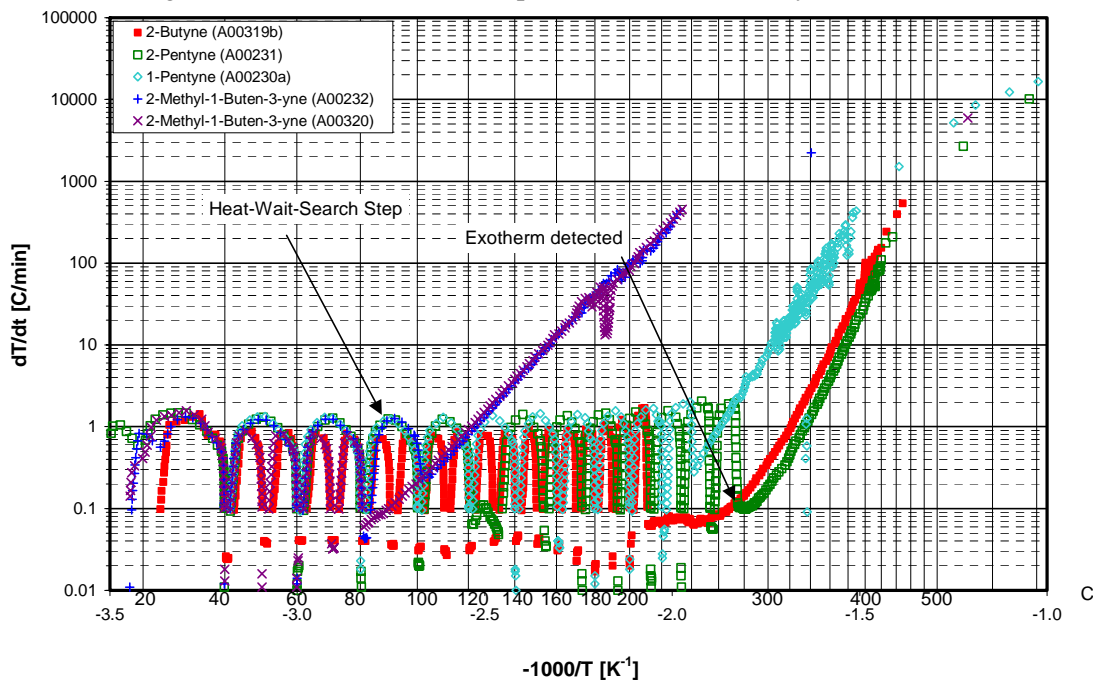


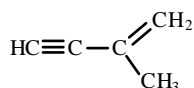
Figure 22: Self-Heat Rate–Temperature Profiles of Alkynes in the APTAC



The pressurization rate trends (Figure 24) of the various alkynes parallel the self-heat rates. Inspection of the pressure-temperature profiles of Figure 25, by comparison of the heatup and cooldown portions, reflects the generation of non-condensable species. In the case of 1-butyne, the sample bomb was ejected from the vessel head followed by bursting of the containment vessel rupture disk. As a result, the pressure reading fell to atmospheric level.

Finally, the time-to-maximum rate plot in Figure 26 illustrates the relative reactivity of these species. Methyl buten-yne heated to 80°C would reach its maximum rate in about four hours. In contrast, temperatures much above 200°C would be required for the other alkynes to react in this timeframe.

The presence of the triple bond in the methyl-buten-yne imposes a steric constraint that is expected to inhibit Diels-Alder condensation. Specifically, the molecule is unable to assume the nearly U-shaped configuration favorable for the reaction pathway.



Nevertheless, it is obvious from the calorimetry data that this alkene-alkyne is substantially more reactive than the alkynes.

To determine the type of molecule being formed initially from methyl-buten-yne, another APTAC test was carried out, but this time, the test was terminated prematurely. Once again the onset temperature was about 80-90°C. The sample was allowed to self-heat for a temperature rise

Figure 23: Self-Heat Rate–Temperature Profiles of Alkynes in the APTAC Heat-Wait-Search Steps Removed

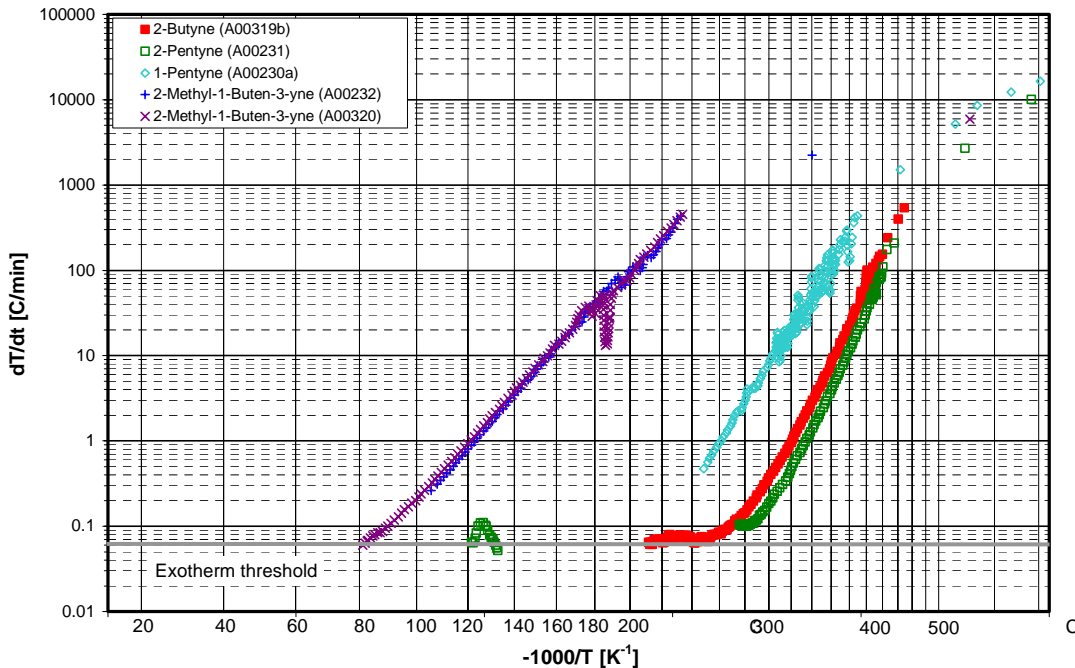


Figure 24: Pressurization Rate-Temperature Profiles of Alkynes in the APTAC

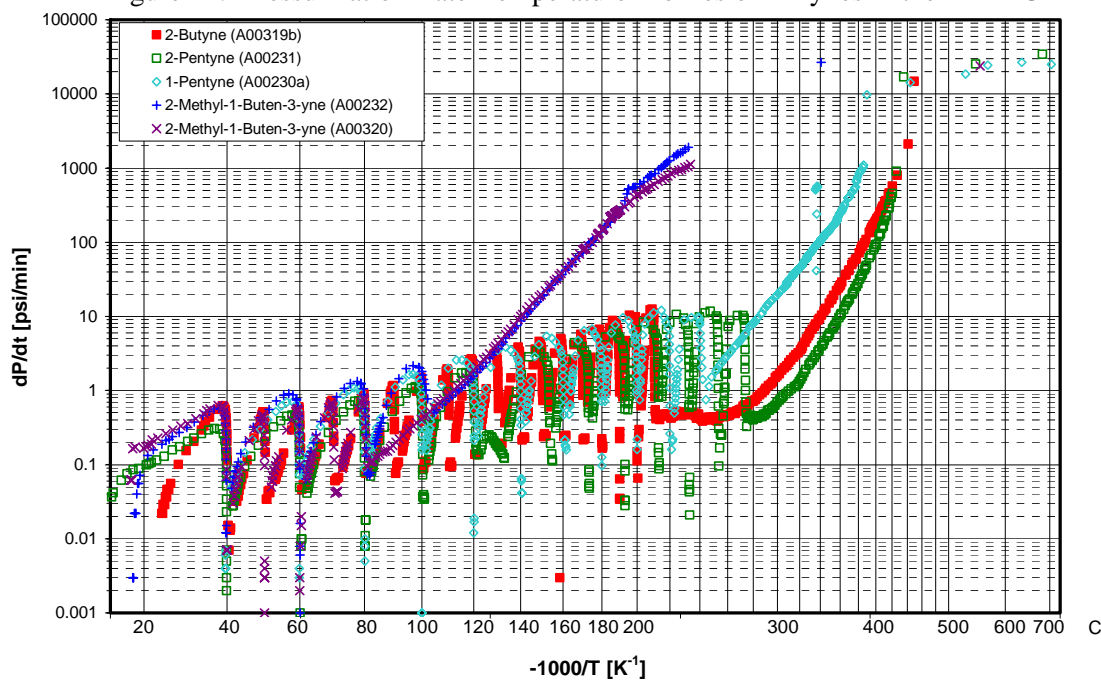


Figure 25: Pressure-Temperature Profiles of Alkynes in the APTAC

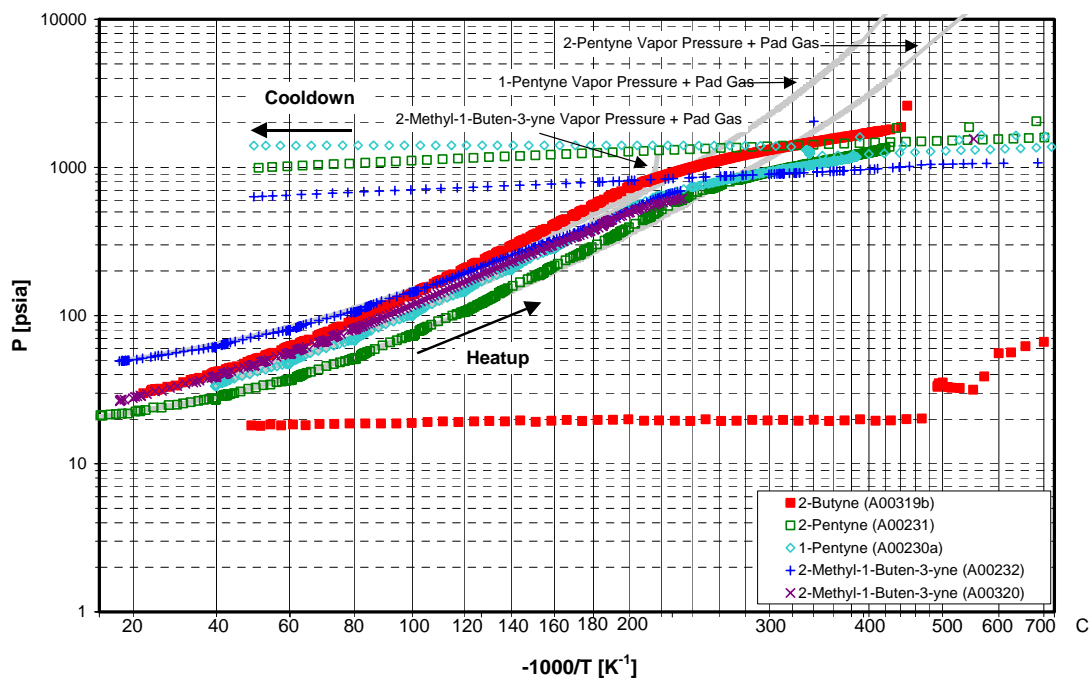
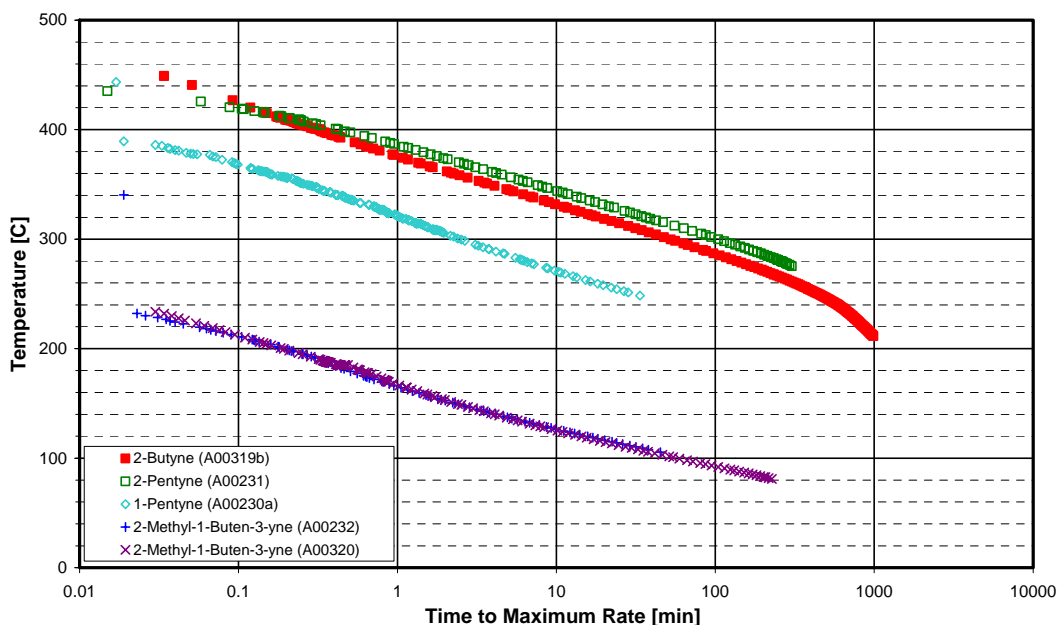
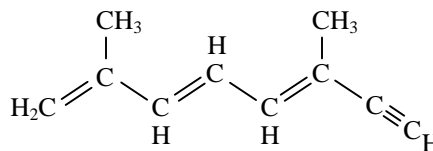
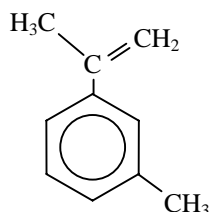




Figure 26: Time-to-Maximum Rate Profiles of Alkynes in the APTAC



of only about 50°C, after which, the sample cooled and was readied for analysis. Preliminary results from GC/IR/MS, GC/FID, and NMR analysis reveal that a collection of dimers and trimers were produced. While most of the sample at this point was still the original methylbuten-yne (ca. 95%w, as expected basis the temperature rise and a rough estimate of dimerization heat), a variety of aromatics and straight-chain compounds of molecular formula  $C_{10}H_{12}$  were formed. For example, the following structures are believed to be present in the product mix.



Aromatics appear to outnumber the straight-chain species by roughly a 3:1 ratio (weight and mass basis being equivalent). Formation of aromatic structures would seem to suggest a Diels-Alder-type reaction pathway, but much more in-depth investigation is required to demonstrate this. The straight-chain hydrocarbon clearly is formed through a different mechanism.

### Thermal Inertia Effects

In this study's experiments, the thermal inertia or phi factor,  $\phi$ , ranges between 1.13 to 1.27 (see Tables 1 and 2). This means that the sample container has a thermal capacitance of 13-27% of that of the sample, or expressed differently, about 12-22% of the total of the bomb plus sample. The *actual* temperature rise experienced in a large-scale adiabatic environment, in which the *relative* wall thermal capacitance might be very small, would be higher by the thermal inertia factor or an additional 13-27%. Thus, the extent of the each exotherm would be greater and may

hasten the transition between exotherms. Furthermore, a greater pressure build-up can be expected to accompany the increased temperature rise.

In addition to the impact of thermal inertia on exotherm temperature rise, the self-heat rates associated with the exotherms would be greater at the commercial scale than those observed in the experiments by a factor larger than the thermal inertia factor. This means that the timeframe for a temperature/pressure excursion beginning at some initial temperature would be correspondingly shorter.

To adjust the current study's results properly for equipment with a lower thermal inertia, a dynamic simulation that takes into account the observed reaction kinetics coupled with material and equipment properties would be required.

## CONCLUSIONS

Evaluation of the *uncatalyzed* reactivity of selected olefins, diolefins, and alkynes has been performed via adiabatic calorimetry. Straight-chain C4 and C5 olefins exhibits no apparent exothermic reactions for temperatures up to 340°C. In contrast, conjugated diolefins readily react at much lower temperatures. For example, cyclopentadiene initiates reaction around room temperature while 1,3-butadiene and isoprene exhibit reaction beginning around 85-100°C. All of the conjugated diolefins tested have the potential for generating temperatures in excess of 600°C.

Several distinct peaks are apparent in the course of cyclopentadiene reaction. Testing of dicyclopentadiene reveals some of the same peaks and confirms that the first cyclopentadiene peak is dimerization. Facets of the same behavior, but with the absence of distinct peaks, are observed when comparing isoprene and limonene. These peaks reflect dimerization, oligomerization, and ultimately, exothermic decomposition taking place. The calorimetric trends are consistent with the Diels-Alder mechanism for dimerization and oligomerization.

The C4 and C5 straight-chain alkynes display exothermic activity at temperatures above 200°C. Once initiated, these exotherms can progress to temperatures approaching 900°C. One particular species, the alkyne analog to isoprene (2-methyl-1-buten-3-yne) shows considerably higher activity. It initiates reaction at 80-90°C (i.e., as reactive as 1,3-butadiene) and also proceeds toward 900°C. Product analysis suggests the aromatic and straight-chain dimers are formed.

The testing results provide a comparison of the relative reactivities of these different classes of unsaturated hydrocarbons as well as an indication of the types of thermal conditions to avoid in handling these species.

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