2-METYLPYRIDINE *N*-OXIDATION RUNAWAY STUDIES

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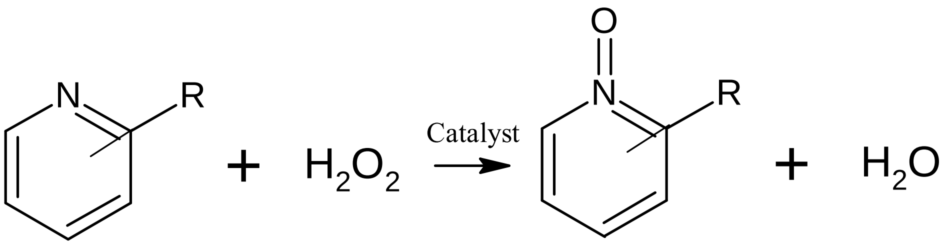
Mary Kay O'Connor Process Safety Center International Symposium

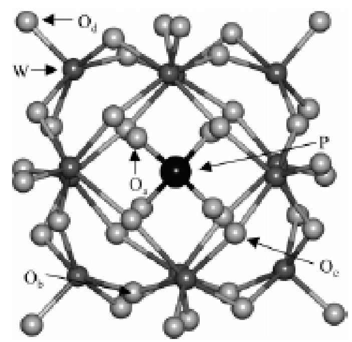
October 28-29, 2008

THE *N*-OXIDATION OF ALKYLPYRIDINES



- Analgesic
- Anti-inflammatory
- Antiulcer → Omeprazole

Phosphotungstic acid



- Nontoxic
- Noncorrosive
- No odor
- Nonvolatile
- High catalytic activities
- Reusable
- Stable in storage

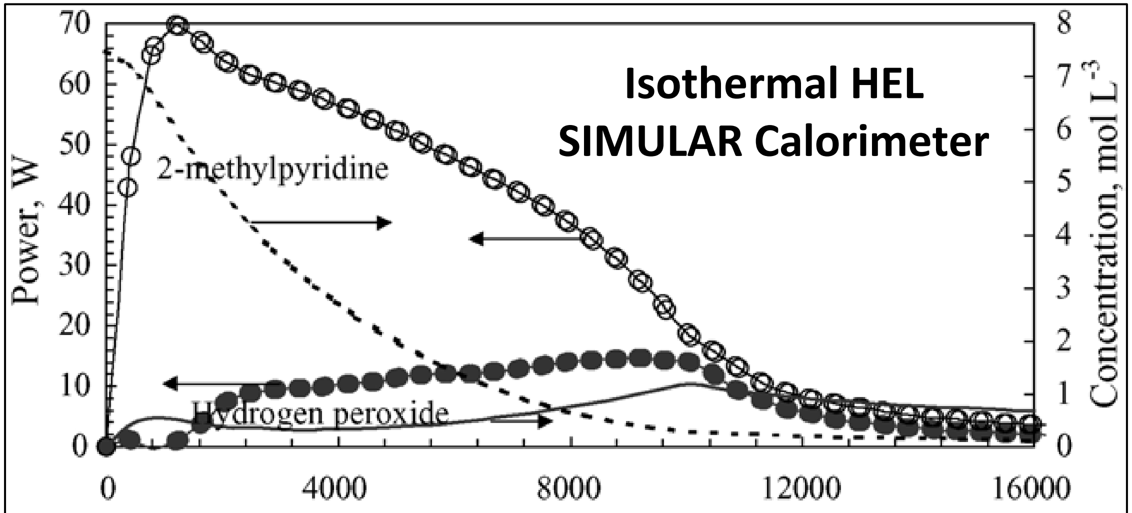
Undesired reaction

$$2H_2O_2 \xrightarrow{\text{Catalyst}} 2H_2O + O_2$$

- Over pressurization
- Oxygen-rich atmosphere
- Condition-sensitivity

Campbell, K.A., Janik, M.J., Davis, R.J., and Neurock, M. Ab Initio and microcalorimetric investigation of alkene adsorption on phosphotunstic acid. Langmuir 2005, 21, 4738-4745

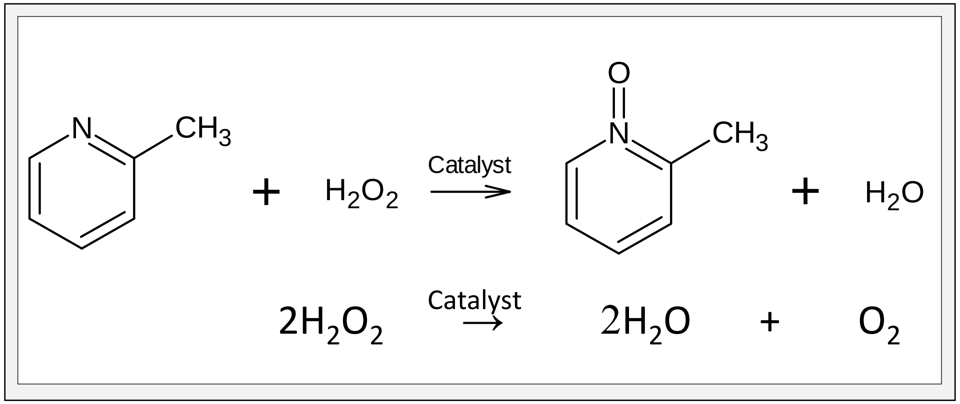
Previous Findings



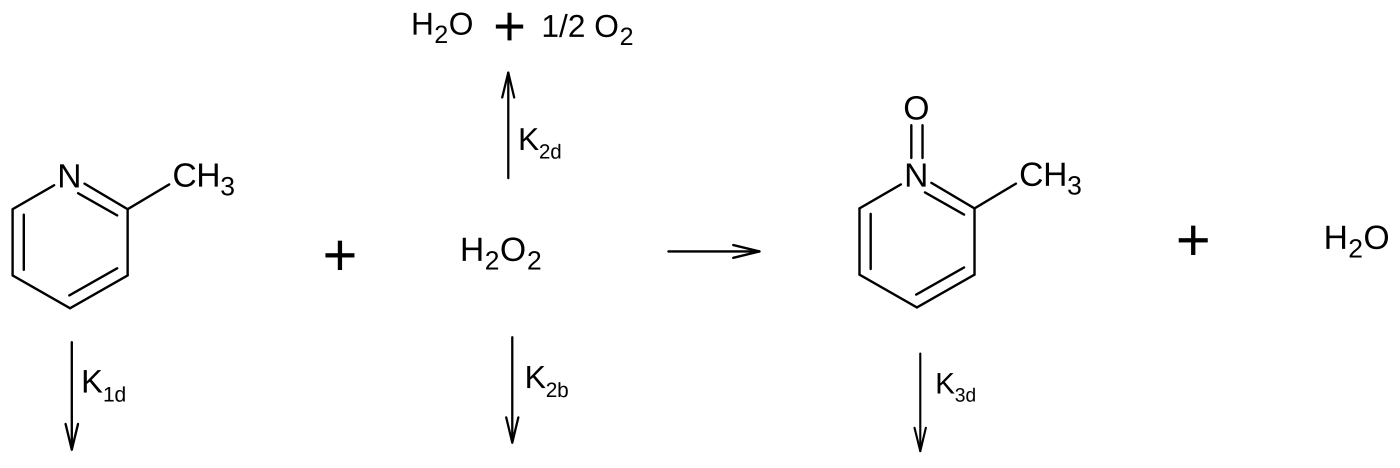
Jun Gao and Maria Papadaki , 2006

- The highly exothermic H_2O_2 decomposition “starts” at temperatures above 50^{o}C.
- Hydrogen peroxide is catalytically and thermally decomposed. However, the rate of the thermal decomposition is insignificant.
- The catalytic decomposition of hydrogen peroxide is slower in the *N*-oxidation reaction.

2-PICOLINE *N*-OXIDATION



$$
\begin{array}{ccccccc}
A_D & & B_D & & & & C_D \\
\uparrow & & \uparrow & & Catalyst & & \uparrow \\
A & + & B & & \rightarrow & & C \\
\downarrow & & \downarrow & & & & \\
A_B & & B_B & & & &
\end{array}
$$



Stable up to 500ºC

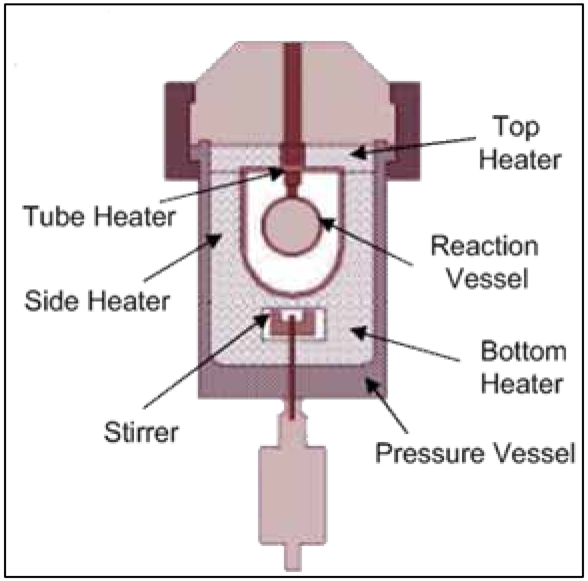
OBJECTIVES

1. Temperature where the 2-picoline *N*-oxide decomposition is significant

2. Effect of the catalyst on the 2-picoline *N*-oxide decomposition

3. Effect of the 2-picoline *N*-oxide and 2-picoline on the hydrogen peroxide decomposition.

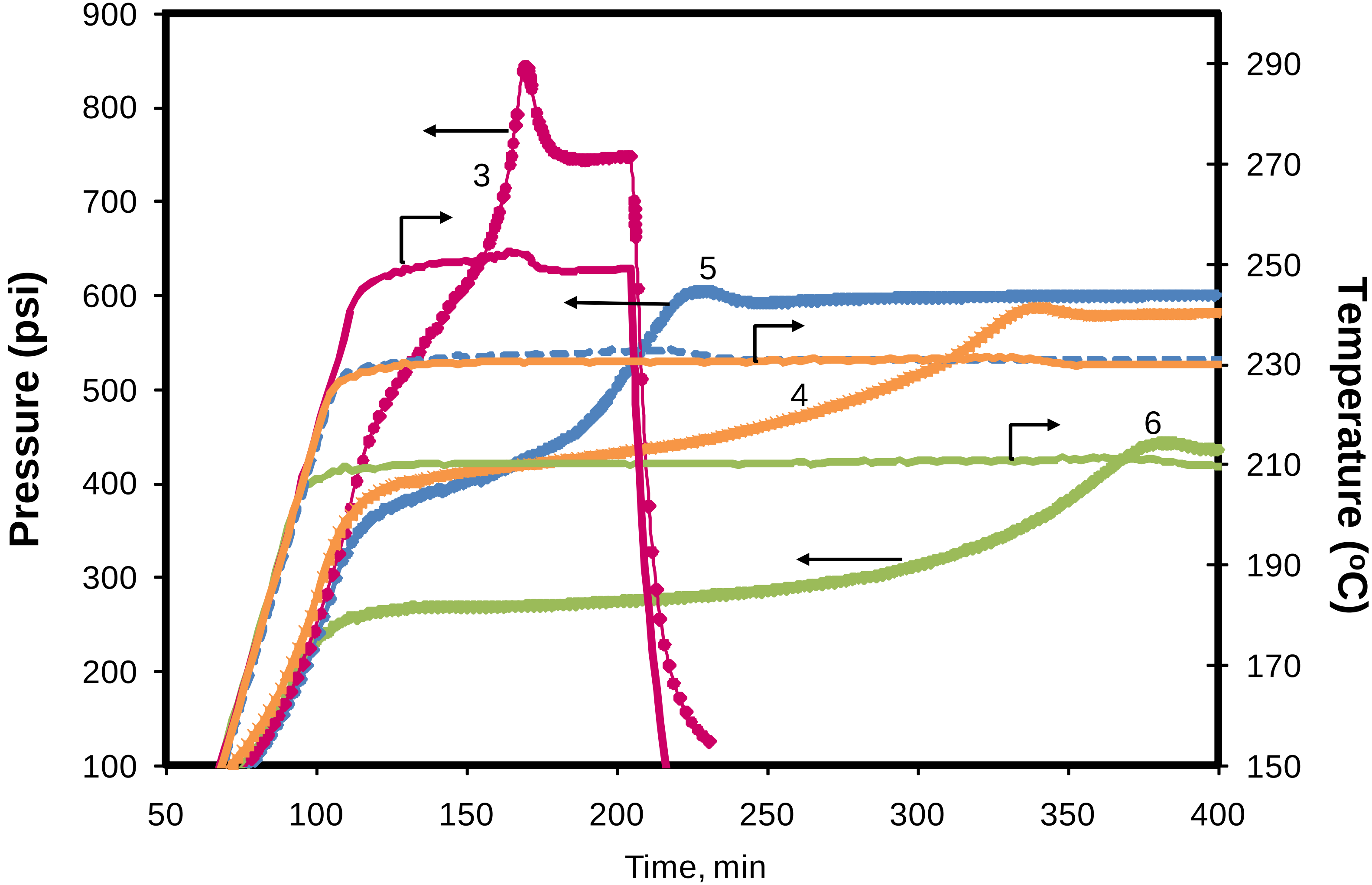
Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)



Aldeeb A. Systematic approach for chemical reactivity evaluation. 2003

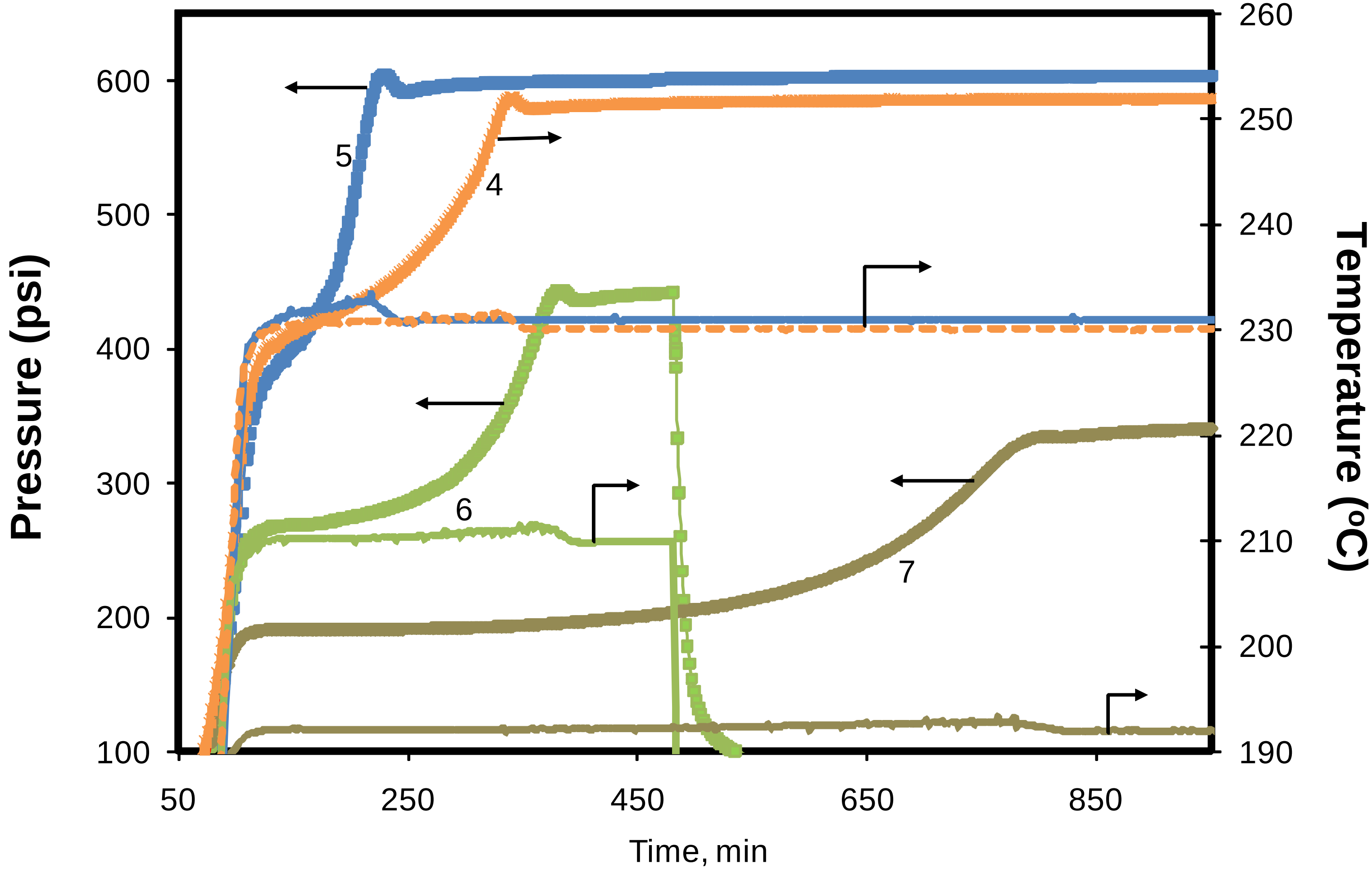
- 16.5 g samples
- 100 ml glass cell
- Isothermal and Heat-Wait-Search (HWS) mode

2-picoline *N*-oxide rate of decomposition: Effect of the catalyst and temperature



	3	4	5	6
2-picoline N-oxide, g	6.89	6.89	6.89	6.88
Catalyst, g	0	0	0.1	0.21
Temperature, °C	249	230	230	210
Heat Mode	Isothermal mode			

2-picoline *N*-oxide rate of decomposition: Effect of the catalyst and temperature



	4	5	6	7
2-picoline N-oxide, g	6.89	6.89	6.88	6.89
Catalyst, g	0	0.1	0.21	0.3
Initial temperature, °C	230	230	210	192
Heat Mode	Isothermal mode			

2-picoline *N*-oxide rate of decomposition: Effect of the catalyst and temperature

	1	2	3	4	5	6	7
2-picoline N-oxide, g	2.28	2.29	6.89	6.89	6.89	6.88	6.89
Catalyst, g	0	0.1	0	0	0.1	0.21	0.3
Initial temperature, ^{o}C	200	200	249	230	230	210	192
Heat Mode	HWS	HWS	Isoth	Isoth	Isoth	Isoth	Isoth
Normalized final P, psi	----	115	166	175	165	145	104
Equiv. ideal gas mole	---	0.022	0.033	0.033	0.033	0.028	0.019
Mass loss, g	---	0.7	1.14	1.03	1.46	1.00	0.95
Equiv. oxygen moles	---	0.022	0.036	0.032	0.046	0.031	0.030
O_2 mole in 2-pic-N-ox	---	0.011	0.032	0.032	0.032	0.032	0.032

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- Oxygen dissociation from the 2-picoline *N*-oxide is the most probable reaction taking place during decomposition.

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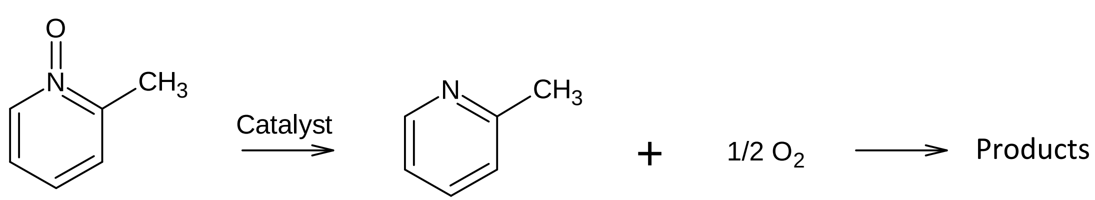
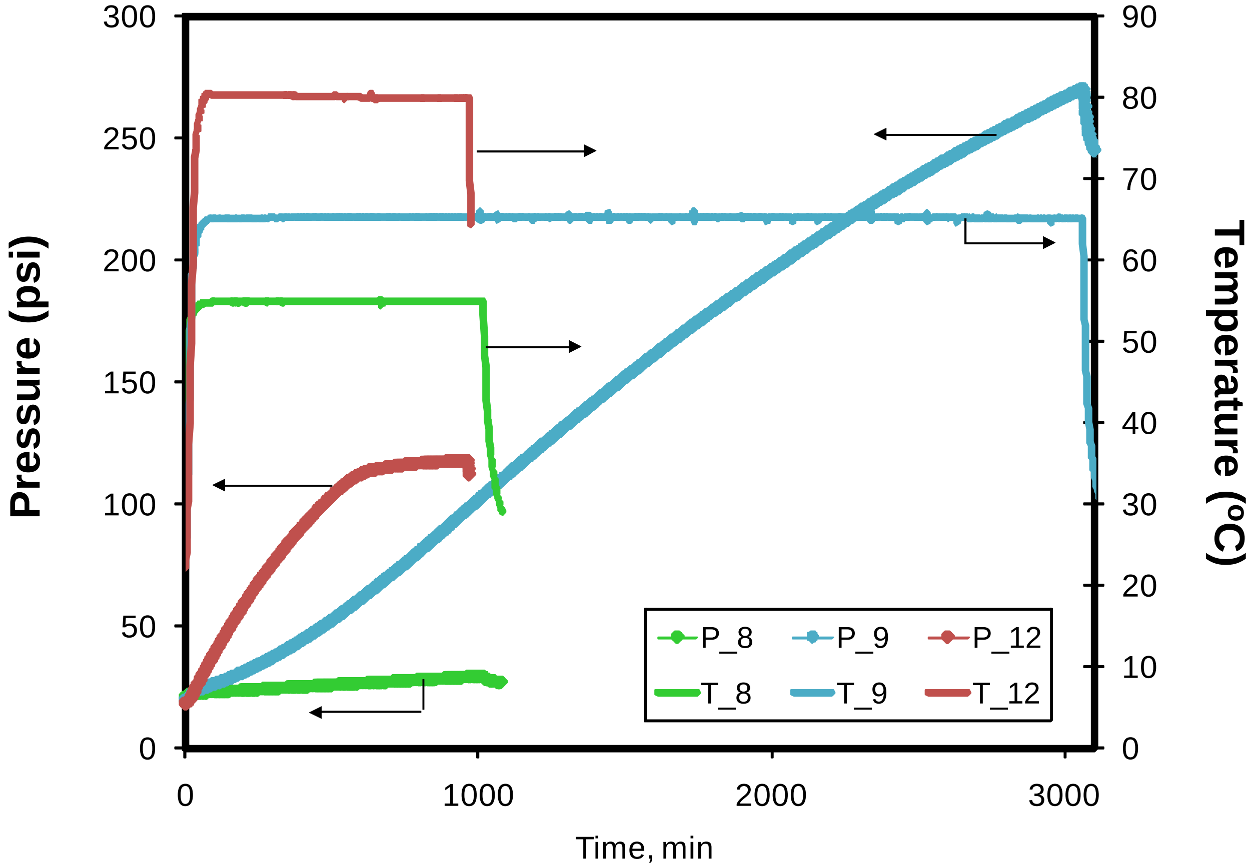
- Oxygen dissociation from the 2-picoline *N*-oxide is the most probable reaction taking place during decomposition.
- Two possible decomposition stages are involved.



✓ Pyridine
✓ Lutidines
✓ Acetic acid

Effect of 2-picoline *N*-oxide decomposition on hydrogen peroxide decomposition



	8	9	12(→9)
2-picoline N-oxide, g	1.6	1.6	→9
Hydrogen peroxide (17.5% wt. in water)	14.4	---	---
Hydrogen peroxide (35% wt. in water)	---	14.4	→9
Catalyst, g	0.09	0.4	→9
Initial temperature, ^oC	55	65	80
Heat Mode	Isothermal mode		

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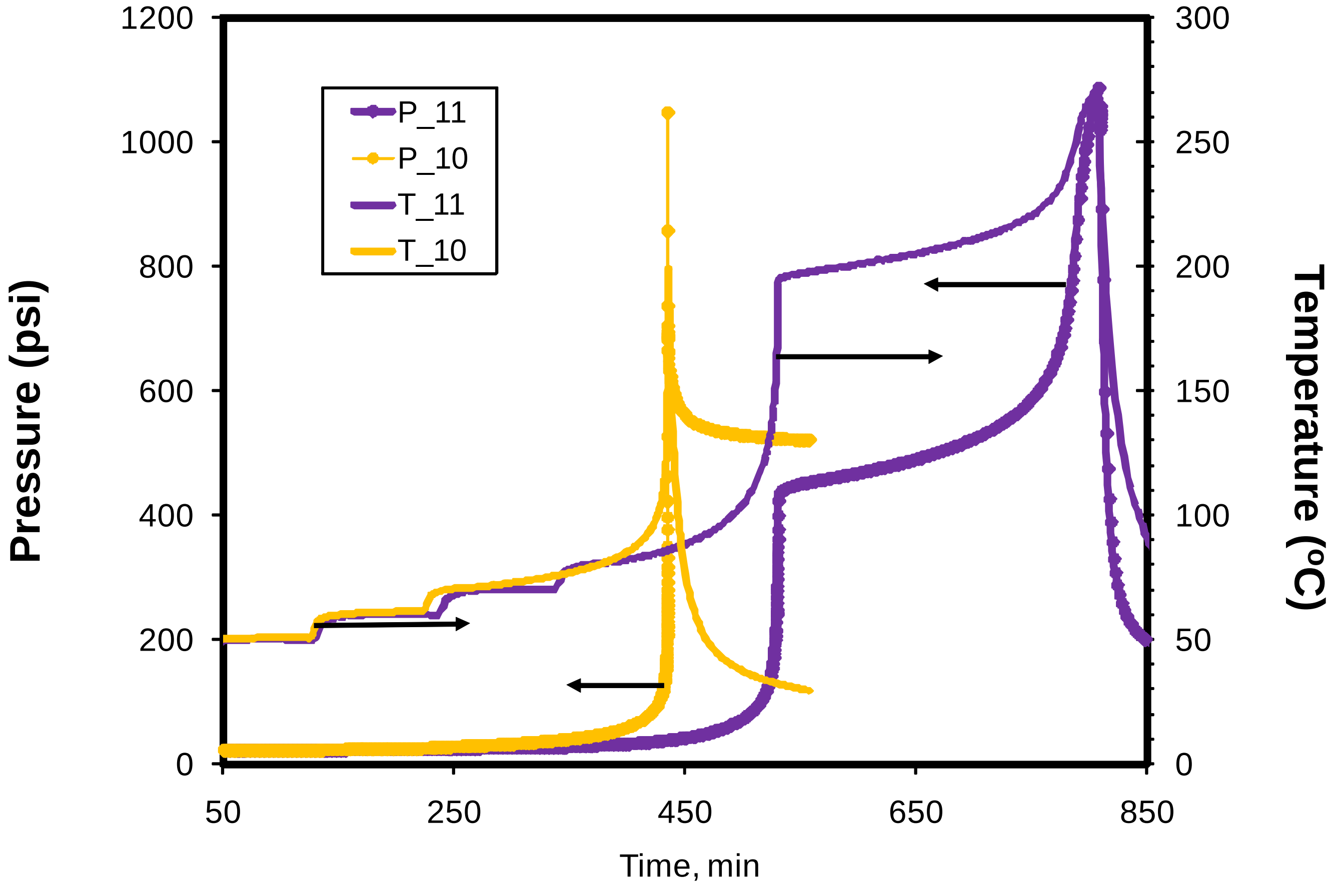

	10	11
2-picoline N-oxide, g	1.6	1.6
Hydrogen peroxide (17.5% wt. in water)	---	14.4
Hydrogen peroxide (35% wt. in water)	14.4	---
Catalyst, g	0.4	0.09
Initial temperature, °C	51	51
Heat Mode	HWS	

Effect of 2-picoline *N*-oxide decomposition on hydrogen peroxide decomposition

	8	10	11	12(→9)
2-picoline N-oxide, g	1.6	1.6	1.6	→9
H_2O_2 (17.5% wt. in water)	14.4	---	14.4	---
H_2O_2 (35% wt. in water)	---	14.4	---	→9
Catalyst, g	0.09	0.4	0.09	→9
Initial temperature, °C	55	51	51	80
Heat Mode	Isoth	HWS	HWS	Isoth
Normalized final press, psi	26.3	510.9	147.2	95.3(+236.6)
Equiv. ideal gas mole	0.005	0.110	0.028	0.016(+0.049)
Mass loss, g	0.18	2.81	2.77	3.28(+2.21)
Equiv. oxygen moles	0.006	0.088	0.087	0.103(+0.069)
O_2 mole in 2-pic-N-ox and H_2O_2	0.082	0.082	0.044	0.082

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- Significant mass loss indicates further decomposition

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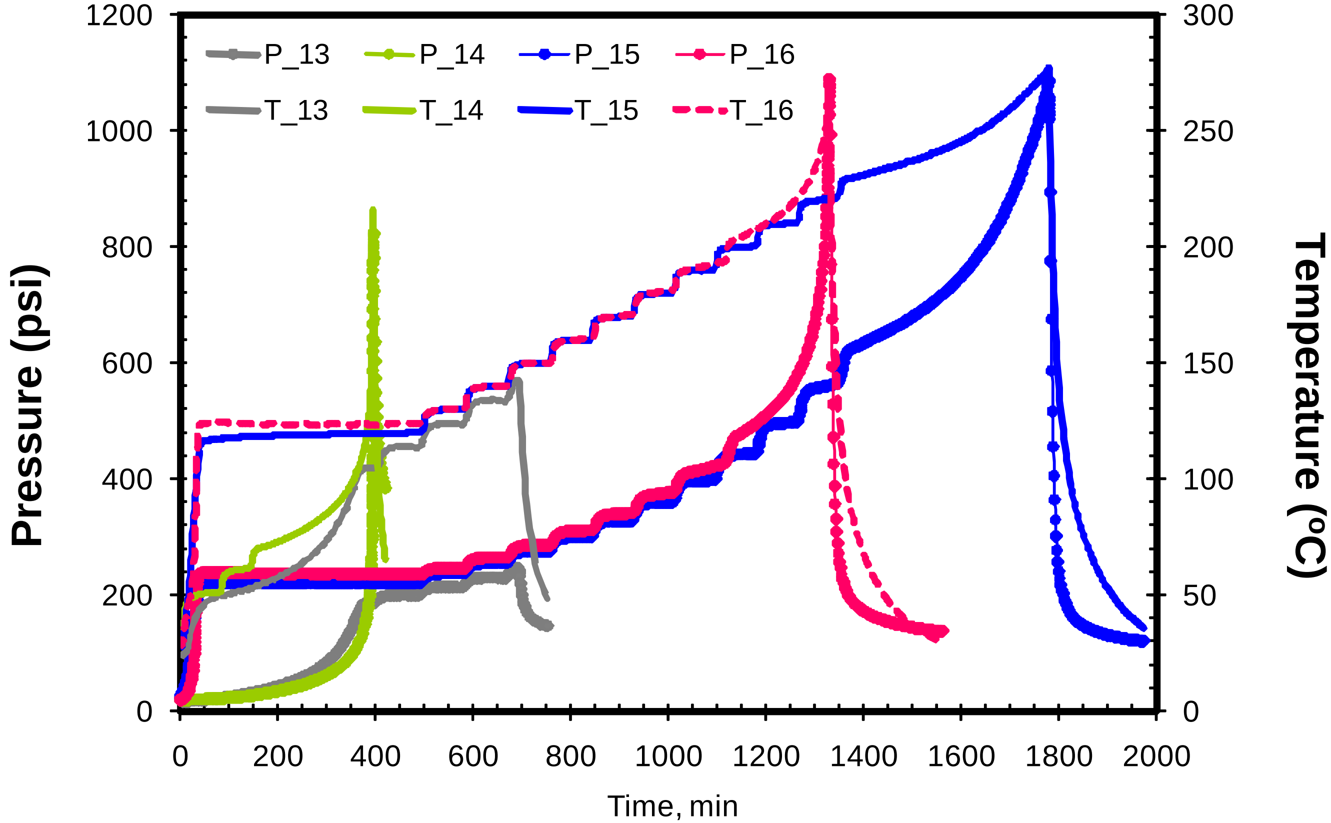
- Significant mass loss indicates further decomposition
- Different mechanisms of decomposition at high catalyst and H_2O_2 concentrations

Effect of the 2-picoline *N*-oxidation on the 2-picoline *N*-oxide and H_2O_2 decompositions



	13 (130 ml cell)*	14	15	16
2-picoline, g	---	---	1.6	1.6
2-picoline N-oxide, g	---	---	---	1.6
Hydrogen peroxide (17.5% wt. in water)	14.52	---	14.4	---
Hydrogen peroxide (35% wt. in water)	---	14.4	---	14.4
Catalyst, g	0.093	0.4	0.09	0.09
Initial temperature, °C	50	51	50	50
Heat Mode		HWS		

*M. Papadaki, et al.,2005.

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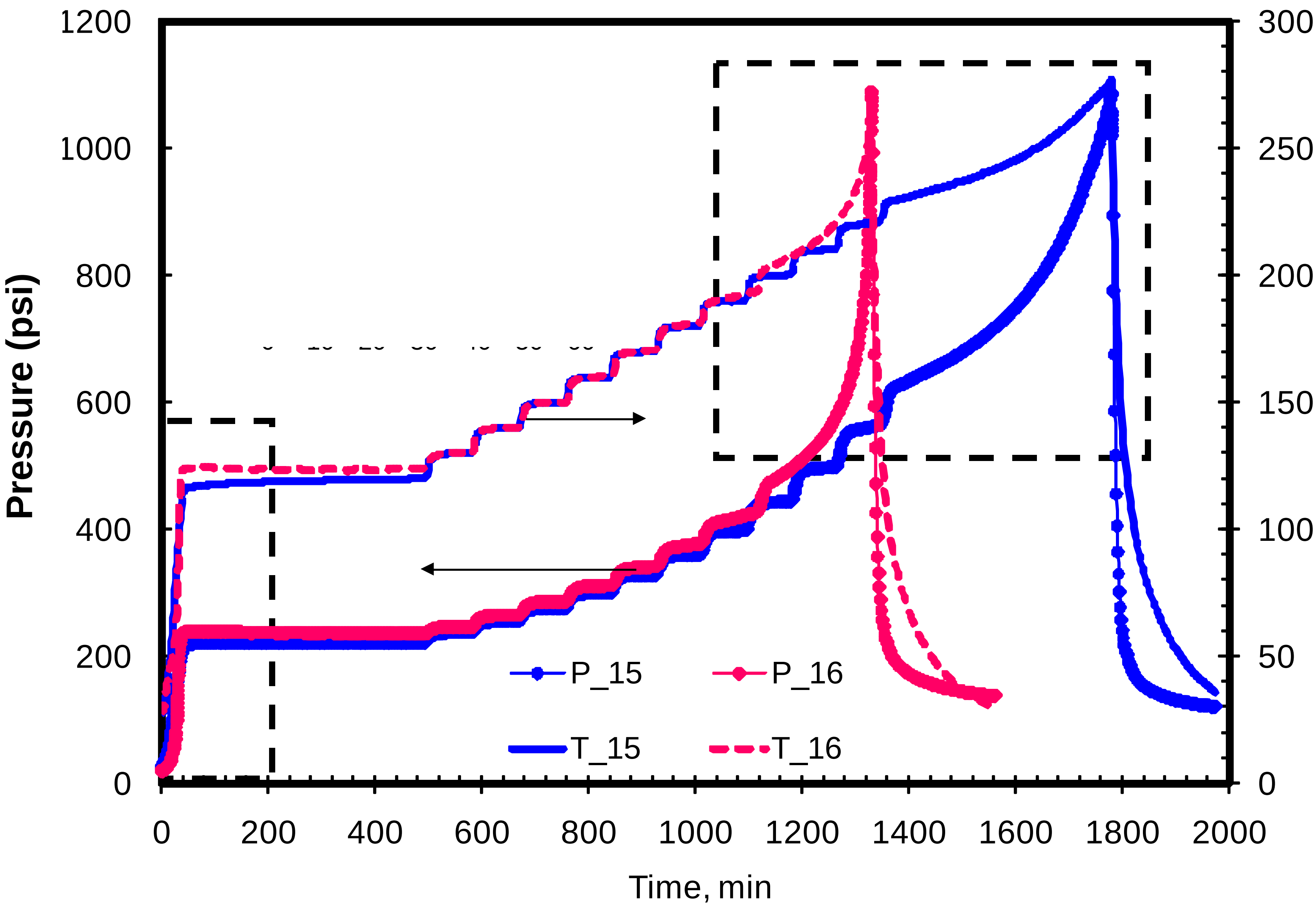

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Initial temperature, ^oC	50	51	50	50
Heat Mode	HWS	HWS	HWS	HWS
Normalized final press	172.9	333.6	115.2	135.6
Equiv_ideal gas mole	0.047	0.071	0.022	0.026
Mass loss, g	---	2.67	1.52	0.73
equiv_oxygen moles	---	0.0834	0.0475	0.0228
O_2 mole in 2-pic-N-ox and H_2O_2	0.048	0.071	0.021	0.026

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- ✓ The catalyst accelerates the decomposition of 2-methylpyridine-*N*-oxide.

- ✓ 2-methylpyridine has a detrimental effect on the rate of decomposition of both hydrogen peroxide and 2-methylpyridine-*N*-oxide.

- ✓ 2-methylpyridine-*N*-oxide affects the rate of hydrogen peroxide decomposition.

- ✓ There are two stages in the decomposition: Oxygen removal from 2-methylpyridine-*N*-oxide and 2-methylpyridine decomposition.

Further research is needed:

- To determine the decomposition products
- To investigate similar behaviors of other alkylpyridines.

AKNOWLEDGEMENTS

- MKOPSC
- Chemical Engineering Department of Texas A&M University

M. Papadaki is indebted to MKOPSC for funding, and Chemical Engineering Department, and Texas A&M for hosting while the present research was conducted

THANKS FOR LISTENING

ANY QUESTIONS?

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