Hydroscience

MONSANTO WASTE THERMAL OXIDATION PROCESS

DISCUSSION REVIEW AND SUMMARY

(INCLUDING NITRO LIQUID ALTERNATIVE)

PROJECT MEETING, MARCH 23, 1979

MONSANTO CHEMICAL

St. Louis, MO

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I. INTRODUCTION

After the process development package (2 volumes) for a rotary-kiln-based waste thermal oxidation process was submitted to Monsanto by Hydroscience on March 6, 1978, several changes were made that affect the scope of the project. Two of these changes were subjects of discussion at a project meeting in St. Louis on March 23, 1979.

The principal change in scope involves an operating temperature of 2200°F as stipulated by the State of Illinois in their permit to construct and potentially supported by the federal government through a future RCRA Standard. The second change involves an updating of the characterization of the Monsanto waste profile for identification of minor changes in the quantity and quality of waste solids and liquids to be destroyed in the process.

A summary of the meeting discussion and the project ramifications of these changes are contained in this document.

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II. CONCLUSIONS AND RECOMMENDATIONS

The minor changes resulting from an updating of the characterization of Monsanto wastes have no significant impact on the design and operation of the thermal oxidation process. The change to an operating temperature of 2200°F in the secondary combustion chamber, however, alters the heat duty requirement of the secondary chamber to the extent that substantial auxiliary fuel would be needed to supplement identified secondary-quality liquids in the Monsanto waste profile previously established. Concurrently, the capacity of the proposed system to handle Monsanto wastes would be reduced by the amount of auxiliary fuel that would be needed if additional secondary-quality waste liquids are not available..

An alternative to the use of auxiliary fuel involves changing the manner in which the nitro liquids are handled so that their heats of combustion can be utilized in the secondary combustion chamber. An alternative concept is suggested in which the nitro liquids would be fired in a reducing combustion chamber addition to the secondary combustion chamber of the main system. The oxidation process would be completed in the secondary combustion chamber, allowing the nitro liquids to provide the heat needed in secondary combustion to operate at 2200°F without auxiliary fuel. It is proposed that the initial combustion of the nitro liquids under reducing conditions will control the formation of NO_x to acceptable levels in the system.

Indicated savings in operating costs along with possible savings in capital costs indicate that the proposed alternative concept for the thermal oxidation of the nitro liquids should be investigated further through pilot tests to demonstrate performance and obtain design data. It is believed that this testing can be conducted satisfactorily in existing vendor pilot equipment.

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III. DISCUSSION

A. UPDATED BASIC WASTE PROFILE

The updated Monsanto waste profile is summarized in Figure 1. This summary identifies the total average heat duty of all waste materials based on 7008 hr of operation annually. It also indicates the distribution of the average heat duty between liquids and solids and identifies those liquids scheduled for firing in the primary chamber (rotary kiln). The remainder of the liquids have suitable physical and chemical characteristics for firing in a secondary combustion chamber. The liquid and solid waste materials scheduled for firing in the primary chamber constitute 53.94% of the total waste profile heat duty.

The previous average waste profile totaled 42.07 MM Btu/hr compared with the updated total of 39.75 MM Btu/hr. Although the total is down slightly, increases can be seen in the heat duty of the solids (26%) and the secondary-quality liquids (10%).

B. SYSTEM HEAT DUTY REQUIREMENTS

The design thermal oxidation temperature in the primary chamber is 1500°F. The combustion gases from the primary chamber are treated in a secondary chamber to destroy residual combustible gases and particulates. Direct firing of secondary-quality fluids in the secondary combustion chamber provides the heat to achieve the desired operating temperature. In the previous plan for design the operating temperature in the secondary combustion chamber was 1800°F, except for a short campaign period for PCBs at 2200°F. The proposed secondary combustion chamber temperature is 2200°F for all modes of operation to meet state and potential federal requirements. The shift in system heat duty distribution when the secondary temperature is raised from 1800°F to 2200°F is illustrated in Figure 2. A comparison of the fraction of the total heat duty required in the secondary combustion chamber (Figure 2) with the fraction of the total heat duty available as secondary-quality fluid (Figure 1) shows that there is a deficiency in secondary-quality fluids for the 2200°F secondary combustion temperature case.

When the updated waste profile (Figure 1) is translated into a heat duty profile for a thermal oxidation system at the previous design capacity of 60 MM Btu/hr and a secondary combustion temperature of 2200°F (Figure 3), it can be seen

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THERMAL OXIDATION SYSTEM
BASIC WASTE PROFILE AND CLASSIFICATION SUMMARY

Classification		Waste ΔHc MM Btu/hr	%
Primary Chamber			
Liquids			
1. PCBs	1.08		
2. NO_2 Tars	9.90		
3. Wet Wastes	5.62		
4. Special Handling	0.13		
Total Liquids		16.73	
Solids			
1. Tars	3.64		
2. Filter C & Cart.	0.90		
3. Lab Wastes	0.17		
Total Solids		4.71	
Total Primary Wastes		21.44	53.94
Secondary Chamber			
Secondary Quality Liquids		18.31	46.06
Total Waste Duty		39.75	100.00

Figure 1

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THERMAL OXIDATION SYSTEM

SYSTEM HEAT DUTY REQUIREMENTS

Item	Heat Duty Distribution, %	
Sec. Combustion Conditions	1800°F 165% XS Air	2200°F 115% XS Air
Primary Chamber	68.7	45.9
Secondary Chamber	31.3	54.1
	100.0	100.0

Figure 2

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THERMAL OXIDATION SYSTEM

System Heat Duty Profile at
60 MM Btu/hr Capacity - 2200°F
Secondary Combustion Temperature.
NO_2 Tars Fired in Primary Chamber.

Item	Heat Duty MM Btu/hr
Primary Chamber	
Primary Liquids and Solids	27.54
Secondary Chamber	
Secondary Quality Liquids	23.52
Auxiliary Fuel	8.94
Total System Capacity	60.00
Total Waste Capacity	51.06

Figure 3

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THERMAL OXIDATION SYSTEM

Basic Waste Profile with NO_2 Tars
Assigned to Secondary Combustion

Classification		Waste ΔHc MM Btu/hr	Waste ΔHc %
Primary - Liquid	6.83		
Solids	4.71		
Primary - Total		11.54	29.03
Secondary Liquids	18.31		
NO_2 Tars	9.90		
Secondary - Total		28.21	70.97
Total Waste Duty		39.75	100.00

Basic Waste Profile Allocation to
Satisfy System Heat Duty Requirements
at 2200°F

Item	System Heat Duty, MM Btu/hr	
Primary Chamber		
Primary Liquids	6.83	
Solids	4.71	
Secondary Liquids	6.71	
Total Primary Chamber		18.25
Secondary Chamber		
Secondary Liquids	11.60	
NO_2 Tars	9.90	
Total Secondary Chamber		21.50
TOTAL SYSTEM		39.75

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Figure 4

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that there is a significant 8.94 MM Btu/hr demand for auxiliary fuel in the secondary combustion chamber, and the total capacity of the system to handle wastes is limited to 51.06 MM Btu/hr. This capacity is only 28% more than the basic profile.

C. NITRO LIQUID CONSIDERATIONS

Through process-development thermal oxidation tests it was determined that the production of NO_x could be limited by firing the nitro liquids in the rotary kiln in a manner that produces a fuel-rich flame envelope. As a result the waste nitro liquids were included in the primary combustion chamber duty in the previous plan for design. In the opinion of Hydroscience this technique cannot be applied successfully to firing directly in the secondary combustion chamber.

Limiting the formation of NO_x, however, was the only consideration in assigning the nitro liquids to the rotary kiln. If a way can be found to utilize the heat from the nitro liquids in the secondary combustion chamber, then 71% of the heat duty in the Monsanto profile is available for secondary combustion, as is illustrated in Figure 4. Since all of this heat is not required, utilizing the nitro liquids for secondary combustion would force a portion of the secondary-quality liquids into the primary chamber, as indicated in a restatement of the basic profile for a system operating at a 2200°F secondary combustion temperature (Figure 4).

D. PRELIMINARY PLAN FOR DESIGN

A preliminary plan for design operating mode for the basic waste profile, with the heat from nitro liquids assumed to be utilized in the secondary combustion chamber, is shown in Figure 5. This plan increases the handling of solids from two shifts/day to three shifts/day during the week because of the reduction from the previous plan in the duty of the primary chamber as a percentage of the total duty. The heat duty in the primary chamber dictates the combustion air flow rate through the kiln which must supply the excess air to absorb the fluctuating heat released from the combustion of the solids. A rotary-kiln heat duty of 20 MM Btu/hr is considered to be minimal for a system handling solids in drums. At this minimum heat duty it becomes increasingly important to restrict the organic contents of the drum to solid materials that will not melt and burn rapidly.

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THERMAL OXIDATION SYSTEM
PRELIMINARY PLAN FOR DESIGN

Base Case - Weekday Operation w/o PCBs
2200°F - 60 MM Btu/hr Capacity

Item	Heat Duty, MM Btu/hr	Comments
Primary Chamber		
Primary Liquids	8.05	
Secondary Liquids	5.35	
Solids	6.60	3 shifts
Total Primary	20.00	
Secondary Chamber		
Secondary Liquids	13.67	
NO_2 Tars	9.90	
Total Secondary	24.56	
TOTAL SYSTEM	43.57	

Weekend Operation

Primary Chamber		
PCB Liquids	3.78	
Secondary Liquids	9.99	
Total Primary	13.77	
Secondary Chamber		
NO_2 Tars	9.90	
Secondary Liquids	6.33	
Total Secondary	16.23	
TOTAL SYSTEM	30.00	2/1 Turndown

Figure 5

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THERMAL OXIDATION SYSTEM

PREVIOUS PLAN FOR DESIGN
Base Case - Weekday Operation w/o PCBs
1800°F - 60 MM Btu/hr Capacity

Item	Heat Duty, MM Btu/hr	Comments
Primary Chamber		
Liquid Wastes	9.4	Primary & Secondary Quality Liquids
NO_2 Tars	11.7	
Solids	8.8	2 shifts/day
Total	29.9	
Secondary Chamber		
Secondary Liquids	13.6	
TOTAL SYSTEM	43.5	

Figure 6

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The plan for design operating mode also illustrates the handling of PCB liquids during the weekends without the fluctuating effects of solids in the system. If weekend operation is restricted initially to 30 MM Btu/hr, which is a 2:1 turndown for a 60 MM Btu/hr capacity system, the average duty for the total week is equal to the basic profile duty of 39.75 MM Btu/hr.

For purposes of comparison the previous plan for design weekday operating mode is illustrated in Figure 6. It can be noted that for the same approximate total system heat duty the heat duty in the rotary kiln is 29.9 MM Btu/hr compared with 20 MM Btu/hr in the present preliminary plan for design operating mode.

E. NITRO LIQUID THERMAL OXIDATION ALTERNATE

One of the considerations in planning for the thermal oxidation of a nitrogen-containing organic is the thermodynamic equilibrium concentration of nitric oxide (NO) at high temperature. Figure 7 illustrates the equilibrium NO:theoretical O_2 ratio as a function of temperature and excess air. As can be seen, this ratio increases rapidly with temperature. Since the excess air in the system is related to the operating temperature, when negligible heat is transferred and no secondary heat sink (such as H_2O injection) is added, the calculated NO equilibrium concentration for various temperatures is shown at corresponding adiabatic excess air values in Figure 8. Without nitrogen in the organic molecule the equilibrium NO values normally are not attained because of reaction rate limitations (Figure 9). With nitrogen in the molecule there is evidence that this nitrogen has a kinetically easier route to NO, and higher concentrations of NO can be expected.

F. TWO-STAGE COMBUSTION CONCEPT

The proposed alternative technical approach to the thermal oxidation of the nitro liquids is to use a burner operating under reducing conditions to reduce all the nitrogen in the waste to elemental nitrogen before the oxidation process is completed in an excess O_2 environment. This concept is illustrated in Figure 10 as a totally separate thermal oxidation system for nitro liquids. This system was presented and discussed in Volume I of the process development package, dated March 6, 1978.

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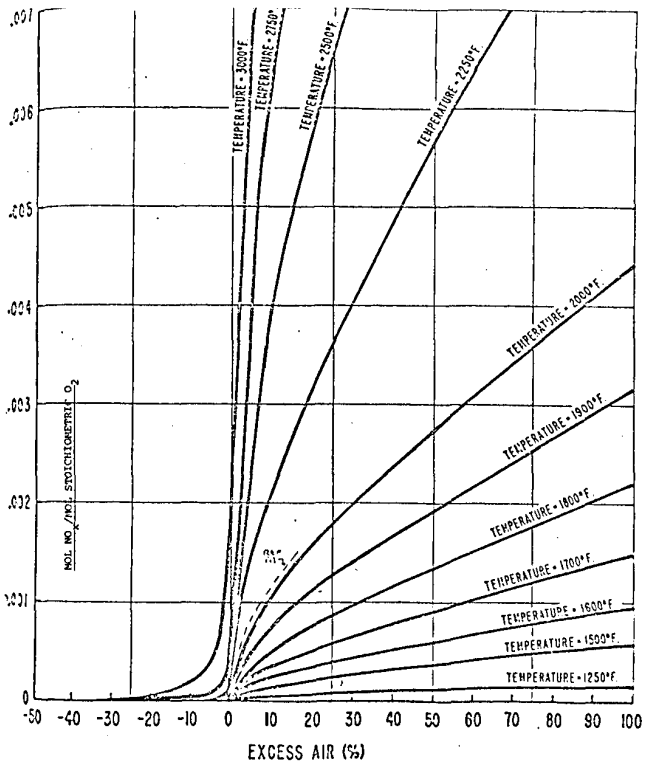


Figure 7

NO_x EQUILIBRIUM CONSIDERATIONS

CONDITIONS		NO_x CONCENTRATION
TEMP, °F	EXCESS AIR, VOL %	PPM BY VOL
1800	164	256
2000	132	529
2200	105	933
2600	50	1733

Figure 8

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Table X. EQUILIBRIUM CONCENTRATIONS AND TIMES OF FORMATION OF NITRIC OXIDE AT ELEVATED TEMPERATURES AT 75 PERCENT NITROGEN AND 3 PERCENT OXYGEN

Temperature, °F	Equilibrium concentration of nitric oxide, ppm[a]	Time of formation of 500 ppm NO, seconds[b]
2,000	180	
2,400	550	1,370
2,800	1,380	16.200
3,200	2,600	1.100
3,600	4,150	0.117

[a]Hougen and Watson, 1945.
[b]Daniels and Gilbert, 1948.

Figure 9

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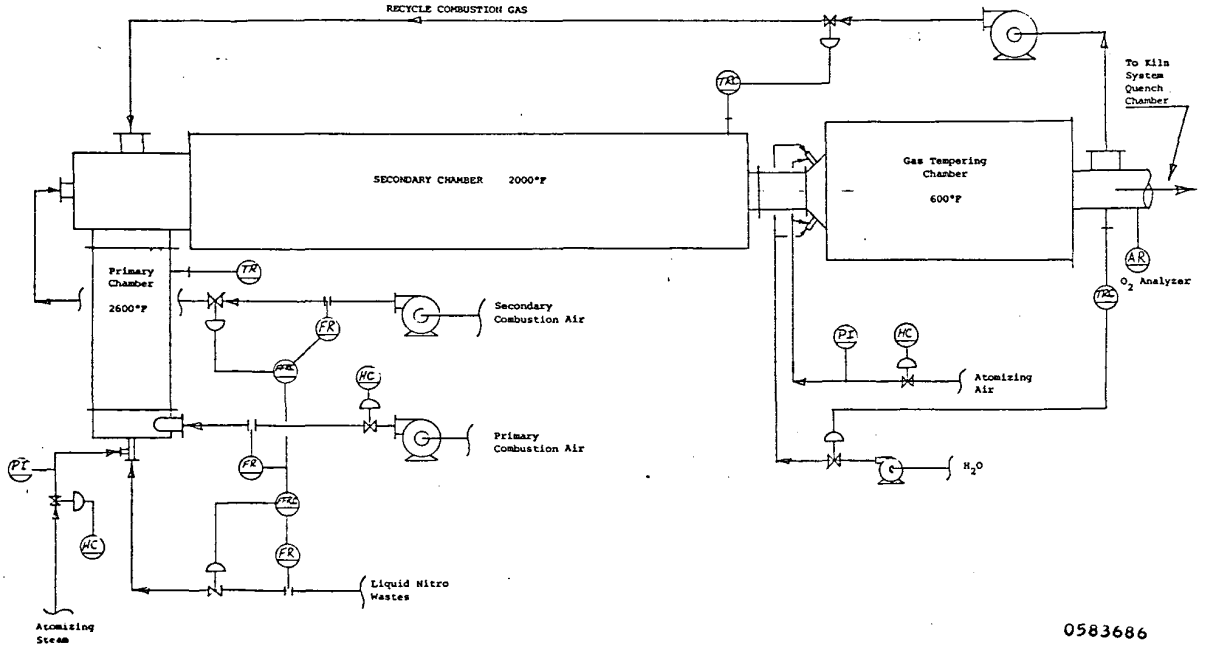


Figure 10

	Hydroscience	CONCEPTUAL DESIGN THERMAL OXIDATION WITH NO_x CONTROL	SUBJECT: LIQUID NITRO WASTES; TWO STAGE COMBUSTION; PAGE OF; JOB NO; BY WEW; DATE 8-16-77

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It is proposed that the two-stage combustion approach be considered again as a means of oxidizing nitro liquids with NO_x control while making the heat available for secondary combustion. In the suggested variation of the alternative concept illustrated, the primary chamber, operating under reducing conditions, would discharge the product gases into the secondary combustion chamber of the rotary-kiln thermal oxidation process, where combustion would be completed in an oxidizing atmosphere at 2200°F. The assumption is that after the nitrogen in the nitro liquid waste is reduced to an elemental form the formation of NO_x would be limited by reaction kinetics similar to the fixation of nitrogen from air under the same conditions.

This concept should be piloted to demonstrate performance and obtain design data before proceeding with a process design.

G. DESTRUCTION EFFICIENCY

At the request of Monsanto, Hydroscience reviewed it's comments to the MCA relative to achieving the proposed principle toxic component destruction efficiencies (DE) of 99.99% for a general, broad based, solid and liquid waste profile. A detailed paper was distributed at the meeting. The conclusions are summarized below.

1. A 99.99% principal toxic component DE is achievable for liquid incinerators that are burning clean low-viscosity fuel oil quality wastes.

2. For a typical industrial liquid and solid waste profile, the 99.99% proposed DE standard can be achieved if the waste materials (which can include bulk or drummed solid residues, sludges, contaminated trash and poor quality waste liquids) are dissolved and upgraded through pretreatment to produce clean solutions of low-viscosity and fuel oil quality.

3. The required pretreatment would be technologically unattainable and economically prohibitive for many industrial waste solid residues, sludges, contaminated trash, and poor quality liquids.

4. The test work performed by EPA under Contract No. 68-01-2966 indicates the following:

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a. Two demonstration test burns indicated that a 99.99% destruction efficiency was obtained for polychlorinated biphenyls (PCB) and nitrochlorobenzenes (NCB) when they made up 4 to 11% of the total energy released in the system and the remainder of the energy was supplied by clean low-viscosity fuel oil rather than typical industrial wastes. Approximately two orders of magnitude greater amounts of auxiliary fuel per pound of waste were used in these two tests than is typical for state-of-the-art practice. Destruction efficiency values for PCBs and NCBs were not determined at higher ratios of waste to fuel oil as would be considered to be typical of state-of-the-art practice. The high auxiliary fuel usage in the PCB and NCB tests does not demonstrate resource conservation.

b. Three other demonstration test burns involved the incineration of aqueous or highly chlorinated liquid wastes and wet polyvinyl chloride (PVC) sludge. Since some of the test data were not included in the report, it was difficult to compare the test conditions with state-of-the-art practice. In general, however, it appears that significant amounts of auxiliary fuels were used relative to the quantity of wastes that were fired. The tests were carried out with supplementary clean fuels of high quality. No attempt was made to utilize actual wastes or to simulate industrial wastes as a source of auxiliary fuel in order to optimize disposal capacity within the incinerators or to conserve energy resources.

c. The DE of the PVC sludge was determined to be >99.99% by measuring total quantities of chlorinated organics in the flue gas. Since PVC starts to dehydrochlorinate at 100°C via a complex decomposition mechanism, much of the chlorine is evolved as inorganic HCl, thereby reducing the potential level of chlorinated organics in the flue gas. The low initial decomposition temperature of PVC and the dehydrochlorination characteristics are not representative of typical industrial wastes.

Monsanto was interested in Hydroscience's opinion of the destruction efficiencies that will be achieved for principle toxic components in their specific waste profile. At this time, Hydroscience can offer only opinions based on their experience in related waste profiles, since the flue gas samples taken during the previous Monsanto test burn were not analyzed. It is

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Hydroscience's professional opinion that destruction efficiencies for principle toxic components in the Monsanto waste profiles may range from a low of 99.9 to greater than 99.99%. If the waste material is readily oxidizable, burns cleanly and is low in ash, such as PNCB, high destruction efficiencies can be expected. However, if combustion proceeds with the generation of large amounts of carbonaceous or inorganic particulate matter, lower destruction efficiencies can be expected due to the potential for adsorption of organics onto the particulate. An average destruction efficiency of 99.95% for principle toxic components is Hydroscience's estimate at this time.

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