

SUPERCRITICAL WATER OXIDATION OF PHENOL AND 2,4 DINITROPHENOL

By

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Abstract

The destruction kinetics of two model compounds has been investigated in the University of British Columbia (UBC) Supercritical Water Oxidation (SCWO) pilot plant. High concentrations of phenol (2.7% and 4% by weight) were oxidized at pressures of 24 to 26 MPa, temperatures of 666 to 778 K, and 0 to 39% oxygen excess. Phenol and Total Organic Carbon (TOC) conversions varied from 92 to 99.98% and 75 to 99.77% respectively.

The second group of wastes studied contained 2,4 dinitrophenol (DNP). Two different solutions that simulated an aromatic nitration facility's wash-water were investigated. The first one contained 2.4% by wt. 2,4 dinitrophenol with 2% by wt. ammonium sulphate and simulated the final wash waters from the nitration plant with no sulphates elimination. The second solution contained 2.27% by wt. as ammonium dinitrophenol, with no sulphates.

For the first DNP waste, at process conditions of 25 MPa, 780 K and 37% oxygen excess, 99.9996% destruction efficiencies were obtained for 2,4 dinitrophenol, and 99.92% for TOC. Mono-nitrophenols were detected as intermediates, but not in the liquid effluent, where residuals of ammonium bicarbonate and sulphates were detected. No NO_x or CO was present in the gaseous effluent streams. This solution resulted to be very corrosive to the system.

The second solution was treated at 22.9 ± 0.1 MPa, 742-813 K and oxygen concentrations ranging from sub-stoichiometric to 69% excess. Destruction efficiencies for 2,4 dinitrophenol were 99.9996% in all cases (not detected). TOC destruction efficiencies ranged from 98.98 to 99.98%, while ammonia destruction ranged from 15 to 50%. Picric acid, mono-nitrophenols, ammonium carbonate and bicarbonate were detected as intermediates, but not in the liquid effluent. No CO or NO_x was present in the effluent gas samples, except in cases with less than stoichiometric oxygen.

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Nomenclature

Acronyms and symbols

%	% Volume of indicated gas, or % wt. of indicated liquid
Ea	Activation energy
A	Area [m ²]
[]	Concentration of indicated specie [mol/L]
C	Concentration of indicated specie [mg/L]
X	Conversion/yield of the indicated species
ρ	Density [g/L]
DRE	Destruction Removal Efficiency
DNP	Dinitrophenol
DNT	Dinitrotoluene
O_{2ex}	Excess oxygen [%]
A	Frequency factor
L	Length [m]
\dot{m}	Mass flow rate of indicated specie [g/min]
x	Mass fraction, or percent fraction
\dot{n}	Molar flow rate of indicated specie [mol/min]
M.W	Molecular weight of indicated specie [g/mol]
n	Number of moles, or number of measurements
N	Number of segments
Ph	Phenol
PH 1	Preheater 1
PH 2	Preheater 2
P	Pressure
r	Rate
K	Rate constant
a, b, c	Reaction orders to the indicated species
RL-2	Reactor length 2
RL-6	Reactor length 6
RHX	Regenerative heat exchanger

Γ	Standard deviation
SCWO	Supercritical Water Oxidation
T	Temperature [K]
TS	Test section
t	Time
TOC	Total of Organic Carbon
w	Uncertainty of individual variables
wR	Uncertainty of measurement
R	Universal gas constant
y	Variables for which w is measured
WAO	Wet Air Oxidation
BCRI	British Columbia Research Institute

Subscripts

a	Air
ex.	Excess
0	Initial
in	Inlet, feed, initial
liquid	Liquid feed into the system (water + waste)
out	Outlet, effluent
oxygen	Oxygen
i	Segment in the SCWO system, or specie
stoich.	Stoichiometric
total	Total
vapor	Vapour
sat	Saturation
gas	Gas

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Chapter 1 Introduction

1.1 Project objectives

Phenol derivatives, often part of industrial wastewaters, are priority pollutants. Supercritical Water Oxidation (SCWO) is a technology developed to treat phenolic wastes, but often, the chemical and physical data needed to design practical systems is lacking.

The supercritical water oxidation research project at UBC currently focuses, among other things, on the destruction of high concentrations of ammonia red waters, specifically the waste waters from a nitrobenzene production plant whose main organic component is 2,4 dinitrophenol (2,4 DNP) ($\text{C}_6\text{H}_3\text{OH}(\text{NO}_2)_2$).

Before exploring the elimination of 2,4 DNP wastes, it was necessary to validate the destruction capabilities of the plant with high concentrations of a simpler organic waste. Phenol represented an ideal component for the operational validation of the pilot plant. Low concentration trials had been reported in literature and phenol was catalogued as difficult to eliminate by SCWO.

The objectives of this project were:

1. To validate the destruction capabilities of the UBC-Noram SCWO pilot plant with high concentrations of phenol; and
2. To complete and report destruction measurements of 2,4 DNP and ammonia wastewaters.

1.2 Thesis Overview

This thesis is composed of five chapters. Following the overview in this section, Chapter 2 provides a brief introduction to phenolic waste streams, the different technologies available for their destruction, and the supercritical water oxidation process. Chapter 3 presents the study of two main groups of wastes: phenol, a simple organic compound, and a second group composed of 2,4 DNP solutions. These included a solution with sulphates and ammonia, and a solution with no sulphates, but containing ammonia. Chapter 4 looks at the corrosion problems faced when treating one of these wastes. Chapter 5 presents final conclusions, and recommendations for future work. Chapter 3 was written so that it could be submitted as a separate article for publication in a technical journal, with little modification, and as such, is intended to be a self-supporting document.

Chapter 2 Supercritical Water Oxidation (SCWO) as a means to destroy phenolic wastes

2.1 Processes that produce phenolic wastes: The mononitrobenzene process.

Phenol, C_6H_5OH , is a colourless or white solid when pure. However, it is usually sold and used as a liquid solution. It is highly flammable, has a sickeningly sweet and irritating odour; and evaporates more slowly than water. Its primary use is in the production of phenolic resins, which are used in the plywood, construction, automotive, and appliance industries. Phenol is highly soluble in water, causing phenolic compounds to be common in a wide variety of industrial wastewaters. Along with substituted phenols, it is a suspected carcinogen, as well as very toxic to aquatic life. The main sources of phenolic wastewater are industries, such as solvent production, petrochemicals, coal gasification, pesticide manufacture, metallurgical and nitration processes.

Mononitrobenzene (MNB) manufacturing is an example of a nitration process that produces nitrophenols as wash water effluents. Mononitrobenzene, the raw material of aniline, is widely used in the production of polyurethane, rubber chemicals, dyes, agrochemicals, and as a solvent in petroleum refining. Its production has increased substantially in the past years, and so have the waste streams that this process generates. For example, in 1960, 73,600 metric tonnes of MNB were produced in the United States alone. By 1986, the production had increased to 434, 900 metric tons.¹

MNB is produced commercially by the exothermic nitration of benzene with nitric acid in the presence of a sulphuric acid catalyst at $110^{\circ}C$. The crude nitrobenzene is passed through washer-separators to remove residual acid and then distilled to remove benzene and

water. Commonly, the nitro-hydroxy-aromatic by-products such as dinitrophenol are extracted from the crude through counter-current washing,² for which alkali chemicals are used, usually caustic soda or aqueous ammonia.¹ This final wash water, called “red water” because of its colour, will be one of the subjects of study in this work. In some cases, certain inorganic compounds are kept out from the red water prior to its treatment. For example, sulphates would produce sulphur dioxide, or non-volatile salts, when treated by incineration and therefore needs to be kept out of disposal systems that use this technology.

2.2 Commonly used methods in the treatment of phenolic wastes

Viable treatment alternatives for phenolic wastes follow different approaches, including biological, physical and chemical and thermal processes. Generally, the choice of treatment depends on local site conditions, volumes and concentration of the wastes, economic feasibility and operator’s preferences. Table 2.1 shows a scheme of the most commonly used techniques.

Table 2.1 Commonly used treatment technologies for phenolic wastes

Type of treatment	Technology
Biological	Anaerobic digestion
	Enzymatic detoxification
	Aerobic digestion (activated sludge)
Physical and chemical	Chemical oxidation
	Activated carbon adsorption
	Ultraviolet (UV) oxidation
Thermal	Incineration
	Wet air oxidation
	Supercritical water oxidation

Anaerobic digestion is a sequential, biologically destructive process in which organics are converted from complex to simpler molecules in the absence of free oxygen, and ultimately to carbon dioxide and methane.³ Phenolic wastes are among the organic chemicals listed as degradable by anaerobic digestion, however, biological removal efficiencies are not always high enough to meet discharge standards and require another secondary treatment method.

Enzymes are complex proteins ubiquitous in nature. A biological method for removal of chlorophenols in drinking water and wastewater is enzymatic detoxification using the horseradish peroxidase enzyme.³ Adding this enzyme together with hydrogen peroxide to the waste solution causes enzymatic cross-linking of the substrate, thus forming insoluble polymers. These then precipitate out of solution and can be removed by filtration. However, the use of enzymes to detoxify chemical pollutants is often dismissed as technologically too challenging.³

In aerobic digestion by activated sludge, oxygen is used by a mixture of different types of micro-organisms as a source of energy for the breakdown of organic substances. This system develops a microbiological community that converts organics into new non-toxic material, CO₂ and water³. Noram Engineering and Constructors Ltd, has developed an aerobic activated sludge process: Vertreat. The Vertreat reactor is capable of treating diluted concentrations of 2,4 DNP, but it needs a sludge specially conditioned to treat this waste stream. Research looking into treating high concentrations of 2,4 DNP is still ongoing.

Chemical oxidation processes applied to the destruction of organic, phenolic wastes include oxidizing agents like hydrogen peroxide, Fentons reagent, ozone, permanganate and peroxidisulphate, a very strong chemical oxidant.⁴ Some of the limitations of chemical

oxidation are that often, large quantities of oxidizing chemicals are needed, thus increasing the cost. Moreover, it is difficult to achieve strict discharge limits without further treatment.^{2, 4}

Activated carbon can be used to treat phenolic wastewaters³. Most carbon-adsorption systems use granular activated carbon in flow through column reactors. The adsorption process is reversible, but even when the activated carbon can be regenerated; the treatment remains very expensive and often develops excessive head loss as the result of suspended-solids accumulation or premature exhaustion of the carbon capacity.³

UV oxidation destroys organics by the addition of strong oxidizers (O_3 and/or H_2O_2) and irradiation with UV light. It generates highly reactive hydroxyl radicals (OH^\bullet) that react with and destroy most organic chemical compounds. UV/ O_3 and UV/ H_2O_2 processes have been proven effective in the treatment of phenol⁵. However, they are not considered cost competitive due to the high energy consumption of the UV lamps. Additionally, turbidity (e.g., cloudiness) of the water can cause interference in the process. Treatment limits range from 10 ppm to over 1000 ppm TOC.

Incineration has been a widely used method of reducing the volume and hazard of organic hazardous wastes since the 1930s.⁴ In the past years, environmental regulators have turned their attention to the concentration of products of incomplete combustion (PICs) from incinerators and their associated risks to human health. Some incineration systems have additional technologies to control the PICs emissions to the required limits. Despite its capability to destroy phenolic wastes, incineration often suffers from poor public image due to potential NO_x and SO_x and other toxic emissions. In the case of wastewaters from the MNB process, incineration is only used in ammonia-washed effluents, as caustic soda

produces ash² and slay which tend to foul the incinerator. Operation costs can be high due to the large amounts of heat needed to evaporate the water and to elevate the temperature of combustion products and air to the point of combustion.

In wet air oxidation (WAO), waste materials in diluted aqueous solution or suspension are mixed with dissolved oxygen at relatively high temperatures (120 to 230°C) and pressures (490 to 21,000 KPa). Oxidation and hydrolysis reactions degrade the initial compound into a series of compounds of simpler structure. A major disadvantage, however, is that very often organic matter is not fully destroyed. Consequently, the effluent requires further treatment.

In 1821 a French scientist, Baron Charles Cagniard de la Tour, showed experimentally that there is a critical temperature above which a single substance can only exist as a fluid and not as either a liquid or gas. Since then, the study of supercritical fluids has advanced considerably. Supercritical water oxidation (SCWO) is one of the principal developments.

Due to its peculiar properties, water at supercritical conditions has been found to be an excellent medium for converting toxic organic substances into benign and environmentally acceptable products. Its density is approximately one order of magnitude less than at ambient conditions, which allows flow systems to operate at very small residence times. Viscosity drops quickly at the critical point, diffusivity increases, and mass transfer limitations become minimal. The static dielectric constant, which is a measure of the hydrogen bonding, is much lower above the critical point than it is at ambient conditions. This causes supercritical water to act like an organic solvent.^{6,7,8} By contrast, inorganic compounds turn insoluble under supercritical conditions.

Supercritical water oxidation (SCWO) can be seen as an extension of wet air oxidation to more severe conditions. It was patented in the 1980s, but research and development is still ongoing. SCWO processes take place at pressures and temperatures above the critical point of water (374.2°C and 22.1 MPa). Since supercritical water is miscible in all proportions with oxygen, oxidation reaction rates will be limited by reaction kinetics rather than by mass transfer. SCWO can usually guarantee complete oxidation of organic compounds without the need for further treatment,⁴ a distinct advantage over WAO. Typical operation temperatures are in the range of 450 to 600°C, much lower than those of incineration processes and less likely to produce NO_x in the gas effluent.

2.2.1 SCWO process description

Figure 2.1 shows a simplified block diagram of a SCWO process for liquid streams. The aqueous organic waste is pressurized and heated above the critical point of water by means of electrical energy or through addition and oxidation of some other kind of fuel; an oxidizer is added to this mixture and, given an adequate reaction time, the organic carbon is converted to CO₂ and the nitrogen species to N₂. Distilled water is used during the warming up, cooling down and rinsing phases of the process.

Even though there are several pilot plants and research facilities, there are not many commercial SCWO plants at the moment. In the late 1990s Eco Waste Technologies implemented and commercialized a process at a site near Austin, Texas. The waste treated there contains long-chain alcohols, glycols and amines, with TOC concentration typically higher than 50,000 mg/L. In April 2001, a SCWO municipal wastewater sludge processing plant started operating in Harlingen, Texas, treating 9.8 tons per day.⁹

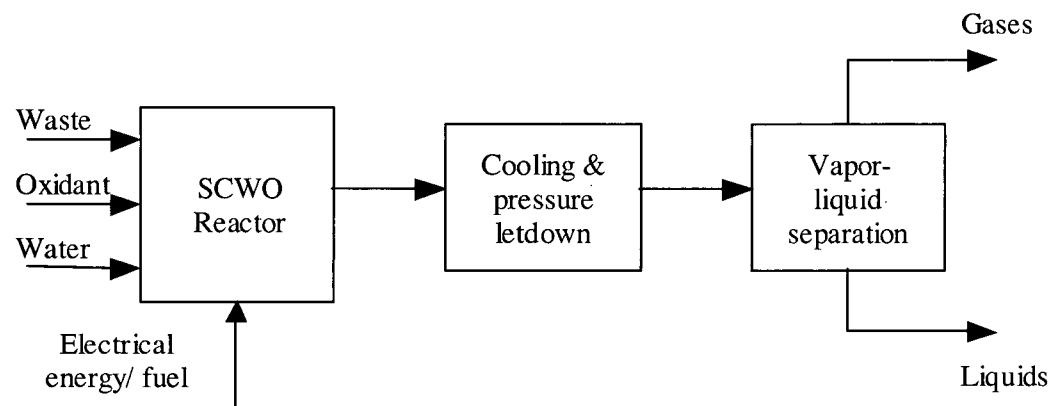


Figure 2.1 Block diagram for SCWO of liquid streams

The industrial scale-up of SCWO has been hindered by some practical problems, such as salts deposition, corrosion and high costs. Careful selection of the wastes that are to be treated by SCWO and of the reactors designs and materials can help reduce the significance of these negative factors.

The next chapter focuses on the treatment of high concentrations of phenolic wastes in the UBC/Noram SCWO pilot plan, followed by a discussion of the system's corrosion from one of the tested wastes.

Chapter 3 Supercritical Water Oxidation of Phenol and 2,4 Dinitrophenol Wastes

3.1 Introduction

Concentrated organic wastewaters are becoming increasingly difficult and costly to treat. To comply with strict disposal standards while maintaining economic viability, waste treatment technologies should be validated for their destruction capabilities under these conditions. Supercritical water oxidation has been proposed as a technology capable of destroying a very wide range of organic, hazardous wastes so that no further treatment is needed. The feasibility of SCWO as a waste destruction technology has been proven in numerous studies,^{10, 11, 12, 13} but not much information exists on the treatment of highly concentrated wastes at moderate oxidant excess; conditions that could be considered more desirable (or practical) in an industrial setting. Matsumura et al.¹⁴ reported the treatment of high concentrations of phenol in a lab-scale facility, finding good agreement between their decomposition conversions and those of the reported literature^{15, 16, 17, 18.}

When bringing SCWO into a practical setting, several factors have to be considered:

- The concentration of the waste to be treated, because the heat released from the oxidation reaction depends on this factor, which will determine both the size of the reactor and the self-sustainability of the process.
- The size of the reactor, so as to obtain the highest destruction removal efficiencies (DRE) with the minimum volume possible, as the reactor accounts for a significant portion of the system cost (50%)¹⁹

- Oxidant excess, which should be enough to allow the destruction of the waste, but not too much, because it represents an important cost factor and un-reacted oxygen will be wasted.
- The formation of partial oxidation products. Besides achieving high Destruction Removal Efficiencies (DREs), a high degree of TOC destruction is mandatory.
- Operating temperature, which should be high enough to achieve the necessary DREs, but not higher.
- The preheater size and preheating strategies, which ought be developed in order to avoid or minimize char formation, which will be more likely to occur with more concentrated wastes.
- Nature of the waste: Some compounds are more likely to promote corrosion and/or fouling, two factors that will influence the operating cost of the facility and define the feasibility of treating a certain waste by SCWO.

In summary, in order to have an economically efficient process, it would be advisable to aim for concentrated feeds with high heating values higher than 300 kJ/kg^{20} , which must be treated at moderate oxidant excess and temperatures, while maintaining the desired destruction efficiencies. Higher concentrations of the waste will mean a lower amount of electrical heat (or other kinds of energy) supplied to the system, with more energy being provided by the heat of reaction of the organic feed. Relatively low oxidant excess would reduce the reactor volume, as well as the operating costs for the oxidant system. Additionally, lower preheating and operation temperatures can be interpreted as lower electricity and/or auxiliary fuel costs and more durability of the materials, and hence, as lower operating costs.

In this work, the destruction of two groups of model wastes (phenol and 2,4-ammonium dinitrophenol (2,4 DNP)) was investigated. The experimental conditions simulated those of a practical process where the excess of oxidant and heats of reactions would be of great importance when accounting for operating costs.

In the case of phenol, a widely investigated waste,^{14, 15, 16, 17, 18, 21, 22, 23} our main goals were:

1. Validate the destruction capabilities of our pilot plant, at practical conditions (high waste concentrations and moderate oxidant excess)
2. Observe the influence of temperature on the residence time and destruction efficiencies.
3. Examine the agreement of rate laws available in the literature^{14, 15, 16, 17, 18, 21, 22, 23} (most commonly for experiments at low waste concentration and very high oxidant excesses) with our experimental results under different conditions.

The second group of wastes modeled contained 2,4 DNP. Two different solutions were treated. The first one, (2.4% by wt. as 2,4 DNP and 2% by wt. as ammonium sulphate), simulated the wash water ("red water") from an aromatic nitration facility without an acid wash to remove the bulk of sulphate. The second solution simulated the wastewaters with 2.27% wt. (as 2,4 DNP), with no sulphates.

For the treatment of these 2,4 DNP solutions, our main goals were:

1. To obtain experimental data on the destruction of a 2,4 DNP waste.
2. To investigate the feasibility of treating 2,4 DNP waste waters with high content of ammonium sulphate.

3. To observe the influence of temperature, residence time and oxygen excess on the destruction of 2,4 DNP and ammonia.

3.2 Studies on phenol, nitrophenols and nitrogenous compounds

3.2.1 Phenol

SCWO of phenol has been extensively investigated, although most of the available literature covers low concentrations (< 0.1% wt.) and high oxidant excess. In all cases^{14, 15, 16, 17, 18, 21, 22, 23}, the overall rate of reaction was determined as:

$$r = -\frac{d[Ph]}{dt} = -A \exp\left(\frac{-Ea}{RT}\right) [Ph]^a [O]^b [H_2O]^c \quad [1]$$

Where A , Ea , R , T , t and $[species]$ express the frequency factor, activation energy, gas constant, absolute temperature, time, and species concentrations in mole per litres, respectively. Ph , O , and H_2O denote phenol, oxidant, and water, with a , b and c as their respective reaction orders. Experimental conditions and coefficients used for the predictions are shown in Table 3.1.

There are significant differences in the reported rate laws despite similar experimental conditions. Many aspects like non-isothermal operation, differing geometry and material of the reactor, operating procedures, or different set of conditions, can lead to a disagreement in model predictions.²⁴

Table 3.1 Conditions and global kinetic models for SCWO of Phenol

Work	[Ph] ₀ [mg/l]	Temperature [K]	Pressure [MPa]	Oxidant excess [%]	Kinetic Parameters					Comments
					Log A	E _a [kJ/mol]	a	b	c	
Li et al. ¹⁵	0.6-0.77	677-715	25	-	1970	60.8	1	0	0	
Thornton & Savage ¹⁶	50-330	573-693	19-28.2	0-1,100	303	51.8	1	0.5	0.7	
Gopalan & Savage ¹⁷	3-37	693-753	27	>200	219	51.8	0.85	0.5	0.42	
Krajnc & Levec ¹⁸	500-1,000	653-723	23-26.5	50-1,000	4.9e8	124.8	1.04	0.38	0	
Koo et al. ²¹	828	653-713	19-27	100-1750	89.12e3	99.6	1	-	1.38	
Oshima et. al. ²²	0.5-12.2	643-703	25.6-33.7	200-900	28.184e3	50.4	1	0.48	-0.45	
Portela et al. ²³	50-593	673-773	25	100-475	22.39	39.2	1	0	0	
Matsumura et al. ¹⁴	20,000	623-723	25	0 ^a	-	-	-	-	-	Experimental study ^a Stoich. Oxidant
This Work	27,000- 40,000	666-778	25	0-35.6	-	-	-	-	-	Experimental study

3.2.2 Nitrogenous compounds

Wastes may contain high levels of nitrogen species^{25, 26, 27}. This nitrogen can be in the forms of ammonia, nitrate/nitrite, or it can be part of the organic waste, as in the case of nitrophenols, which are separately referred to below.

Ammonia oxidation is often the slowest reaction for the final decomposition of the nitrogenous waste into CO_2 , N_2 and H_2O ^{28, 29}, and for this reason a lot of attention has been given to it. Killilea et al.³⁰ and Cocero et al.²⁹ found that ammonia destruction increased with temperature and with the presence of organic compounds. According to their findings, SCWO systems favoured N_2 formation over N_2O , while no NO_x was produced; this is corroborated by other authors³¹. Even though it is not favoured by SCWO, N_2O can be observed in the gas effluent. Operating at high temperatures in the range of 873 K can eliminate this effect^{29, 30}.

Due to its slow rate of disappearance in O_2 , the destruction of ammonia in different environments has been extensively studied. Luan et al.³² treated organic/ammonia mixtures and observed an enhanced reactivity when using hydrogen peroxide (H_2O_2) as the oxidant. They also pointed out that a co-oxidant system using both nitrate and hydrogen peroxide was more effective and guaranteed the destruction of organics and ammonia. Aymonier et al.³³ observed the same when treating fenuron ($\text{C}_6\text{H}_5\text{-NH-CO-NH}(\text{CH}_3)_2$) by using H_2O_2 as the oxidizing agent. The nitrogen atoms from the fenuron were first transformed into ammonia, nitrate ions (NO_3^-) and nitrobenzene. NO_3^- and H_2O_2 created a powerful oxidant system that allowed the complete degradation of the nitrogenous organic.

Proesmans et al.²⁸ showed that ammonium nitrate was an effective oxidizer for some organic compounds, with better conversions for higher feed TOC concentrations. This last point coincided with the findings of Killilea et al.³⁰

Gidner et al.³¹ treated wastewaters from amine manufacturing. They developed a method of adding nitric acid to the feed tank, in a stoichiometric ratio to the amount of total nitrogen contained in it, and using oxygen as the other oxidizing agent. They also developed a process of continuous injection of nitric acid in the reactor. Lee et al.³⁴ corroborated that the coexistence of the nitro group and oxygen had a positive effect on reducing ammonia concentration in the treatment of organic wastes. There was the possibility that oxygen could be consumed for oxidizing the organic compound, and the nitro groups, in addition to the decomposition products from the nitrogenous organic, could oxidize the ammonia.

Ding et al.³⁵ have explored catalytic destruction of ammonia as a way to reduce the temperature needed for ammonia conversion. Using $\text{MnO}_2/\text{CeO}_2$ as a catalyst at 27.6 MPa and temperatures ranging from 410 to 470°C, the rate of ammonia conversion increased considerably as compared to that of non-catalytic oxidation.

3.2.2.1 Nitrophenols

While there is no information available on the SCWO of dinitrophenols, the destruction of mono-nitro phenols has been discussed in literature. Martino and Savage^{36, 37} investigated the thermolysis (pyrolysis and/or hydrolysis) and oxidation of 2-, 3- and 4- nitrophenol. Both types of reactions revealed that NO_2 -substituted phenols are very reactive in SCW.

From the thermolysis reactions, phenol was proven to be the major aqueous-phase product, the order of reactivity being 2-nitrophenol > 4-nitrophenol > 3-nitrophenol. During

all these experiments, some of the reacted carbon was deposited in the reactor in the form of a solid residue.

The contribution of thermolysis and oxidation as well as the yields of CO and CO₂ was quantified. The nitrogenous species yields were not quantified. Oxidation also produced phenol as the major product, although the phenol yield during oxidation was not much higher than that of thermolysis.

According to their findings, thermolysis accounted for up to 25% of the total amount of destruction for 3- and 4-nitrophenol, and was higher for 2-nitrophenol, implying that the SCWO of NO₂-substituted phenols would involve a significant purely thermal component, and that a great portion of the oxidation would be of the thermal reactions products, rather than the NO₂- substituted phenols. Martino and Savage discovered two major primary paths for the SCWO process of the investigated nitrophenols: the first one leading to phenol, and the other one leading to ring-opening products and ultimately to CO and CO₂, as shown in Figure 3.1

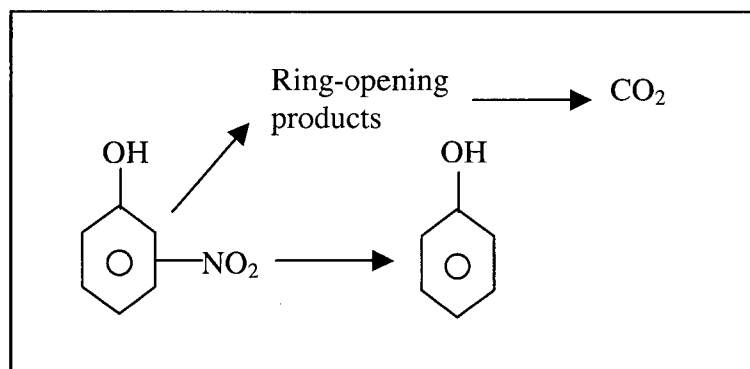


Figure 3.1 Primary reaction paths for SCWO of nitrophenols (Martino and Savage)³⁶

In 1993, Li et al.²⁶ treated dinitrotoluene (DNT) process wastewaters. The major organic components in these wastewaters were: DNT, phenol, 4,6-dinitro-ortho-cresol, 2,4 dinitrophenol, 2-nitrophenol and 4-nitrophenol, as shown in Table 3.2. Tests were conducted in batch and continuous flow systems, under subcritical and supercritical conditions, and with two choices of oxidant (oxygen and hydrogen peroxide). Oxidant excess was in the order of 100%, and in some cases biological sludge was added to provide additional heat.

No numerical data were reported on the destruction of any of the individual components. However, it was described that the destruction of the higher molecular weight organic compounds in the influent generally occurred rapidly, and that the lighter weight transformation compounds (such as acetic acid) required longer residence times, higher temperatures and/or catalysis. TOC removals at supercritical conditions were higher for both batch and continuous flow reactors than those at subcritical.

Table 3.2 Influent characteristics for DNT wastewater experiments. (Li et al.)²⁶

Composition	Concentration [mg/l]	
	Waste without sludge solids	Waste with 3% wt sludge solids
Dinitrotoluene (DNT)	346	179.1
2-Nitrophenol	0.466	0.243
4-Nitrophenol	0.471	0.346
2,4 Dinitrophenol (DNP)	3.93	2.03
4,6-dinitro-ortho-cresol (DNOC)	15.18	7.84
Phenol	16.11	8.83
Acetate	2.1	40.04
Chloride	3.9	473.1
Nitrite	37.2	19.25
Nitrate	1224	631.8
Sulphate	1391	854.4
Total Organic Carbon (TOC)	1840	-
Chemical Oxygen Demand (COD)	-	38970

3.2.2.1.1 2,4 DNP

Destruction kinetics for 2,4 DNP wastes have not been reported in literature, although experiments were conducted at the UBC-Noram pilot plant in 1999³⁸. These tests treated a low concentration, synthetic solution of ammonium 2,4 dinitrophenolate at very high oxygen excesses, according to Table 3.3. Instabilities in the pilot plant were observed due to poor regulation of the system's pressure and oxygen flow fluctuations, at times resulting in poor or unstable conversions of the waste. Likewise, foaming in the effluent was observed due to poor performance of the gas-liquid separator. Nevertheless, the tests yielded encouraging

results: No CO or NO_x was detected in the vent gas and both TOC and nitrophenols were below the detection limits (see Table 3.3). In the aqueous effluent with a pH of 8.0, ammonium bicarbonate was observed.

Taking into consideration experience from the 1999 experimental runs, some changes in the system were made, which will be discussed in the following section.

Table 3.3 Experimental conditions for DNP experiments at UBC/Noram pilot plant, 1999.

Composition	Feed concentration [mg/l]	DRE [%]	Operating parameters		
			Oxygen excess [%]	Pressure [MPa]	Temperature in reactor [K]
2,4 DNP	11,188	99.99	601	25.5	800
Total ammonia (as NH ₃)	5,543	53.13			
TOC	5,500	99.89			

3.3 Experimental apparatus and methods

3.3.1 Apparatus

The oxidation experiments were conducted in a pilot-scale plant, designed to treat a maximum waste flow of 2 L/min. The system, a simplified schematic of which is shown in Figure 3.2, consisted of a high-pressure pump, an oxygen vessel with a compressed air-driven oxygen compressor, and a tubular system, (Inconel 625, high pressure tubing, 0.622 cm ID and 0.952 cm OD (3/8")) formed by the following sections:

- Regenerative Heat Exchanger (1/2"x 3/8" counter flow tube in tube exchanger): 6.2 m in length
- Preheater 1: 4.7 m in length
- Preheater 2: 4.7 m in length
- Test Section: 3.8 m in length
- Reactor: 120 m in length
- Process Cooler (5/8"x 3/8", counter flow tube in tube, SS316): 6.2 m in length,

All hot sections of the system were insulated in 15.2 cm x 15.2 cm boxes of ceramic board (Kaowool).

One polyethylene storage tank (550 L capacity) supplied distilled water to the system, which was used during system warm up. Another tank (250 L capacity) contained the waste mixture that was fed into the system once steady state was reached. A steam coil was used during the red water tests to keep the feed in solution. Liquids were pumped into the system by a high pressure, triplex, positive displacement, metering pump (GIANT P57), followed by a pulsation damper (Hydrodynamics Flowguard DS-10-NBR-A-1/2" NPT). The flow from the pump was controlled by a variable frequency drive (VFD, Reliance ISU21002). Steam tracing maintained the feed line at 60-70 °C during red water tests.

A compressed-air-driven booster pressurized gaseous oxygen from a liquid oxygen tank (equipped with a vaporizer) up to 324 bar. The delivery pressure to the SCWO system was regulated at 270 bar, allowing the oxygen to flow by pressure difference between this delivery system and the SCWO unit (normally 250 bar). The oxygen flow was controlled by a metering valve and measured by a 1.14 mm orifice meter, which was connected to a differential pressure transmitter (FOXBORO ID P10). Uncertainty in the calibration of this

orifice meter depended on the oxygen pressure and voltage reading (See Appendix A for details and system calibration), but in practice always was of the order of 1.3 to 1.6%.

The aqueous and oxygen mixture first passed through a regenerative heat exchanger. The cold, incoming fluid flowed through the tube side, and the hot fluid left through the shell side.

After the heat exchanger, two separately controlled preheaters were used to continue heating the fluid until it reached the desired temperature. The test section and the reactor were similarly heated, and together with the preheaters and the regenerative heat exchanger formed a 150-meter long tubular system, in which oxidation reactions started as soon as conditions allowed it.

After leaving the reactor, the process fluid flowed through the shell side of the regenerative heat exchanger, and then through the process cooler, which took the bulk temperature down to 40-50 °C. When leaving the system, the fluid passed through a gas-liquid separator. Then, the gaseous stream passed through a carbon bed filter that eliminated odours. Its flow rate was measured by a dry gas flow meter (AL 425 Canadian Meter Company Limited) (see Appendix B for flow meter calibrations).

A 310 bar nitrogen tank and the main body of a backpressure regulator Tescom 54-2100 series (without the spring element) formed the backpressure regulation system. The nitrogen tank was set to the pressure desired in the SCWO system, allowing it to operate with a pressure oscillation of no more than 1 bar. This stability in the system pressure could be translated into stable oxygen flow and better control over the operating conditions.

Figure 3.3 shows an example of pressure and oxygen vs. time during a real oxidation experiment. In this case, samples were taken only from the effluent. Consequently, there was

no chance of pressure fluctuations due to sudden changes in the system's flow rate, which could occur when the intermediate sampling ports were in use. According to this figure, the maximum variation in the system pressure was 0.029 MPa, causing a variation of 0.02 kg/h in terms of oxygen flow. Since the system generally operated at relatively low oxidant excess, an accurate oxidant flow control was of vital importance for the proper oxidation of the waste. However, Figure 3.4 shows a case in which there was a noticeable pressure (and subsequently oxygen flow) fluctuation. This was due to opening the intermediate sampling valves, which destabilized the system pressure.

After finishing each experiment, the system was rinsed and cooled down with distilled water, then depressurized.

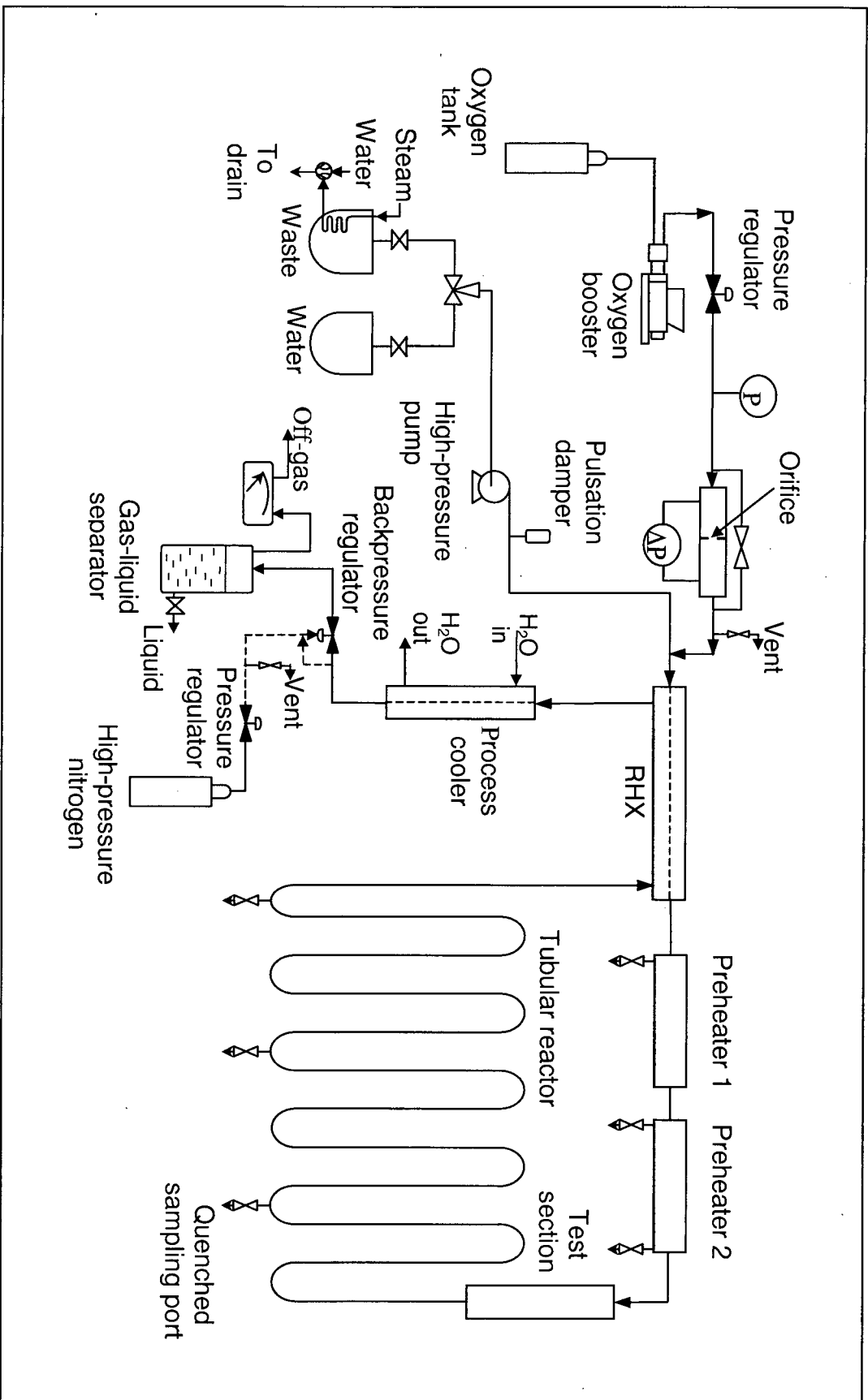


Figure 3.2 Schematic flow sheet of the UBC-Noram SCWO reactor

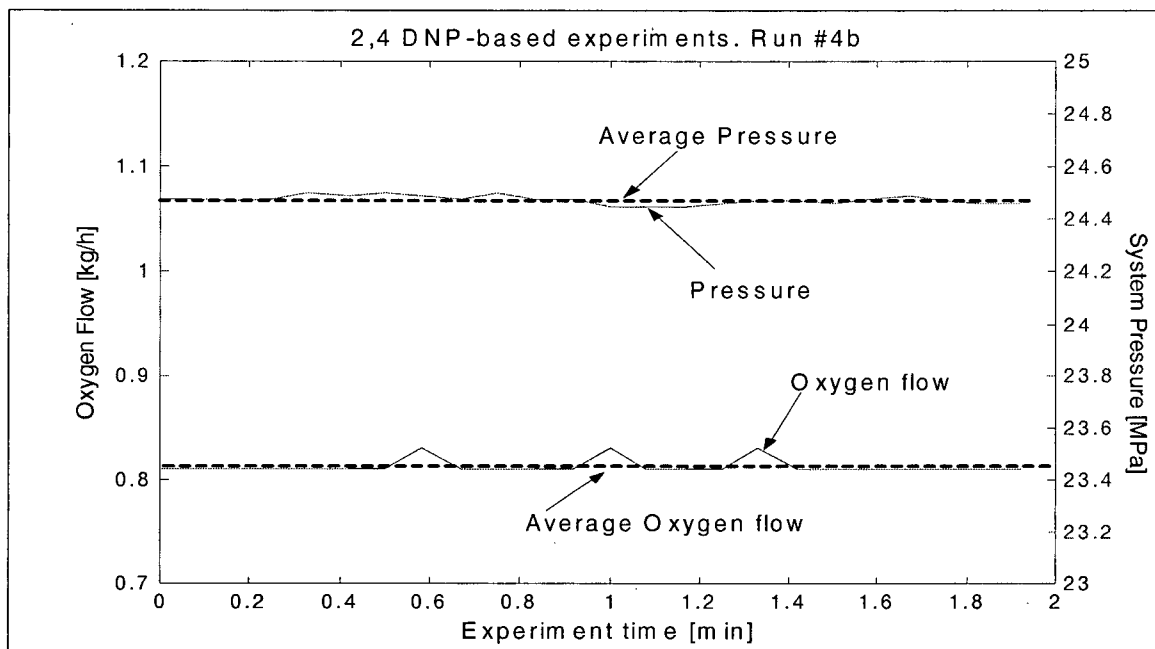


Figure 3.3 Pressure and oxygen flows. Samples only taken from the effluent.

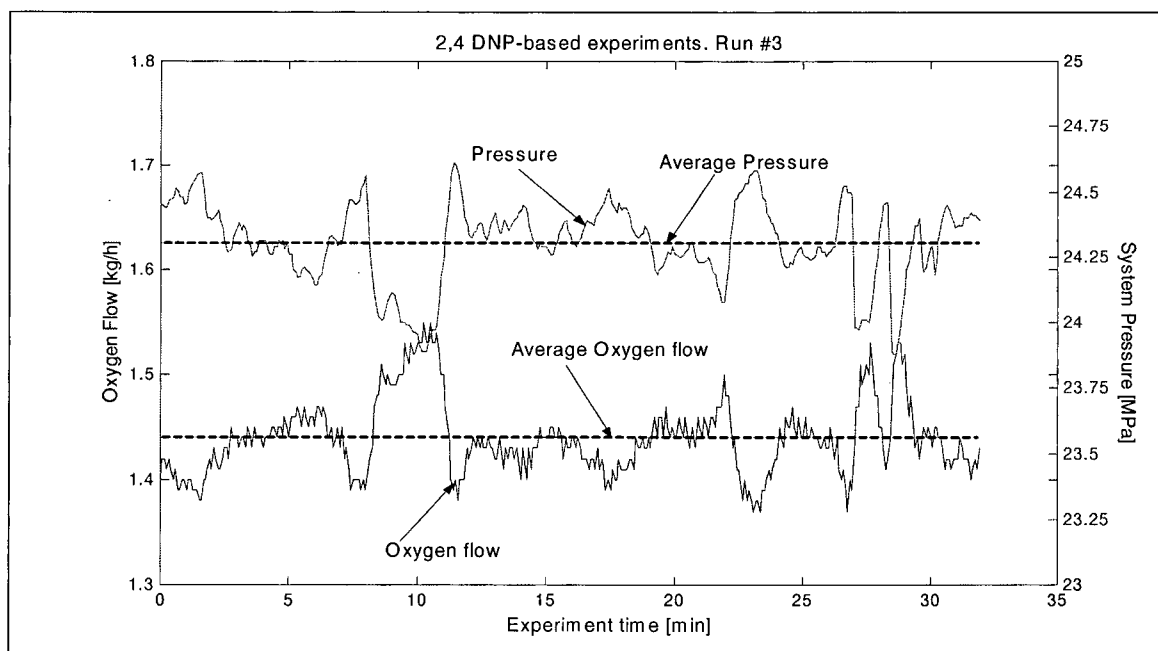


Figure 3.4 Pressure and oxygen flow. Samples taken from sampling ports and the effluent

3.3.2 *Fluid temperature measurements*

Bulk and surface temperatures were monitored during the experiments. A table describing the thermocouples distribution throughout the system is provided in Appendix C. Bulk and surface thermocouples were K-type, Inconel sheathed, and ungrounded. Their uncertainty was $\pm 5^{\circ}\text{C}$.

3.3.3 *Sampling system*

In order to learn about the destruction of the wastes studied, it was necessary to take samples not only from the effluent port, but also from several intermediate locations. This allowed us to follow the course of the SCWO reaction process in terms of destruction efficiency and intermediate species.

For this purpose, a new, water-cooled, jacketed sampling system was installed and validated. It is imperative that the samples be instantly quenched, because otherwise the analysis of results could be deceiving, yielding false conversions that did not really take place in the system, but in the sampling ports.

Each sampling port, (Figure 3.5) was purged for more than two sampling port residence times before taking a sample (typically a sampling time of 2 minutes). Additionally, the sampling ports were rinsed with distilled water between each experimental run, to make sure that no organics remained in the sampling line. Random samples of the final rinse water were taken and analysed for TOC in order to confirm the absence of organics (see Appendix D for calculations of the necessary rinsing times for each sampling port and other details). After assuring that the sampling lines were completely clean, the next experimental run started, and

the organic waste was again fed into the system. All jackets were made with Swagelok reducing tees and lengths of copper tube.

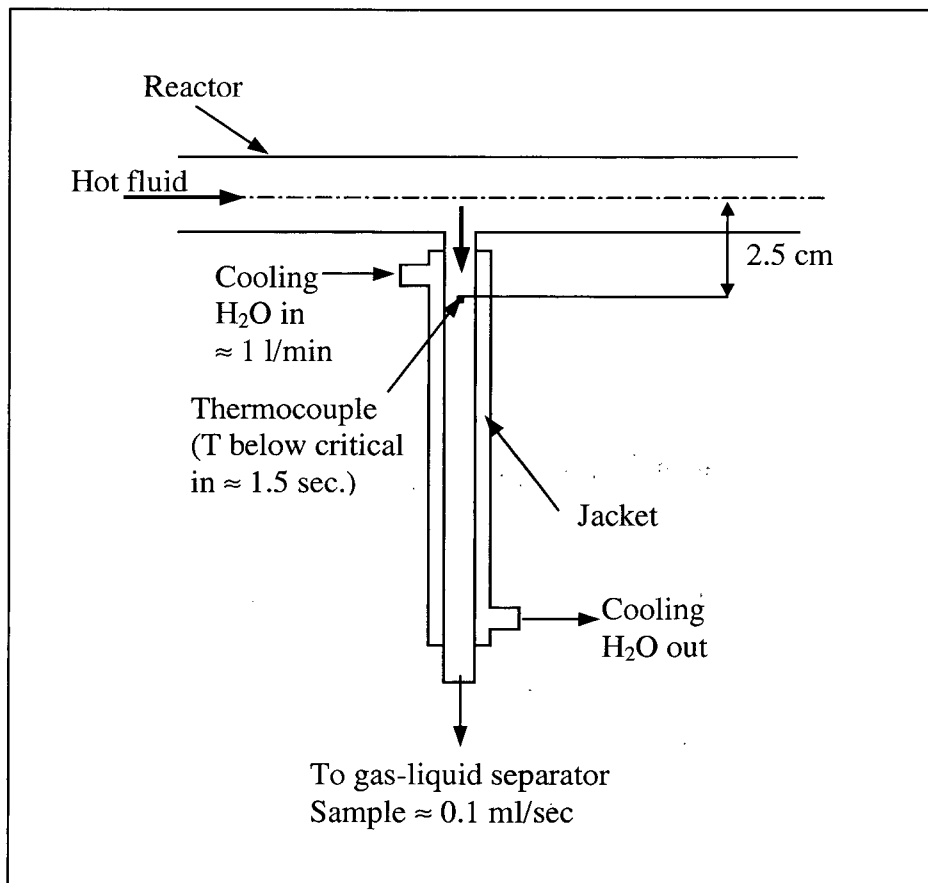


Figure 3.5 Sample cooler for intermediate sampling port.

3.3.4 Analytical procedures

Given that chemical analyses methods have an important effect in the accuracy of the results, a brief discussion is in order here.

Nitrophenols (including phenol) were analyzed with a HP HPLC 1100, with a detection limit 0.5 mg/L and an accuracy of $\pm 10\%$. TOC was analyzed by a Shimadzu TOC-500 Carbon analyzer, with a detection limit of 1 mg/L and an accuracy of 10%.

Ammonia was analyzed by a colorimetric method, with a detection limit of 0.01 mg/L and an accuracy of $\pm 13\%$. It is important to mention that samples containing ammonia should be analyzed immediately after being taken, or be acidified and properly stored. Otherwise, the results from the analyses yield falsely low ammonia concentrations, due to the ammonia volatilization. Not observing this caused differences with the ammonia measured in two different labs. The values used for all calculations in this work corresponded to those of the lab that observed the proper treatment of the samples (see appendix H).

Gas analyses were done by GC with a thermal conductivity detector in a HP packed column gas chromatograph (GC), with an accuracy of $\pm 10\%$ and detection limits ranging from 0.1 to 0.5 % (by volume).

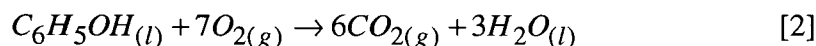
Carbonates and bicarbonates were obtained by pH titration; the accuracy was of the order of 10%. Nitrates and nitrites were analyzed in a Dionex ion chromatograph, with a detection limit of 0.1 mg/L and an accuracy of $\pm 10\%$.

Finally, metals were obtained by an inductively coupled plasma (ICP) method, with detection limits ranging from 0.02 to 0.1 mg/L and accuracies from ± 1.3 to 7.5%. The accuracies of the analytical methods were considered for the calculations of errors in the yields and conversion of the different compounds.

3.4 Calculations

3.4.1 Oxygen excess

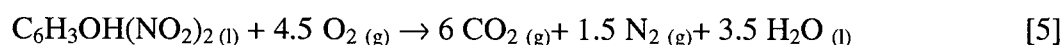
The stoichiometric relation for the complete destruction of phenol is given by Equation [2]. The stoichiometric requirement for oxygen in g/min at a given concentration is provided by Equation [3] below, where Ph_{in} represents the feed concentration in wt. %, \dot{m}_{liquid} the liquid feed mass flow rate in g/min and $M.W_{phenol}$ and $M.W_{O_2}$ the molecular weights in g/mol of phenol and oxygen respectively. The percentage in oxygen excess was calculated as shown in Equation [4].



$$\dot{m}_{oxygen\ stoich.ph} = \frac{\%Ph_{in} / 100 \cdot \dot{m}_{liquid}}{M.W_{phenol}} * 7M.W_{O_2} \quad [3]$$

$$O_{2ex} = \frac{(\dot{m}_{oxygen} - \dot{m}_{oxygen\ stoich.})}{\dot{m}_{oxygen\ stoich.}} * 100 \quad [4]$$

The stoichiometric relation for complete oxidation of 2,4DNP is:



In this equation, it is assumed that nitrogenous compounds were converted to $N_2 (g)$, and not to nitrous oxide (N_2O), as could also have been the case. The assumption was made based on the experience from the experiments conducted in 1999, in which practically no N_2O was detected.

The stoichiometric oxygen requirement could be calculated similarly to equation [3]:

$$\dot{m}_{oxygen\ stoich.DNP} = \frac{\%DNP_{in} / 100 \cdot \dot{m}_{liquid}}{M.W_{DNP}} * 4.5M.W_{O_2} \quad [6]$$

Where DNP_{in} was the feed concentration of 2,4 DNP in % wt., and $M.W_{DNP}$ was the molecular weight of 2,4 dinitrophenol.

3.4.2 Residence times

The residence time dt in a differential length of reactor dL is given by Equation [7], where A represents the area of the tubular cross sections in m^2 , L the length of the system, $\rho(T)$ the density in g/L at its corresponding temperature T (in K) and \dot{m}_{total} the total feed mass flow rate, including both the waste-water mixture and the oxygen fed into the system.

$$dt = \frac{A dL}{\dot{m}_{total}} \rho(T) \quad [7]$$

When the elements of the system are divided into a number of segments N , the cumulative residence time through out the system, for every position “ i ”, can be represented as in Equation [8].

$$t_i = \sum \left(\frac{L_{(i)} - L_{(i-1)}}{N * \dot{m}_{total}} \right) A \rho_i + t_{(i-1)} \quad [8]$$

All residence time calculations were performed in Matlab by forward integration over a number of segments of the tubular system (see Appendix J). Each element of the system (preheaters, test section, reactor and regenerative heat exchanger) was divided into 100-300 segments of constant enthalpy increments, and the water properties were obtained by interpolation from a lookup table from the IAPWS-95 Scientific Formulation of Water Properties.³⁹ The data files loaded into the Matlab program included the readings from the thermocouples at different locations throughout the system. With this data, the program was able to calculate the residence time at each specific location in the system.

The densities used for the calculations corresponded to those of water because no data were available for density of water-phenol-oxygen or water-dinitrophenols-oxygen mixtures. However, using water densities is a reasonable assumption, considering that the mass percentages of oxygen and organics in the feed were still very low compared with those of water. For example, for a water-4% by wt phenol feed flow rate of 0.78 L/min and an oxygen flow of 0.23 l/min at 269 bar, the total flow entering the system would be 1.01 L/min, of which 74.26% of the volume would correspond to water, 3% to phenol, and 23.5 % to oxygen.

Figure 3.6 presents an example of the progress of the residence time throughout the system. The experiments conducted at higher temperatures generated lower residence times. The progress in time of the destruction of both phenol and 2,4 DNP will be shown in different plots in the following sections.

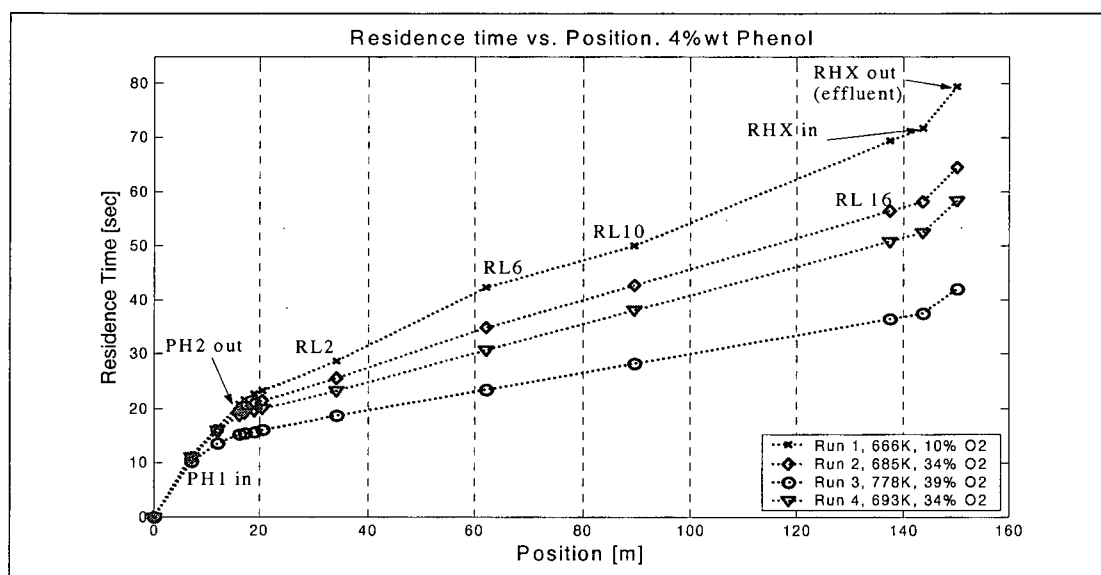


Figure 3.6 Plot of residence time vs. system length at different conditions

3.4.3 Yields and Conversions

Conversion X at some location was calculated from the concentration C at that location and the initial concentration C_{in} :

$$X = \frac{C_{in} - C}{C_{in}} \quad [9]$$

For example, the TOC destruction efficiency was

$$X_{TOC} = \frac{C_{TOC_{in}} - C_{TOC}}{C_{TOC_{in}}} \quad [10]$$

The destruction of other compounds in the feed, (e.g. ammonia) was calculated in the same way.

Yields of CO , CO_2 , N_2 and N_2O were calculated as the molar flow rate of CO or CO_2 at the sampled point divided by the TOC molar flow rate in the feed, and the molar flow rate of N_2 and N_2O divided by the molar flow rate of N in the feed, respectively. For example:

$$X_{CO_2} = \frac{\dot{n}_{CO_2}}{\dot{n}_{TOC_{in}}} \quad [11]$$

$$X_{N_2} = \frac{\dot{n}_N}{2\dot{n}_{N_{in}}} \quad [12]$$

Gas compositions were normally given in percent, on a per volume basis. Therefore, their molar flow rates could be obtained by simply multiplying their corresponding percentage in the gas sample by the gas flow rate, in $gmol/min$, for example:

$$\dot{n}_{CO_2} = \frac{\%CO_2}{100} \dot{n}_{gas} \quad [13]$$

The molar flows of TOC or N in the feed were given as their corresponding concentrations in the feed, in g/L multiplied by the total liquid feed flow rate in L/min and divided by their respective molecular weight. For example:

$$\dot{n}_{TOC} = \frac{C_{TOC_{in}} \dot{m}_{liquid}}{M.W_C} \quad [14]$$

3.4.4 Calculations for the comparison with other studies of the phenol experiments

The global reaction rate for phenol destruction [1], with the kinetic parameters from Table 1, was used to compare other authors' predictions with our experimental results.

Equation [1] was integrated in Matlab over each segment of the tubular system, using our own system's temperature profiles and residence times calculated as previously explained.

In the program, (see Appendix J), the system was divided into a number of segments z , and the rate from Equation [1] was expressed in the following form:

$$r_{(i)} = -K_{(i-1)} [Ph]_{(i-1)}^a [O]_{(i-1)}^b [H_2O]_{(i-1)}^c \quad [15]$$

Where K was the rate law constant given by $A \exp\left(\frac{-Ea}{RT}\right)$ and water concentration varied according to its density at each different point in the system. All elements concentrations were entered in mol/L.

The initial phenol concentration $[Ph]_{in}$ at the system's pressure and temperature was defined as:

$$[Ph]_{in} = x_{Ph_{in}} \frac{\rho_{in}}{M.W_{Phenol}} \quad [16]$$

Where ρ_{in} was the initial water density at the initial temperature and $x_{Ph\ in}$ the phenol mass fraction at initial conditions:

$$x_{Ph\ in} = \frac{\dot{m}_{Phenol}}{(\dot{m}_{liquid} + \dot{m}_{Oxygen})} \quad [17]$$

\dot{m}_{Phenol} , \dot{m}_{liquid} , and \dot{m}_{Oxygen} were the feed mass flows of phenol, liquid and oxygen, respectively. The phenol mass flow rate was a function of the feed concentration $Ph_{,in}$ in weight percent and the total liquid flow rate \dot{m}_{Liquid} :

$$\dot{m}_{Phenol} = \frac{Ph_{in}}{100} \dot{m}_{liquid} \quad [18]$$

The initial water concentration in moles/L was represented by the relation of its initial density divided by the molecular weight of water:

$$[H_2O]_{in} = \frac{\rho_{in}}{M.W_{H_2O}} \quad [19]$$

The initial oxygen concentration was a function of the initial concentration of phenol and the molar relation oxygen-phenol:

$$[O_2]_{in} = [Ph]_{in} \frac{\dot{m}_{Oxygen} / M.W_{Oxygen}}{\dot{m}_{Phenol} / M.W_{Phenol}} \quad [20]$$

Phenol concentration during the experiment varied as:

$$[Ph]_{(i)} = [Ph]_{(i-1)} + d[Ph]_{(i-1)} \quad [21]$$

$$d[Ph]_{(i)} = r_{(i)} dt_{(i-1)} \quad [22]$$

With $d[Ph]$ being the differential changes in phenol concentration per system segment i, and time was the residence time per segment i and the oxygen concentration was assumed to vary according to the stoichiometric relation:

$$[O_2]_{(i)} = [O_2]_{(i-1)} + 7 \, d[Ph]_{(i-1)} \quad [23]$$

This stoichiometric assumption is not accurate when carbon-containing products different from CO_2 appear.^{16, 40} In such a case, the oxygen consumption would be different than that of the stoichiometric relation [2]. Nevertheless, the effective stoichiometric coefficients for the formation of carbon compounds will increase with conversion, to finally reach the stoichiometric value of Equation [2]. Since the effective stoichiometry for the incomplete oxidation of phenol is not known, the oxygen concentrations cannot be calculated by using this approach. This situation would leave us with two alternatives:

1. Use the stoichiometric relation to calculate the oxygen concentration (a reasonable assumption when working with global rates); or
2. Use very high excess oxygen during the experiments, to assume that its concentration is either constant or changes only by a small fraction.

Since the main objective of this work was to investigate and validate the supercritical water oxidation destruction of organics at practical conditions it was decided to maintain a low oxygen excess and use the stoichiometric relationship to calculate oxygen concentrations.

The phenol conversions in the system were calculated according to Equation [9] from the previous section.

This procedure was followed for the authors referred to in Table 3.1.^{14, 15, 16, 17, 18, 21, 22, 23}
The results obtained will be discussed in section 3.2.1

3.4.5 Error analysis

Errors in controlling experimental conditions also have an effect on the overall accuracy of the experiments. The measurement of temperatures, pressures and liquid and oxygen feed flow rates directly affect the calculated residence times. The control of the gaseous stream flow rates and sample collection techniques, together with the analytical uncertainties, affect the reported conversions and yields.

3.4.5.1 Residence times

The calculation of system pressure and oxygen flow uncertainties have been described in the experimental conditions sections, and in Appendixes A, F, G, and H.

According to Equation [7], in section 3.4.2, residence time can be calculated as a function of the area of the tubular system, its length, the relation between the density of the fluid, and the total mass flow rate of the fluid:

Equation [7] was used as the basis of the calculation of the residence time's uncertainties. It was considered that the uncertainties in the densities were mostly given by the uncertainties in the temperature, and to a lesser extent, by the uncertainties in the system's pressure.

As explained in section 3.4.2, \dot{m}_{total} included the liquid and the oxygen mass flow rates that were fed into the system (\dot{m}_{liquid} and \dot{m}_{oxygen}). The uncertainty in measuring the liquid flow rate was neglected, as it was considered very small (0.5 mL/min, for feed flow rates of approximately 0.8 L/min in all experiments) in comparison with those of the oxygen flow rates. Therefore, the factors influencing the residence time were the system's temperatures

and pressure (affecting the density) and the oxygen mass flow rate (affecting the total feed flow rate).

Considering the residence time as a general function $R=f(y_1, y_2, \dots y_n)$, its uncertainty (w_R) was expressed by the Equation [24]⁴¹ below, where w_1, w_2, w_n were the uncertainties of the individual equation variables, $y_1, y_2, \dots y_n$. Taking \dot{m}_{total} as y_1 and $\rho(T, P)$ as y_2 , w_1 was taken as the uncertainty in the oxygen mass flow rates (section 3.4.2 and Appendix A), and w_2 as the uncertainty in the density.

$$w_R = \left[\left(\frac{\partial R}{\partial y_1} w_1 \right)^2 + \left(\frac{\partial R}{\partial y_2} w_2 \right)^2 + \dots \left(\frac{\partial R}{\partial y_n} w_n \right)^2 \right]^{1/2} \quad [24]$$

The calculations of residence time uncertainties for each experiment were performed in Matlab (see Appendix J).

The overall uncertainty in the density (w_2) was calculated in several steps. First, the uncertainty due to the accuracy in temperature was obtained, then the uncertainty due to the oscillation in pressures.

For the temperature component, it was assumed that the temperature readings were accurate within ± 5 degrees, as already explained in section 3.3.2. The densities at $T+5$ and $T-5$ degrees were calculated for each temperature reading. The same was done for their correspondent unbiased standard deviation, according to Equation [25], where n was the number of measurements, 3 for each temperature reading T , ($\rho(T)$, $\rho(T+5)$ and $\rho(T-5)$). y_1 and y_2 were $\rho(T+5)$ and $\rho(T-5)$ respectively, and y_m was the density at the temperature reading $\rho(T)$.

$$\Gamma = \left[\frac{1}{n-1} \sum_{i=1}^n (y_i - y_m)^2 \right]^{1/2} \quad [25]$$

To calculate the uncertainty in the density due to the fluctuations in pressure (δP), the same procedure was followed, but in this case, the uncertainty in the pressure varied for each case (refer to Tables 3.4 and 3.6 in the experimental conditions section). The densities at $P+(\delta P)$ and $P-(\delta P)$ were calculated, as well as the corresponding unbiased standard deviation, by Equation [25]. It was observed that the uncertainties due to the changes in pressure were lower than those from the changes in temperature, with their values always being maximum at temperatures/pressures close to the critical point. This was to be expected due to the sudden change in the water density around the critical point. Finally, the total uncertainty in the density measurements (w_2) was calculated as the sum of the uncertainties caused by the temperatures and the pressures.

Equation [24] was then used to calculate the total uncertainty in the residence time. As it was observed with the densities, the uncertainty in the residence time was maximum at locations with temperatures around the critical point.

3.4.5.2 Yields and conversions

Conversion of organics, TOC and ammonia were calculated as shown in equation [9] of section 3.4.3. Using this equation, equation [24] and the procedure explained before, the uncertainty in the conversions was calculated in Matlab (Appendix J). The uncertainty in the destruction of these compounds was given by the uncertainty in the corresponding analytical technique.

For the case of the gas yields, they were represented according to Equations [11] to [14] of section 3.4.3. In one formula, the gas yields were expressed, for example, as Equation [26]:

$$X_{CO_2} = \frac{\frac{\%CO_2}{100} \dot{m}_{gas}}{\frac{C_{TOC\ in} \dot{m}_{liquid}}{M.W_{TOC}}} \quad [26]$$

Following a procedure similar to the one described for the residence times, Equation [24] was used to obtain the uncertainties in the gas yields, taking y_1 as the volume percent in the gas sample (%), y_2 as the gas flow rate, y_3 as the TOC or N concentration in the feed and y_4 as the total liquid feed flow rate. In the same way, all calculations were performed in Matlab, and can be seen in Appendix J.

As shown, gas yield uncertainties depended both on analytical measurements and on the system's accuracy when measuring the liquid and gaseous flow rates. The uncertainty of the liquid flow rate was 0.5 mL/min, as explained before, and it was not neglected in this case. The uncertainty in measuring the gaseous streams flow rates varied with the experiments and appears explained in each of the correspondent discussion of results section.

3.5 Discussion of results

3.5.1 Phenol Experiments

3.5.1.1 Experimental conditions

High concentrations of phenol were treated, in all cases maintaining the oxygen excess at a relatively low level.

Uncertainties in the system pressure and oxygen excess were obtained from the uncertainties in the voltages recorded by the data acquisition system, (see Appendix F for more details on these calculations). At the time of the tests, a different orifice meter from the one described in section 3.3.1 was used. In this case, no uncertainties in its calibration

equation were considered (see Appendix A for more information). The precision with which the feed flow rate was measured was within ± 5 ml/min. The purity of the phenol used was > 99% (ultra pure grade). The investigated conditions are shown in Table 3.4.

Table 3.4 Experimental conditions for phenol destruction.

Phenol conc. [%wt]	# of Runs	Run	Feed flow rate [l/min]	Temperature in reactor [K]	Absolute Pressure [MPa]	Oxygen excess [%]
4	4	1	0.78 ± 0.005	666	25.67 ± 0.02	10 ± 5
		2		685	25.78 ± 0.18	34 ± 8
		3		778	25.48 ± 0.21	39 ± 8
		4		693	25.69 ± 0.2	34 ± 5
2.7	5	5	0.8 ± 0.005	681	25.67 ± 0.45	34 ± 34
		6		690	25.54 ± 0.87	-1 ± 80
		7		703	25.69 ± 0.4	21 ± 10
		8		726	25.61 ± 0.26	19 ± 6
		9		737	25.61 ± 0.26	19 ± 6

3.5.1.2 Observations

Phenol, TOC and GC analyses were carried out to obtain the destruction efficiencies (conversions) and gas yields, as described in section 3.4.3. Gaseous flow rates were measured with an AL 425 Canadian Meter Company Limited volume flow meter (Appendix B), and it was considered to have an uncertainty of 5%.

As stated before, our objectives during these experiments were not to perform a kinetic analysis to determine a rate constant, its associate Arrhenius parameters or the reactant's reaction orders. We focused our attention on proving the pilot plant performance with high

concentrations of a hard to destroy simple compound, with practical (moderately low) excesses of oxygen.

Table 3.5 shows TOC and phenol conversions and gas yields for all different runs. Please refer to Appendix G for more details on each experimental run. Conversions and gas yields were calculated as explained in 3.4.3.

Table 3.5 Conversions and yields for phenol experiments

Run	Conditions T [K], Excess O ₂ [%]	Sampling Point	Distance from feed [m]	X _{Phenol}	X _{TOC}	CO yield	CO ₂ yield	Carbon Balance
<i>Feed concentration = 4 %wt as Phenol</i>								
1	666, 10	PH 2 in	11.8	-	0.328	-	-	-
		PH2 out	16.07	0.669	0.49	0.034	0.28	-
		RL-2	34.18	-	0.656	-	-	-
		RL-6	61.91	-	0.744	-	-	-
		Effluent	150.14	0.98	0.815	0.12	0.786	1.15
2	685, 34	Effluent	150.14	0.95	0.784	0.094	0.55	0.94
3	778, 39	Effluent	150.14	0.9998	0.9977	-	-	-
4	693, 6	Effluent	150.14	0.977	0.858	-	-	-
<i>Feed concentration = 2.7 %wt as Phenol</i>								
5	681, 34	PH 2 in	11.8	0.41	0.3	-	-	-
		PH2 out	16.07	0.565	0.47	0	0.108	-
		RL-2	34.18	0.65	0.59	-	-	-
		RL-6	61.91	0.79	0.65	-	-	-
		Effluent	150.14	0.97	0.79	0.082	0.402	0.74
6	690, stoich.	PH 2 in	11.8	0.25	0.24	-	-	-
		PH2 out	16.07	0.4	0.24	0	0	-
		RL-2	34.18	0.61	0.43	-	-	-
		RL-6	61.91	0.75	0.61	-	-	-
		Effluent	150.14	0.94	0.75	0.169	0.801	1.32
7	703, 21	PH 2 in	11.8	0.52	0.34			-
		PH2 out	16.07	0.61	0.48	0.027	0.201	-
		RL-2	34.18	0.73	0.59			-
		RL-6	61.91	0.8	0.68			-
		Effluent	150.14	-	0.81	0.097	0.458	0.87
8	726, 19	Effluent	150.14	0.98	0.94	-	-	-
9	737, 19	Effluent	150.14	0.993	0.89	0.032	0.614	0.78

As can be seen, there is a difference between the TOC and the phenol conversions. In every case, the TOC conversion is lower than that of phenol. This shows that in all cases organic species different from phenol remained in the aqueous effluent. It was not the objective of this work to identify such intermediate species. From the runs in which intermediate samples were taken, it was observed that by the end of the Preheater 2 (PH 2 out), a good amount of phenol had already been converted into intermediate species and a smaller portion had been converted into CO or CO₂. However, for most of the runs, final TOC conversions were considerably lower than phenol conversions. Considering how fast phenol started to break down into other species, it could be speculated that the new intermediates were less reactive and hence more difficult to eliminate. This is consistent with results obtained by both Kranjc and Levec¹⁸ and Rice and Steeper⁴², who observed complete disappearance of intermediates long after phenol had been destroyed. Gopalan and Savage¹⁷ have presented a quantitative reaction model that showed that longer residence times and higher temperatures could favour the destruction of intermediates and the formation of CO₂.

Relatively good carbon balances were achieved in the effluent streams, although they usually did not completely close. One possible reason for this could have been the formation of tarry materials (organic intermediates that could have been formed and were not destroyed), which remained in the system. This is likely to occur at high concentrations.^{14, 17} In our system, small amounts of tar were observed in the back pressure regulator when opened for cleaning.

Traces of CO were obtained in the gas effluent samples, indicating that the oxidation of CO was relatively slow. Nevertheless, the yield of CO was less than that of CO₂ at all times. Moreover, the yield of CO was always lower than unconverted TOC. This observation

suggests that even though $\text{CO} \rightarrow \text{CO}_2$ is a relatively slow reaction, it is not a rate-determining step. Rather, the rate-determining step is the further destruction of one (or more) of the oxidation intermediates. This agrees with the results repeatedly obtained by Li et al.⁴³ and Martino and Savage^{44, 40}, in which it was concluded that the main path for CO_2 formation by -passed CO. A suggested path to CO_2 was via decarboxylation of carboxylic acid intermediates, which are formed via ring-opening reactions.³⁶

No consistent temperature-CO yield production trend was observed, but no gas samples were taken at the highest temperature (run 3, 778 K). Run 9 (464 K) produced the smallest amounts of CO, with a yield of 0.032 (1.26 g/min).

3.5.1.3 *Effect of temperature*

Figures 3.7 and 3.8 show plots of phenol and TOC conversions versus temperatures for all runs at both concentrations treated. In general it was observed that higher temperatures yielded higher phenol and TOC conversions for both the 4% and 2.7 % runs. One possible reason for not having observed a consistent increase in the conversion with temperature could have been some remaining contamination in the sampling ports, which suggests that they should be allowed more rinsing time. Taking this experience as base for the following 2,4 DNP experiments, it was decided to rinse the whole system with water after each experimental run. The sampling ports were rinsed out for as long as 5 minutes, with occasional steam flushing, in order to remove any remaining organic contaminants

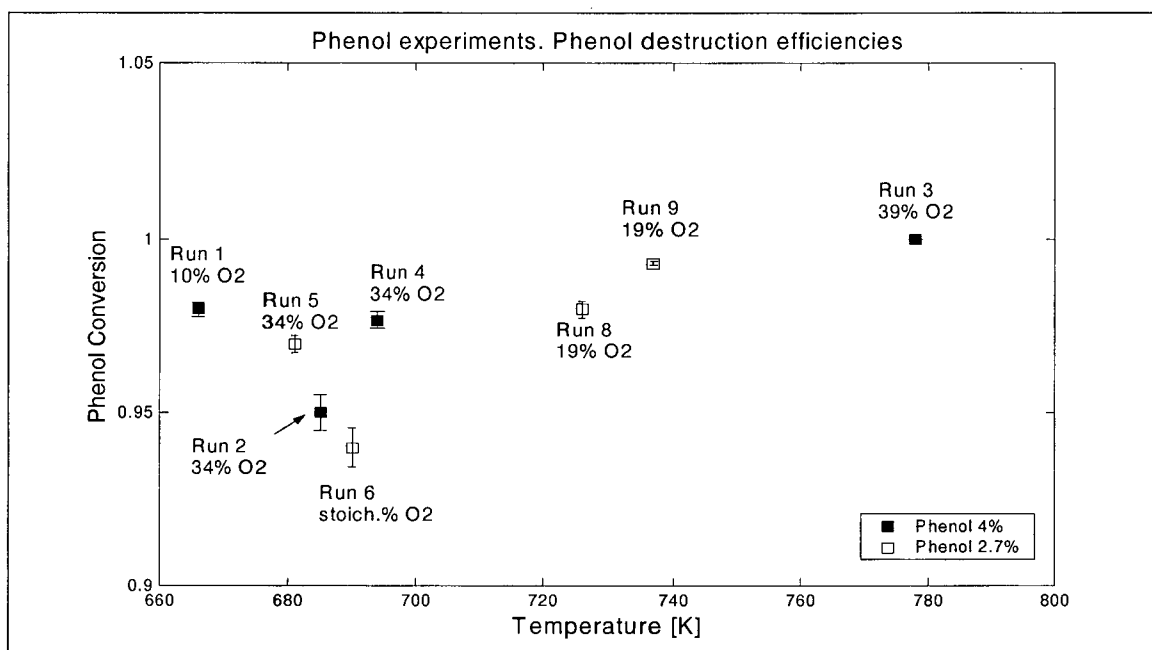


Figure 3.7 Effect of temperature, feed concentration and oxygen excess on phenol DREs

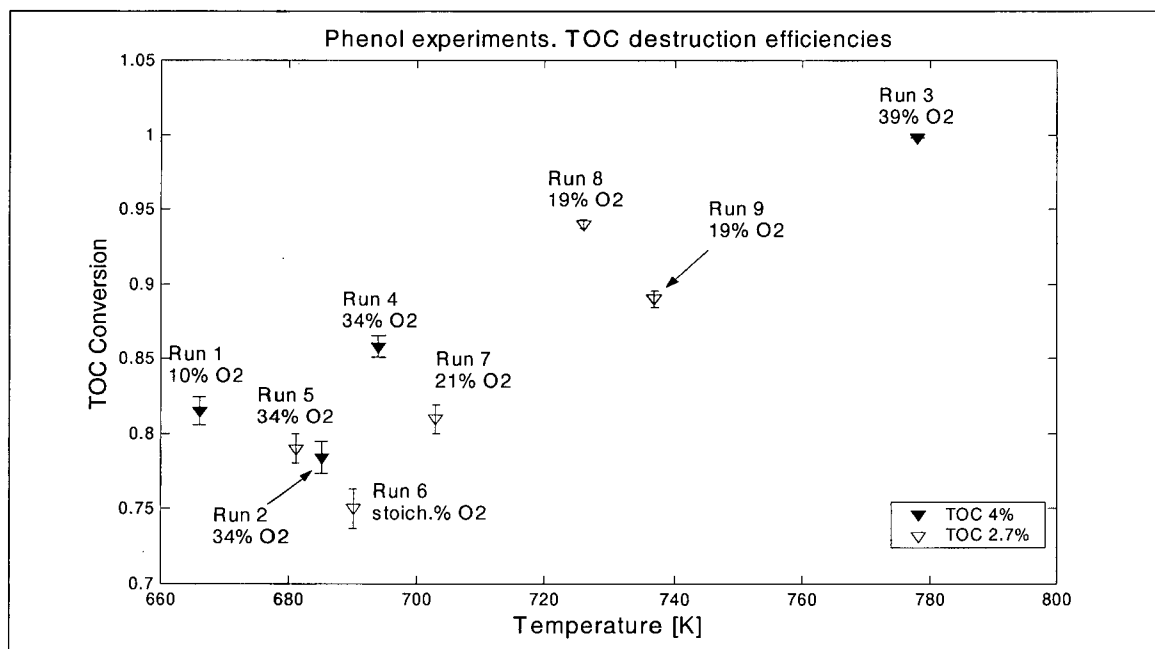


Figure 3.8 Effect of temperature, feed concentration and oxygen excess on TOC DREs

3.5.1.4 Effect of Residence time

Figures 3.9 and 3.10 show the temperature profiles vs. residence time for the 4 % wt. and 2.7 % wt. experiments, respectively. From left to right, the graph symbols correspond to the feed, PH1 in, PH2 in, PH2 out, points on the test section, the reactor and the finally RHX out (effluent). Residence times for higher temperature runs were lower. This was caused by the decrease in the water density with the increase in temperature, which directly affected the residence time.

Phenol and TOC conversions, as well as the CO₂ yield for each individual run, increased with residence time. However, there were still traces of CO, even though the CO₂ yield proved to increase. Figures 3.11 to 3.14 show the conversions and yields profiles for runs in which the effect of residence time was studied. Phenol conversions increased more rapidly than those of TOC, and still some organic intermediate were obtained in the effluent. CO₂ production was faster than that of CO.

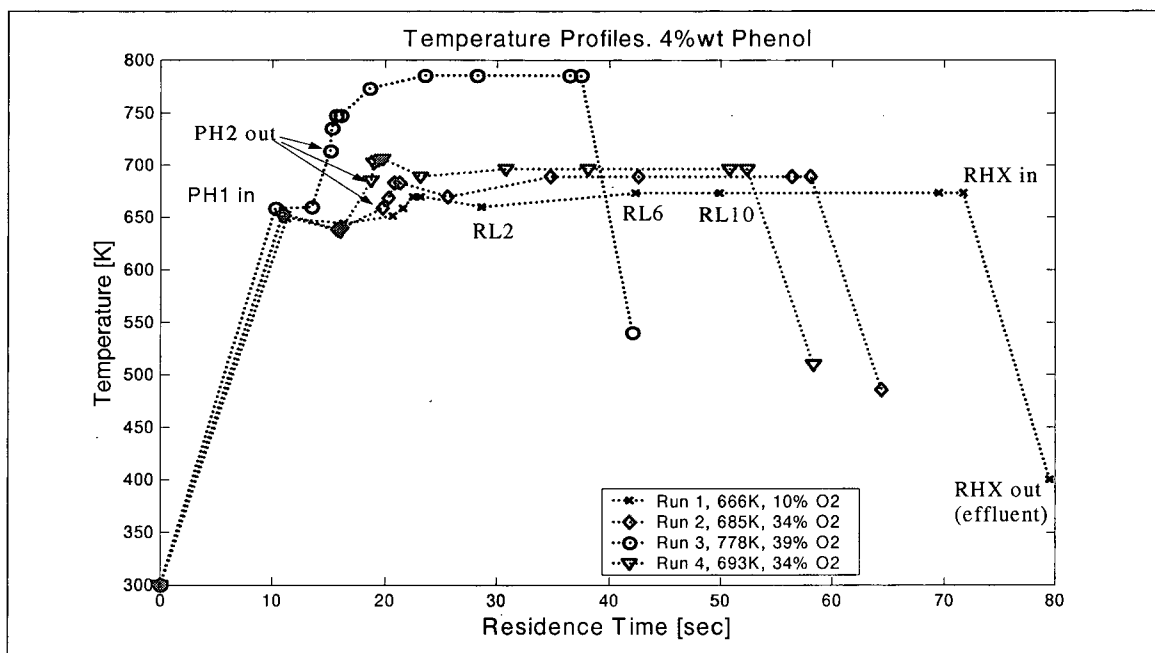


Figure 3.9 Phenol experiments. Temperature profiles for 4% wt runs

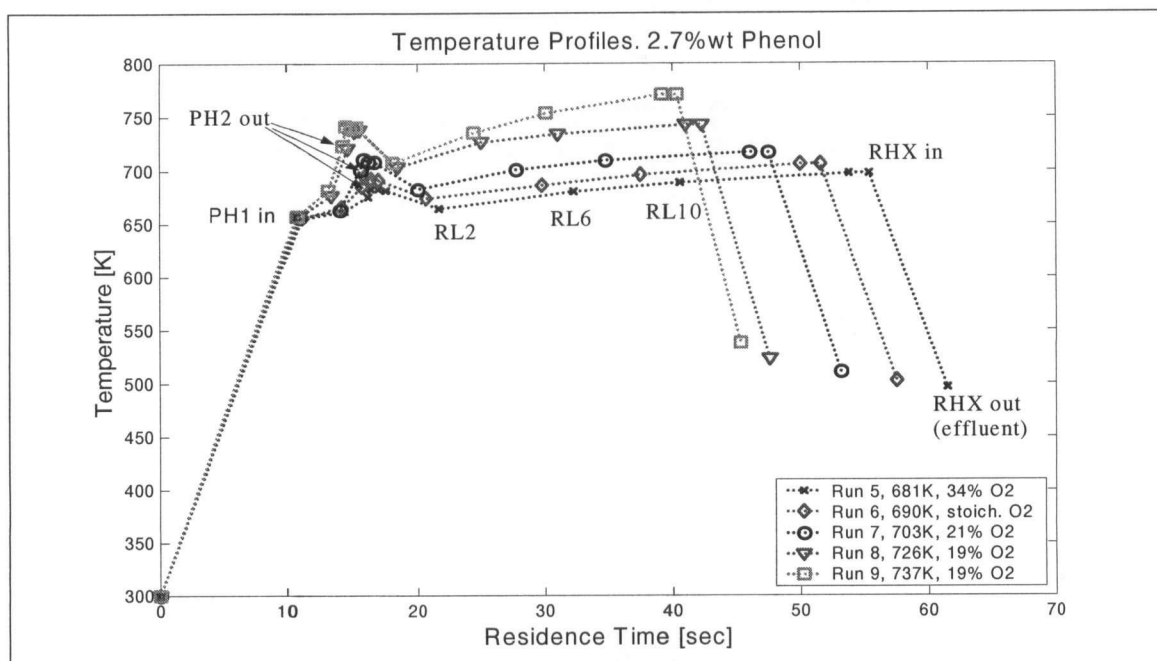


Figure 3.10 Phenol experiments Temperature profiles for 2.7% wt runs

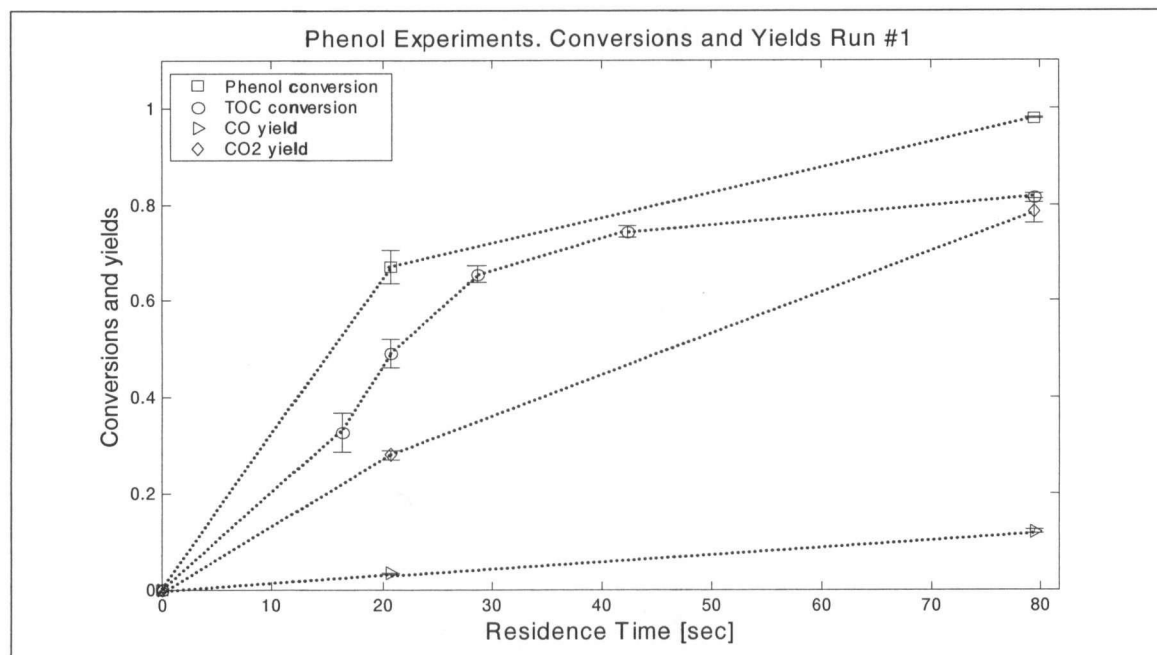


Figure 3.11 Phenol experiments. Conversions and yields for Run 1 (666K, 10% O₂ excess)

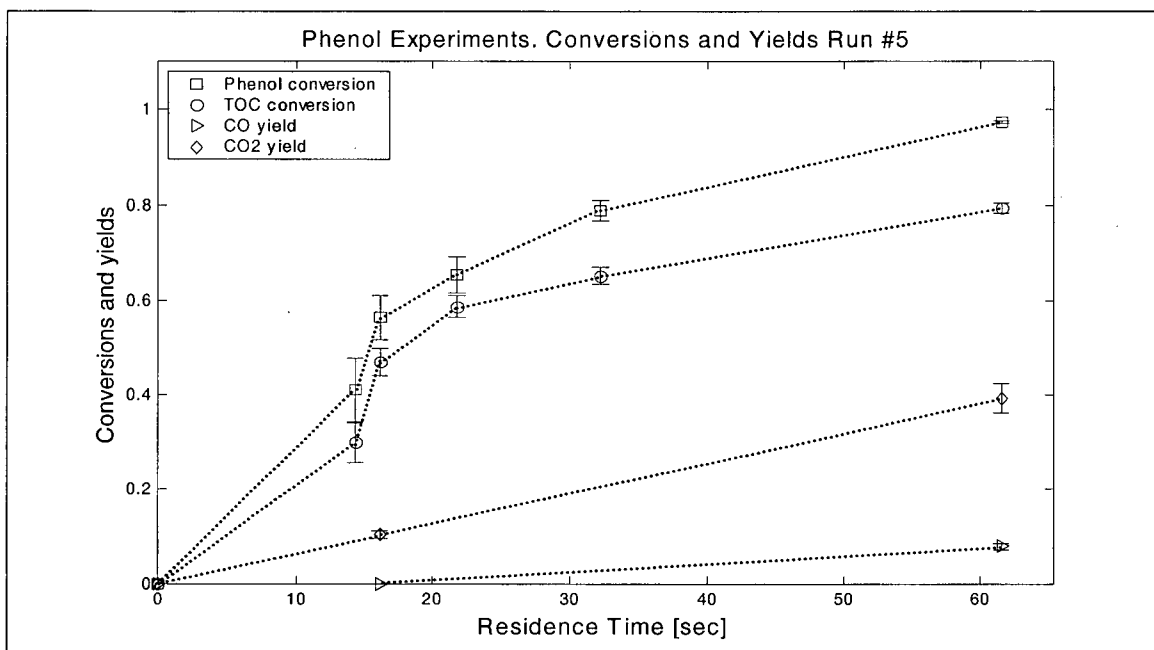


Figure 3.12 Phenol experiments. Conversions and yields for Run 5 (681 K, 34% O₂ excess)

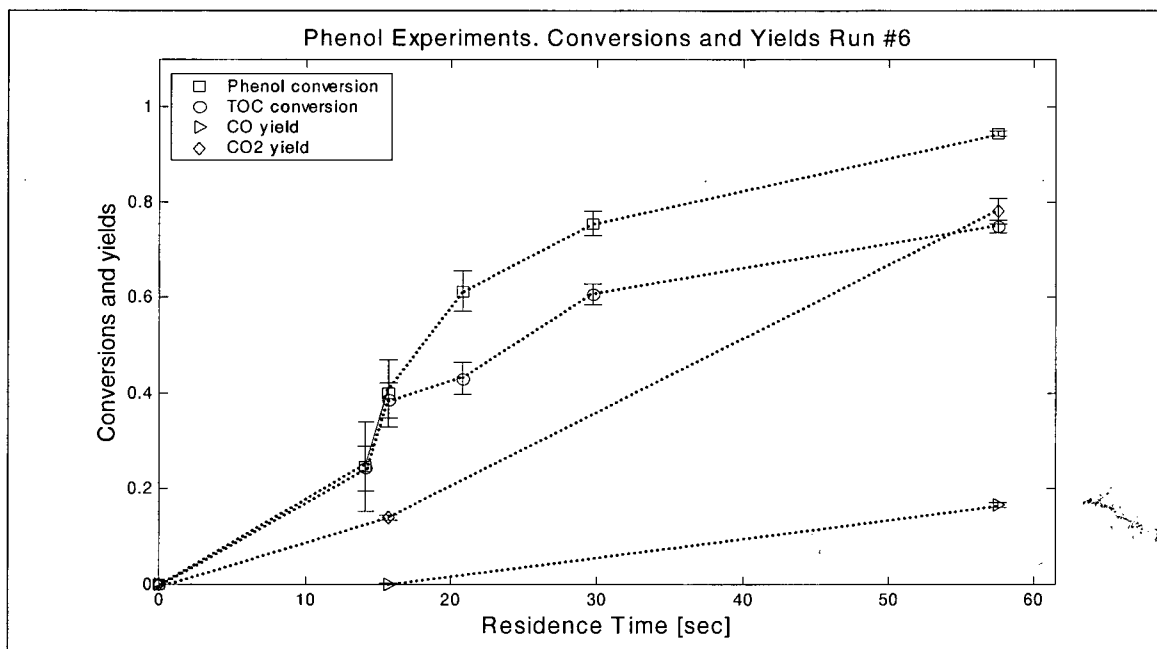


Figure 3.13 Phenol experiments. Conversions and yields for Run 6 (690 K, 0% O₂ excess)

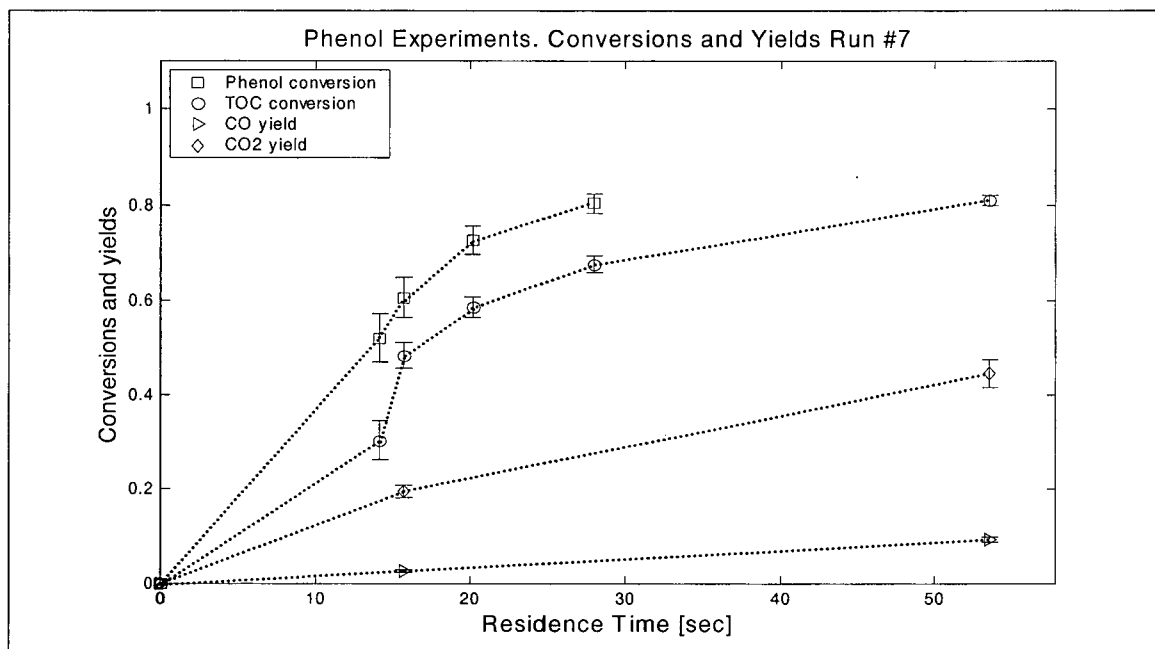


Figure 3.14 Phenol experiments. Conversions and yields for Run 7 (703 K, 21% O₂ excess)

3.5.1.5 *Effect of excess oxygen*

Figures 3.7 and 3.8 show that with stoichiometric amounts of oxygen, phenol and TOC conversions were the poorest, but for runs with higher than stoichiometric oxygen, there was no apparent effect. Not achieving high conversions at stoichiometric oxygen amounts agrees with the findings of Koo et al.²¹ and Thornton and Savage¹⁶. However, both Koo et al and Thornton and Savage found that the conversions increased with increasing the oxygen excess.

3.5.1.6 *Effect of phenol concentration*

As a general trend, phenol destruction was not affected much by the feed concentration, but TOC destruction tended to be lower at lower phenol concentrations.

Consistent with most of the previous work on SCWO of phenol,^{14, 15, 16, 17, 18, 21, 22, 23} there appears to be little dependence of phenol conversion on the feed concentration. In most

of the previous work, the global reaction orders with respect to phenol are close to unity. A higher dependence of TOC concentration in the feed was observed by Krajnc and Levec,¹⁸ who obtained a second order relation with respect to TOC conversion in phenol experiments.

3.5.1.7 Comparison with other studies

Even though it is known that global rate laws are mainly applicable for the operating conditions at which they were obtained, we decided to conduct a comparison study of the predictions of the existing rate laws at our experimental conditions. Most of the rate laws used in this comparison study,^{14, 15, 16, 17, 18, 21, 22, 23} whose kinetic parameters are shown in Table 3.1, describe the SCWO of phenol under low concentrations and high oxygen excess. Nevertheless, previous studies²³ observed disagreements among these rate laws for differences in excess oxygen of 200 and 300 % excess, concentrations of 50 and 100 mg/L and temperatures between 673 and 693 K. This confirms that global rate laws are quite sensitive to changes in operating conditions.

Figures 3.15 to 3.18 show the results obtained as a function of residence time for several runs by following the procedure described in section 3.4.4 (refer to Appendix F for other comparisons). From the graphs, it can be seen that there are some discrepancies in the predicted conversions at these conditions, although very good agreements were obtained with the rate laws proposed by Krajnc & Levec¹⁸ and Gopalan and Savage¹⁷, and in some cases with Koo et al.²¹ Some of the other global rate laws either over predicted or underestimated the phenol conversion, which, if used in the design of a SCWO reactor, would lead to either too small or too big devices, respectively. Other reasons for possible discrepancies could have been possible contamination of the sampling ports, only justifying the disagreement with the rate laws that over predicted the phenol conversions. Very fast pyrolysis reactions

that also occur during the heating are not accounted for when evaluating the proposed oxidation rates. This would have justified the disagreement with the rate laws that underestimated the phenol conversions.

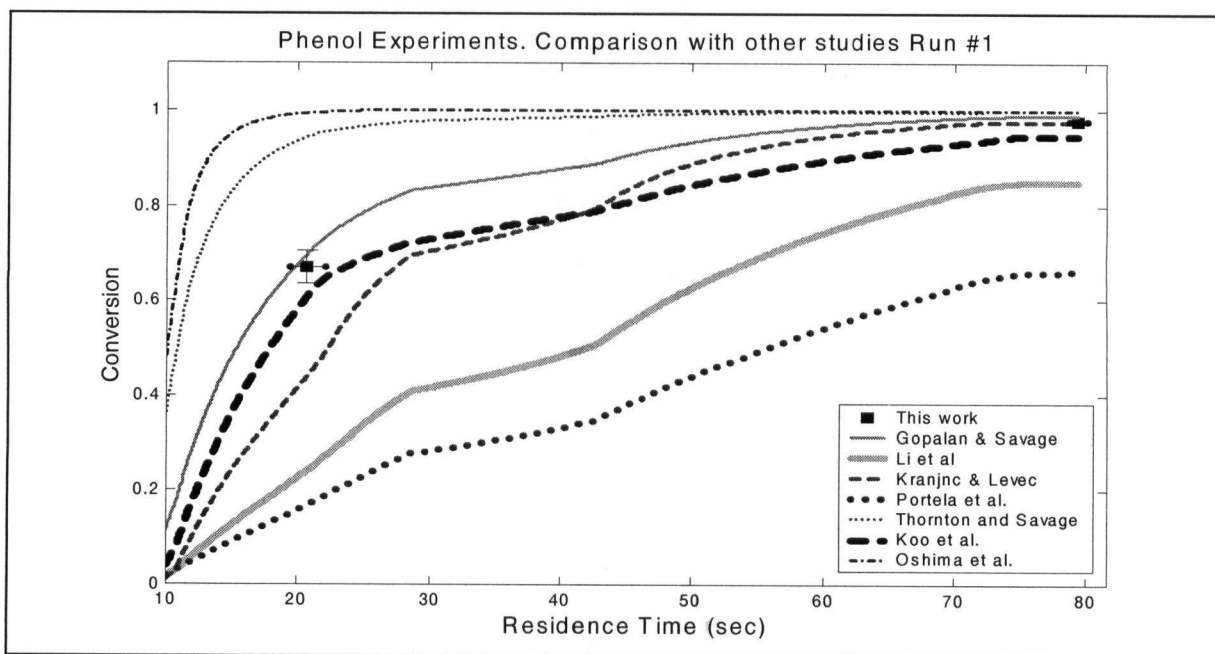


Figure 3.15 Phenol experiments. Agreement study. Run 1 (666K, 10% O₂ excess)

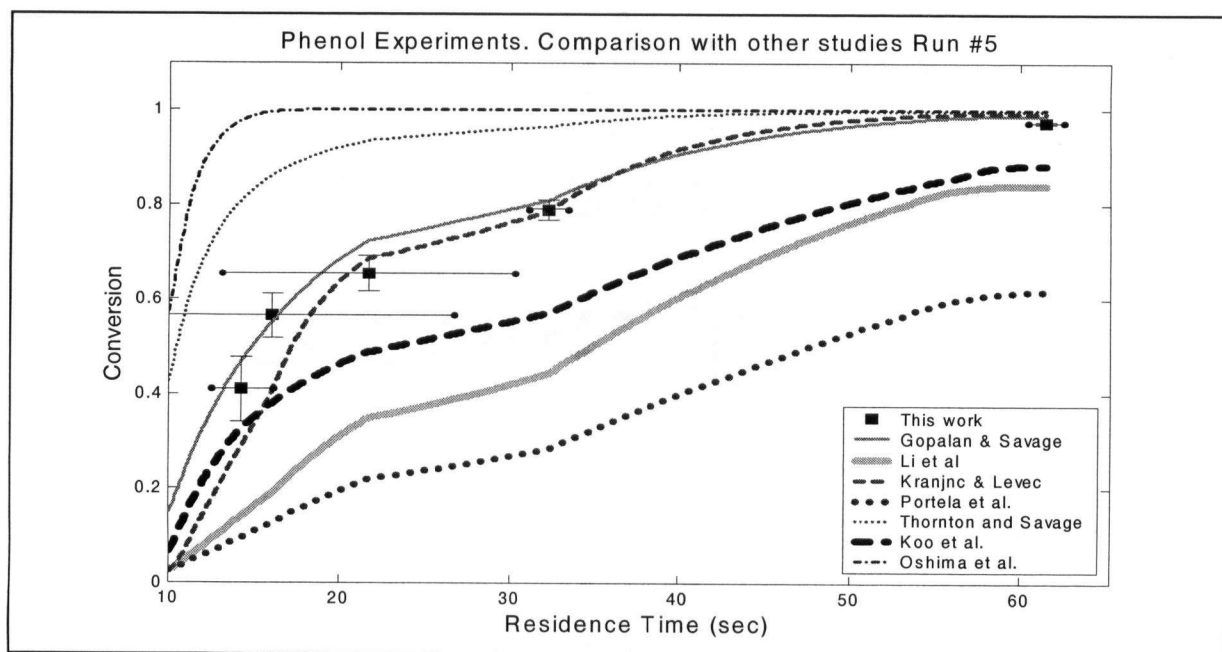


Figure 3.16 Phenol experiments. Agreement study. Run 5 (681 K, 34% O₂ excess)

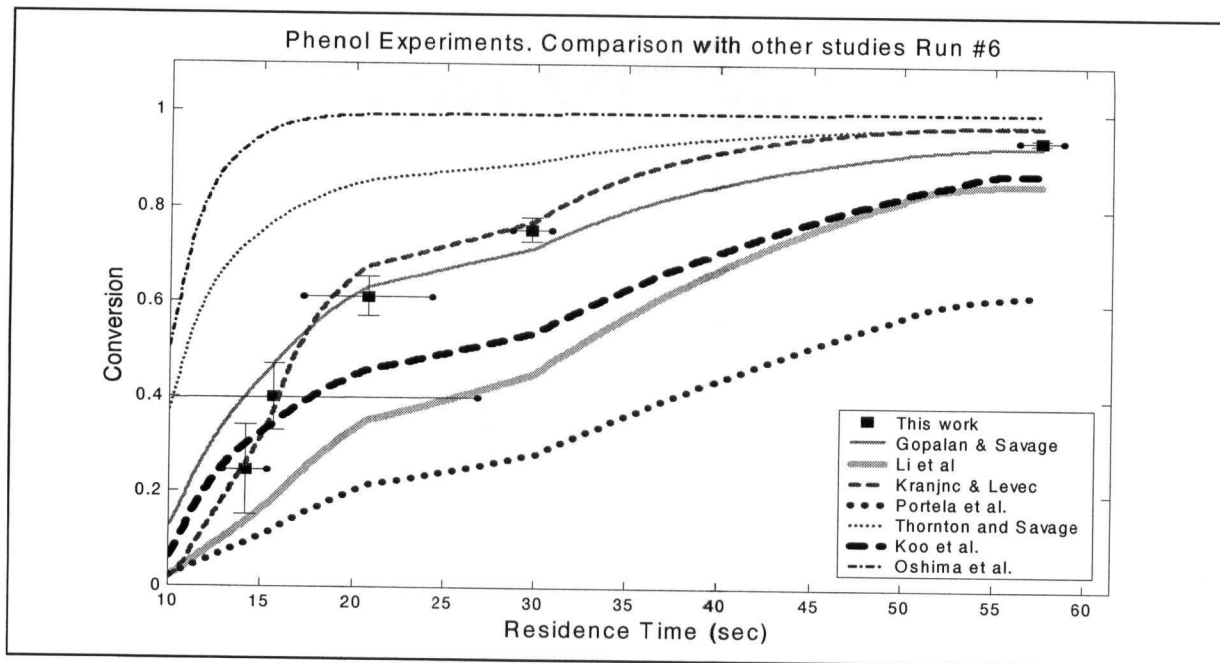


Figure 3.17 Phenol experiments. Agreement study. Run 6 (690 K, 0% O₂ excess)

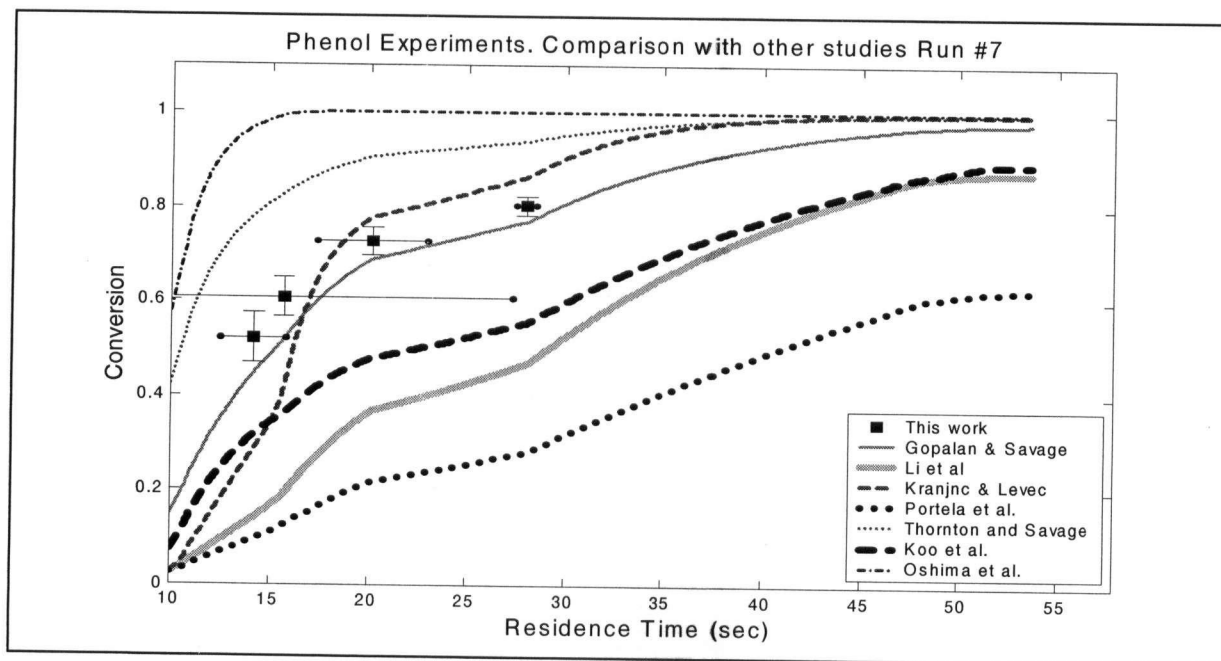


Figure 3.18 Phenol experiments. Agreement study. Run 7 (703 K, 21% O₂ excess)

3.5.2 *2,4 DNP based wastes*

3.5.2.1 Experimental conditions

Since 2,4 DNP has reduced solubility at ambient temperature compared to the elevated temperature at which real red water is produced and processed, the waste to be fed to the SCWO reactor was heated by using a steam coil (See Figure 3.2). During the heating process, steam at close to atmospheric pressure heated the insulated waste tank through a 3/8" stainless steel coil. A tap-water-driven aspirator pump then took it out of the system. This kept the steam circulating and provided temperatures up to 90°C in the waste tank. The stock preparation procedures and solubility conditions are discussed in Appendix E. The feed temperatures were set based on the criteria shown in Table E.1 of that appendix.

The compositions and conditions explored are shown in Table 3.6. A total of 13 experimental runs were carried out, with 5 different temperatures and several oxygen excesses in most of them. This allowed for the study of both the influence of temperature and oxidant excess in the destruction of the waste.

Uncertainties in the oxygen excess for runs 0, 1, 3 and 5 (in which intermediate samples were taken) were obtained from the uncertainties in the voltages recorded by the data acquisition system. For the other runs, in which pressures and voltages were considered to be more stable, oxygen excess uncertainties were taken from the uncertainties in the oxygen flow calibration equation (see Appendix A for the oxygen flow meter calibration, and Appendixes G and H for oxygen excess uncertainties in each run).

Table 3.6 2,4 DNP experimental conditions.

Feed Composition [% wt]	# of Runs	Run #	Feed Flow Rate [L/min]	Temp. in reactor [K]	Feed Temp. [K]	Absolute Pressure [MPa]	Oxygen excess [%]
2.4% wt. as 2,4 DNP 2.1% wt. as (NH ₄) ₂ SO ₄ 6.67 % wt. as NH ₃	1	0	0.78± 0.005	780	358	24.9 ^{+ 0.26} - 1.22	198.9 ^{+ 21.65} - 17.9
2.26 % wt. as 2,4 DNP 0.23 % wt as NH ₃	12	1	0.78± 0.005	813	330	24.4 ^{+ 0.2} - 0.5	74.73 ^{+ 21.2} - 9.5
		2			330.6	24.48± 0.01	22.44± 1.62
		2b			331	24.48± 0.01	0.36± 1.57
		2c			331.7	24.54± 0.05	-28.93± 1.76
		3		791	335.3	24.4 ^{+ 0.2} - 0.41	73.27 ^{+ 14} - 8.53
		4			336.8	24.39± 0.02	21.05± 1.61
		4b			338	24.47± 0.02	-1.9± 1.57
		5		769	335.5	24.3 ^{+ 0.25} - 0.99	78.62 ^{+ 29.6} - 8.9
		6			332.1	24.36± 0.01	16.08± 1.59
		6b			330.7	24.36± 0.01	-3.43± 1.57
		6c			327.8	24.32± 0.03	-18.4± 1.64
		7		742	327.8	24.33± 0.03	73.15± 1.98

3.5.2.2 2,4 Dinitrophenol, ammonium sulphate and excess ammonia

3.5.2.2.1 Observations

Table 3.7 shows the conversions of 2,4 DNP, ammonia and TOC conversions, gas yields, and carbonates, nitrates and sulphates obtained during the experiment (see Appendix G for mass balances).

The mass balances for the different species were not completely closed, although in the case of carbon, the balance was much better than for nitrogen and sulphur. Destruction efficiencies, along with gas yields are shown in Figure 3.19 and conversion profiles and intermediate species formation are shown in Figure 3.20. The intermediate species observed were 2-nitrophenol and 4-nitrophenol, which were not detected in the final effluent, and neither was 2,4 DNP. Ammonia was found in the effluent, in the form of ammonium sulphate, ammonium carbonate and ammonium bicarbonate.

No phenol was obtained at any stage as an intermediate. From both figures it can be observed that most of the 2,4 DNP breaks into mono-nitrophenols during the first 18 seconds. Then, the process continues mostly as the oxidation of 2- and 4-nitrophenol.

In an attempt of a second, higher temperature run, the system became unstable. Pressure and oxygen flows fluctuated, making it impossible to reach steady state; consequently no samples could be taken. A large amount of char deposited in the preheaters, throughout the system and in the backpressure regulator. The char accumulated in the system was observed once it was opened for repair and inspection of damages caused by corrosion. This waste resulted in a highly corrosive environment for the system, provoking the later failure of the regenerative heat exchanger (RHX) and the first preheater (PH 1). High levels of metals-

mostly nickel, chromium and cobalt- were found in the aqueous effluent (see Appendix H and I). This topic is more thoroughly addressed in Chapter 4.

Since only one experiment was conducted with 2,4 DNP and ammonium sulphate, the effect of temperature was not studied. The system was operated at high temperatures, with an average of 780 K in the reactor. These temperatures proved to be enough to destroy the organic feed and achieve high TOC and ammonia conversions. Even though the 2,4 DNP concentration in the feed was expected to be 4%wt. (see Appendix E), only 2,4 %wt. was obtained. This suggested that 2,4 DNP in the feed tank did not reach the necessary temperature to completely dissolve in water (in which case the solubility data from Table E.1 should be revised), and/or that the mixing was poor.

Despite the observed instabilities, the feasibility of destroying the organic component of the waste was proven. The experiments provided useful insights in how to perform the subsequent experiments. Figure 3.21 shows a picture of the samples taken at different points in the system. From the change in colour the progress of the destruction of the feed can be observed. Slightly red in the beginning, the feed turns green-brown in the intermediate stages, and completely clear in the effluent stream.

Table 3.7 2,4 DNP and ammonium sulphate experiments. Conversions and yields

	PH2 in	PH2 out	RL-2	RL-6	Effluent
Distance from the feed [m]	11.8	16.07	34.18	61.91	150.14
$X_{2,4 \text{ DNP}}$	0.997	0.993	0.9999	0.99996	0.99996
X_{TOC}	0.85	0.93	0.977	0.992	0.9992
X_{NH_3}	-	-	-	-	0.9855
CO yield	-	0.06	-	-	< 0.017
CO ₂ yield	-	0.322	-	-	0.54
N ₂ O yield	-	0.002	-	-	< 0.0016
N ₂ yield	-	0.106	-	-	0.21
Carbon mass balance [%]	-	-	-	-	86.59
Nitrogen mass balance [%]	-	-	-	-	41.26
Oxygen mass balance [%]	-	-	-	-	40.01
Sulphur mass balance [%]	-	-	-	-	25.52

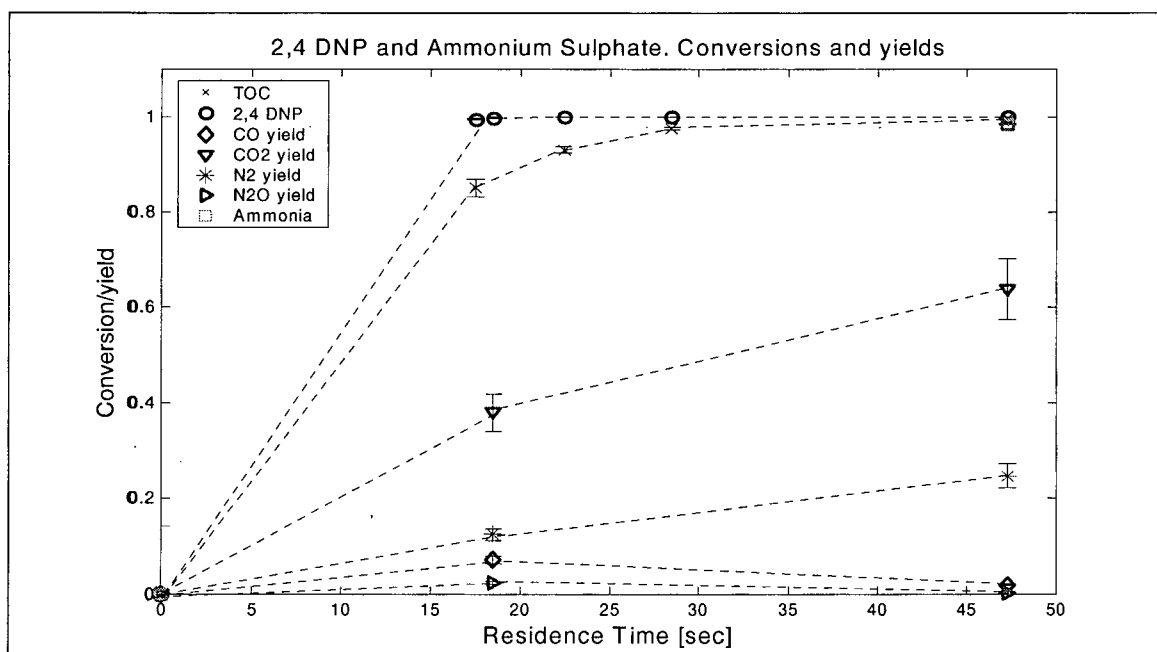


Figure 3.19 2,4 DNP and ammonium sulphate. Conversions and yields (780 K, 199% O₂ excess)

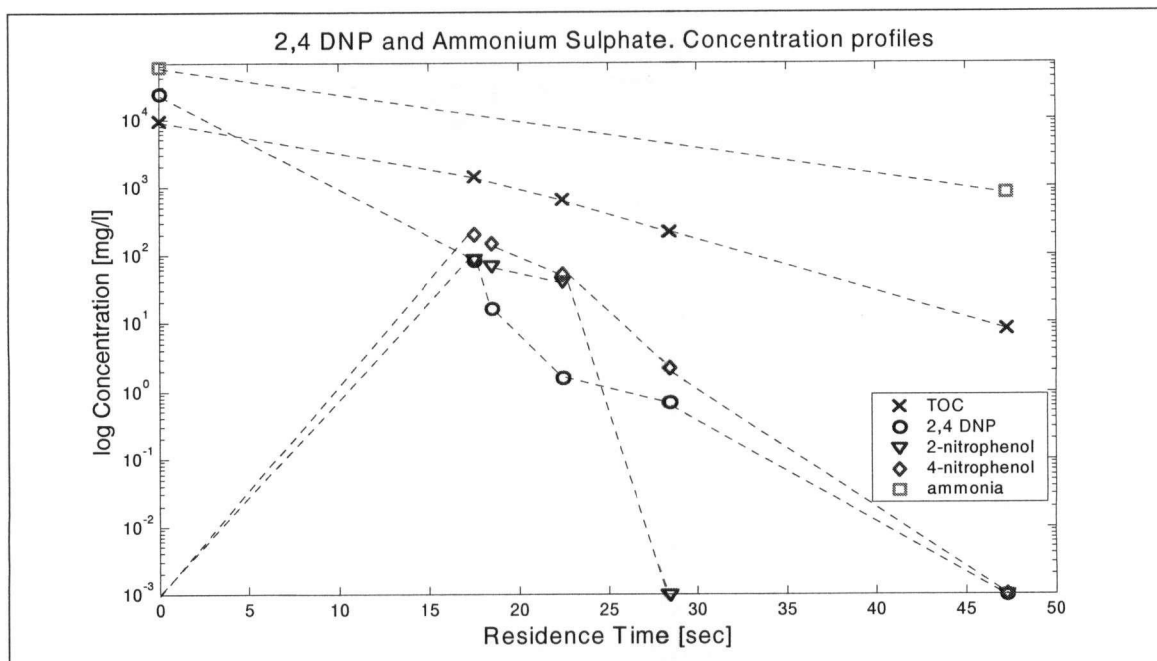


Figure 3.20 2,4 DNP and ammonium sulphate. Intermediates formation

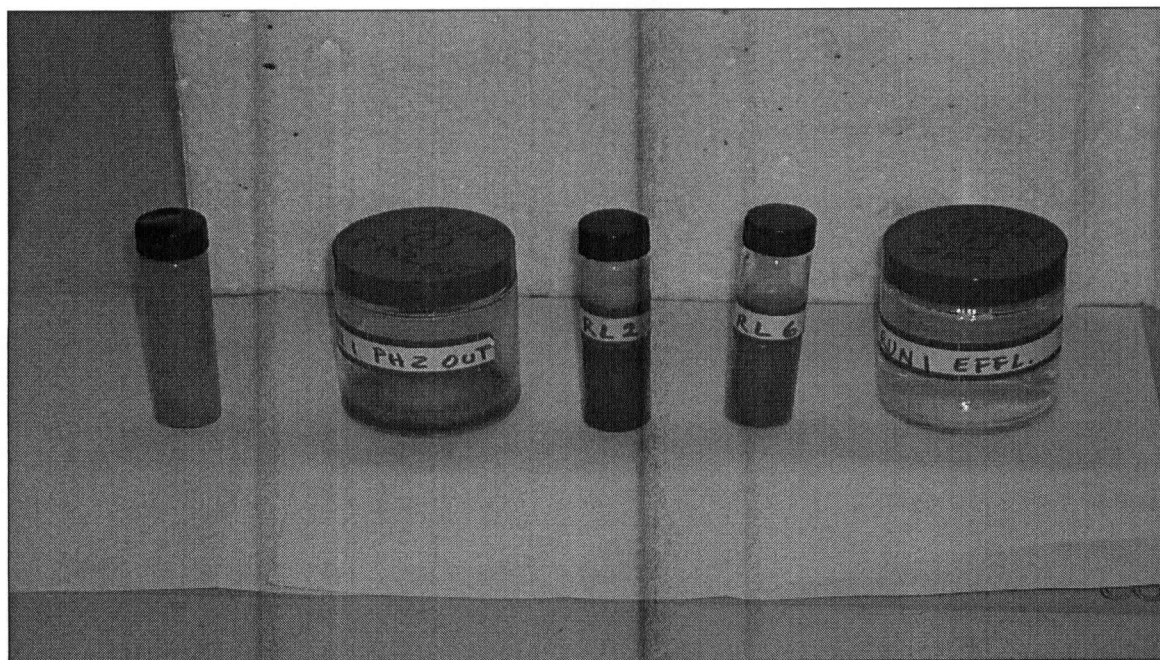


Figure 3.21 Appearance change. (From left to right: Feed, PH2 out, RL-2, RL-6, effluent)

3.5.2.3 2,4 DNP and Ammonia

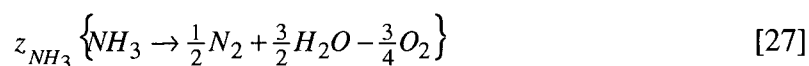
3.5.2.3.1 *Observations*

The temperature rise observed when the waste fed into the system began to release heat from combustion, was not very high, from 10 to 15 °C (see Electronic Files, “red water no sulphate.xls”). The possibility of treating higher concentration wastes could still be explored.

During the experiments, the gas samples became contaminated with atmospheric air that had remained in the gas liquid separators of the sampling ports. Nitrogen, oxygen and carbon balances were made to try to estimate the effects of this contamination and to calculate the amount of atmospheric nitrogen and oxygen contained in the sample bags. The procedure used is explained next (see Appendix H for more details and a sample calculation for one of the experimental runs).

After finishing the experiments, the effluent rinsing water was collected in a separate container, followed by an analysis of its TOC and ammonia contents. Given the results that TOC was < 20 mg/L and $\text{NH}_3 = 12 \text{ mg/L}$, we assumed that we could account for all of the carbon and nitrogen by material balances. Based on this assumption, the oxygen and nitrogen contents in the gas effluent could be calculated and any additional volumes from the contaminating air could be determined. The volumetric composition of air was assumed to be 79% nitrogen and 21% oxygen.

As mentioned before, the feed contained both 2,4 DNP and ammonia. The total feed destruction equation included the oxidation of 2,4 DNP, (see Equation [5]) and the destruction of ammonia:



Where z_{NH_3} is the ratio of ammonia and 2,4 DNP molar flows.

Equation [28] was used to obtain a stoichiometric table (Table 3.8) that was used to obtain a mole balance that considered the conversions of both 2,4 DNP and ammonia, with n_{ex} as the excess of oxygen moles fed into the system, and is X_{NH_3} the ammonia conversion:

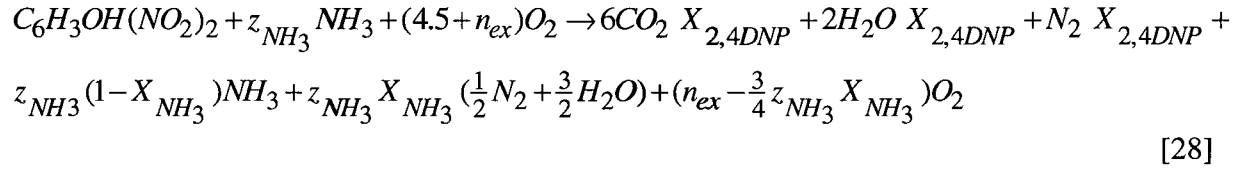


Table 3.8 Stoichiometric table for Equation [28]

Specie	In [mol]	Change [mol]	Out [mol]
$C_6H_3OH(NO_2)_2$	1	$-X_{2,4DNP}$	$1 - X_{2,4DNP}$
O_2	$4.5 + n_{ex}$	$-4.5 X_{2,4DNP} - \frac{3}{4} z_{NH_3} X_{NH_3}$	$4.5 + n_{ex} - 4.5 X_{2,4DNP} - \frac{3}{4} z_{NH_3} X_{NH_3}$
CO_2	0	$+6 X_{2,4DNP}$	$6 X_{2,4DNP}$
H_2O	0	$+2 X_{2,4DNP} + \frac{3}{2} z_{NH_3} X_{NH_3}$	$2 X_{2,4DNP} + \frac{3}{2} z_{NH_3} X_{NH_3}$
N_2	0	$+X_{2,4DNP} + \frac{1}{2} z_{NH_3} X_{NH_3}$	$X_{2,4DNP} + \frac{1}{2} z_{NH_3} X_{NH_3}$
NH_3	z_{NH_3}	$-z_{NH_3} X_{NH_3}$	$z_{NH_3} (1 - X_{NH_3})$

Equations [29]-[33], obtained from the stoichiometric table, were used to predict the molar flows in the effluent and intermediate streams:

$$\dot{n}_{CO_2 out} = 6 \dot{n}_{2,4DNP, in} X_{2,4DNP} \quad [29]$$

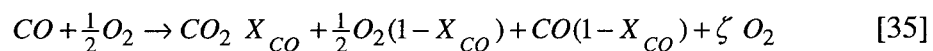
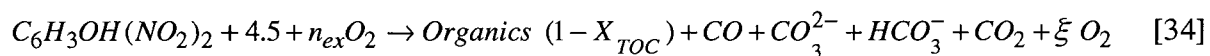
$$\dot{n}_{N_2 out} = \dot{n}_{2,4DNP in} X_{2,4DNP} + \frac{1}{2} \dot{n}_{NH_3 in} X_{NH_3} \quad [30]$$

$$\dot{n}_{H_2O out} = 2 \dot{n}_{2,4DNP in} X_{2,4DNP} + \frac{3}{2} \dot{n}_{NH_3 in} X_{NH_3} \quad [31]$$

$$\dot{n}_{NH_3 out} = \dot{n}_{NH_3 in} (1 - X_{NH_3}) \quad [32]$$

$$\dot{n}_{O_2 out} = \dot{n}_{2,4DNP in} (4.5 + n_{ex} - 4.5X_{2,4DNP}) - \frac{3}{4} \dot{n}_{NH_3 in} (1 - X_{NH_3}) \quad [33]$$

The formation of CO₂ and N₂, however, depended on the conversion of other intermediate carbonic and nitrogenous compounds to CO₂ and N₂, respectively. The main carbon containing by-products found were organics (e.g. 2-nitrophenol, 4-nitrophenol and picric acid), CO, carbonates and bicarbonates. None of the previously mentioned organics were observed in the aqueous effluent in any of the experiments. Nitrogenous compounds were mostly nitrates, nitrites, ammonia and N₂O. Attempts to write equations for the formation of some such compounds are shown in Equations [34]-[37], where ξ and ζ would represent arithmetic values to balance the oxygen moles in the equations. A detailed study of the formation of all intermediate species was beyond the scope of this thesis.



The ratios of CO/CO₂ and N₂O/CO₂ (referred to as CO/CO₂ (BCRI) and N₂O/ CO₂ (BCRI) respectively) in the contaminated samples were used to account for CO and N₂O. It was assumed that the values of their relative ratios did not change after accounting for the contaminating air. Equations [29] and [30] were respectively transformed into equations [38] and [41]; CO and N₂O flows were obtained according to Equations [39] and [40]:

$$\dot{n}_{CO_2 out} = \frac{6 \dot{n}_{2,4DNP, in} X_{2,4DNP} - \dot{n}_{CO_3} - \dot{n}_{TOC} (1 - X_{TOC})}{1 + \frac{CO}{CO_2 (BCRI)}} \quad [38]$$

$$\dot{n}_{CO_{out}} = \dot{n}_{CO_{2out}} \frac{CO}{CO_2 (BCRI)} \quad [39]$$

$$\dot{n}_{N_2O_{out}} = \dot{n}_{CO_{2out}} \frac{N_2O}{CO_2 (BCRI)} \quad [40]$$

$$\dot{n}_{N_2_{out}} = \dot{n}_{2,4DNP_{in}} X_{2,4DNP} + \frac{1}{2} \dot{n}_{NH_3_{in}} X_{NH_3} - \dot{n}_{NO_3} - \dot{n}_{NO_2} - \dot{n}_{N_2O} \quad [41]$$

The pressure vapour at the ambient temperature during the experiments (26 °C) was used to find the percentage of water vapour in the gas samples:

$$H_2O_{vapor} = \frac{P_{sat, 26^\circ C}}{P_{atm}} 100 = 3.32\% \quad [42]$$

Finally, the total molar gas flows were obtained as the sum of all gaseous components and water vapour (Equation [43]). Molar rates for all runs are shown in Table 3.9.

$$\dot{n}_{gas\ total} = \sum \dot{n}_i \quad [43]$$

During the experiments, gas flow rates were measured with a volume gas flow meter model Equimeter RC-M-415. Measurement of pure oxygen flows showed that the gas flow meter was reading values much lower than those that were being fed into the system. For example, according to the voltage reading and Equation [A.6] of Appendix A, the flow fed into the system was of $\dot{n}_{O_2} = 0.758$ mol/min. However, according to the reading from the vent gas flow meter, the flow rate was $= 0.554$ mol/min, 73 % of the measured feed O_2 . For this reason, the predicted total molar flow rates from Table 3.9 were considered to be more reliable and were used in subsequent calculations.

The fractions of air contamination in the samples (x_a) were obtained as the best fit with the fractions of the O_2 , N_2 and CO_2 obtained in the contaminated analyses, as shown in Equations [44] to [46]:

$$x_{O_2 \text{ BCRI}} = 0.21x_a + (1 - x_a) \frac{\dot{n}_{O_2 \text{out}}}{\sum \dot{n}_i} \quad [44]$$

$$x_{N_2 \text{ BCRI}} = 0.79x_a + (1 - x_a) \frac{\dot{n}_{N_2 \text{out}}}{\sum \dot{n}_i} \quad [45]$$

$$x_{CO_2 \text{ BCRI}} = (1 - x_a) \frac{\dot{n}_{CO_2 \text{out}}}{\sum \dot{n}_i} \quad [46]$$

The percentages of gaseous components, after accounting for air contamination were calculated as:

$$\%_{N_2} = \left(\frac{\dot{n}_{N_2 \text{out}}}{\sum \dot{n}_i} + 0.79 x_a \right) 100 \quad [47]$$

$$\%_{O_2} = \left(\frac{\dot{n}_{O_2 \text{out}}}{\sum \dot{n}_i} + 0.21 x_a \right) 100 \quad [48]$$

$$\%_{CO_2} = \frac{(100 - \%_{N_2} - \%_{O_2} - \%_{H_2O \text{vapor}})}{1 + \frac{\dot{n}_{CO_2 \text{out}}}{\dot{n}_{CO_2 \text{out}}} + \frac{\dot{n}_{N_2O \text{out}}}{\dot{n}_{CO_2 \text{out}}}} \quad [49]$$

$$\%_{CO} = \%_{CO_2} \frac{\dot{n}_{CO \text{out}}}{\dot{n}_{CO_2 \text{out}}} \quad [50]$$

$$\%_{N_2O} = \%_{CO_2} \frac{\dot{n}_{N_2O}}{\dot{n}_{CO_2}} \quad [51]$$

Table 3.10 shows the percentage of air contamination in the samples, the predicted composition after accounting for the air contamination, and the results of the gas analyses given by BCRI. The errors in the percentage of air contamination were obtained from the average deviation of the individual errors from O₂, N₂ and CO₂ (see Appendix H).

As a general trend, the percentage of air increased from intermediates to effluent and from higher to lower oxygen excesses. A considerable portion of air from the gas-liquid separators was evacuated when taking intermediate samples, but not when sampling from the effluent. Furthermore, samples were commonly taken during a fixed period of time. Thus with low oxygen excess levels, or sub stoichiometric runs, there was less total gas flow from the system and so air contamination was higher.

Table 3.9 Predicted gaseous molar flows

Run	Location	CO ₂ [mol/min]	CO [mol/min]	N ₂ [mol/min]	N ₂ O [mol/min]	O ₂ [mol/min]	$\sum \dot{n}_i$ (With water vapour) [mol/min]
1	PH1	0.419	0.012	0.123	0.000	0.304	0.886
	PH2	0.477	0.013	0.096	0.023	0.279	0.917
	Effluent	0.530	0.000	0.087	0.036	0.281	0.966
2	Effluent	0.525	0.000	0.077	0.044	0.052	0.721
2b	Effluent	0.519	0.000	0.081	0.035	0.000	0.656
2c	Effluent	0.325	0.017	0.091	0.013	0.000	0.461
3	PH1	0.309	0.020	0.110	0.000	0.296	0.761
	PH2	0.462	0.017	0.123	0.014	0.299	0.945
	Effluent	0.532	0.000	0.075	0.048	0.275	0.961
4	Effluent	0.525	0.000	0.080	0.040	0.042	0.709
4b	Effluent	0.517	0.000	0.081	0.033	0.000	0.653
5	PH1	0.318	0.026	0.109	0.000	0.317	0.795
	PH2	0.369	0.063	0.108	0.009	0.303	0.880
	Effluent	0.526	0.000	0.068	0.051	0.292	0.968
6	Effluent	0.524	0.000	0.076	0.041	0.017	0.680
6b	Effluent	0.515	0.000	0.074	0.041	0.000	0.652
6c	Effluent	0.499	0.008	0.080	0.030	0.000	0.638
7	Effluent	0.523	0.000	0.079	0.041	0.269	0.942

Aqueous feed analyses showed the presence of high amounts of carbonates/bicarbonates, which, according to our knowledge, should have not been part of the feed (see Appendix E, stock preparation). These levels of carbonates in the feed were suspected to be erroneous and were not included in the above balances (see Appendix H).

In general, TOC, CO and N₂O yields in the effluent remained very low, whereas ammonia conversions were found to be very poor. Table 3.11 shows a summary of conversions and yields for every sampling location at each experimental run. Metals concentrations in all aqueous samples were very low (Appendix H), indicating that no corrosion occurred during the experiments.

Table 3.10 Air contamination. BCRI results and balance predictions

Run	Location	Air [%]	Location	CO ₂ [%]		CO [%]		N ₂ [%]		N ₂ O [%]		O ₂ [%]		H ₂ O vapour [%]	Error _a [%]
				Predicted	BCRI	Predicted	BCRI	Predicted	BCRI	Predicted	BCRI	Predicted	BCRI		
	PH 1	28	PH 1	19.92	14.32	0.57	0.41	36.00	30.21	0.00	<0.5	40.19	52.58	3.32	14.53
	PH 2	10	PH 2	42.60	43.64	1.18	1.21	18.32	11.24	2.02	2.07	32.56	38.60	3.32	6.10
	Effluent	36	Effluent	21.12	32.10	0.00	0.00	37.43	33.34	1.45	2.20	36.68	29.23	3.32	2.30
2	Effluent	42	Effluent	33.98	40.13	0.00	0.00	43.81	29.86	2.86	3.38	16.03	23.50	3.32	7.37
2b	Effluent	54	Effluent	28.38	31.32	0.00	0.00	55.05	47.09	1.90	2.10	11.34	16.30	3.32	3.80
2c	Effluent	66	Effluent	10.03	22.67	0.51	1.15	71.87	58.09	0.42	0.94	13.86	14.00	3.32	0.73
	PH 1	12	PH 1	29.30	19.96	1.94	1.32	23.99	18.57	0.00	<0.5	41.46	57.07	3.32	13.27
	PH 2	10	PH 2	39.41	40.20	1.47	1.50	20.89	17.44	1.20	1.22	33.72	36.50	3.32	3.93
	Effluent	44	Effluent	14.88	26.36	0.00	0.00	42.59	38.87	1.34	2.38	37.87	29.33	3.32	3.00
3	Effluent	60	Effluent	18.11	23.14	0.00	0.00	58.68	50.68	1.38	1.76	18.51	21.32	3.32	4.67
4	Effluent	76	Effluent	7.70	15.42	0.00	0.00	72.53	62.34	0.49	0.99	15.96	18.09	3.32	2.13
4b	PH 1	10	PH 1	30.59	20.39	2.49	1.66	21.63	19.38	0.00	<0.5	41.97	55.48	3.32	11.33
	PH 2	12	PH 2	31.79	18.38	5.40	3.12	21.74	19.52	0.74	0.43	37.01	55.52	3.32	13.93
	Effluent	24	Effluent	32.34	32.18	0.00	0.00	25.94	22.57	3.17	3.15	35.23	39.25	3.32	7.37
5	Effluent	44	Effluent	36.18	41.55	0.00	0.00	45.92	28.41	2.85	3.27	11.74	23.59	3.32	9.07
6	Effluent	30	Effluent	51.22	44.36	0.00	0.00	35.07	31.02	4.09	3.54	6.30	17.92	3.32	7.73
6b	Effluent	26	Effluent	53.97	56.43	0.89	0.90	33.07	29.51	3.29	3.44	5.46	6.46	3.32	0.90
6c	Effluent	16	Effluent	40.64	33.54	0.00	0.00	20.99	17.37	3.16	2.61	31.89	43.38	3.32	10.50
7	Effluent														

Notes: Predicted percentages from molar balances and assumed air contamination on the third column

$$Error_a = \frac{\sum(predicted - BCRI)}{3}$$

Table 3.11 2,4DNP and ammonia experiments. Conversions and yields

Run	Conditions T [K], Oxygen excess [%]	Sampling point	Distance from the feed [m]	X _{2,4DNP}	X _{TOC}	X _{NH3}	CO yield*	CO ₂ yield*	N ₂ O yield*	N ₂ yield*
1	813, 74.73	PH ₁ in	6.9	0.961	0.832	0.566	0.026	0.87	0	0.54
		PH ₂ in	11.80	0.978	0.891	0.638	-	-	-	-
		PH ₂ out	16.07	0.993	0.934	0.435	0.027	0.95	0.13	0.34
		RL-2	34.18	0.99996	-	0.5	-	-	-	-
		RL-6	61.91	0.99996	0.9997	0.49	-	-	-	-
		Effluent	150.14	0.99996	0.9998	0.495	0.002	1	0.11	0.45
2	813, 22.44	Effluent	150.14	0.99996	0.9998	0.455	0.002	1	0.14	0.41
2b	813, 0.36	Effluent	150.14	0.99996	0.9998	0.37	0.001	1	0.07	0.45
2c	813, -28.93	Effluent	150.14	0.99996	0.9898	0.155	0.03	0.84	0.03	0.44
3	791, 73.27	PH1	6.9	0.93	0.71	0.385	0.05	0.71	0	0.49
		PH ₂ in	11.80	0.981	0.875	0.36	-	-	-	-
		PH ₂ out	16.07	0.996	0.915	0.76	0.036	0.94	0.07	0.53
		RL-2	34.18	0.99996	0.9949	0.81	-	-	-	-
		RL-6	61.91	0.99996	0.9994	0.5	-	-	-	-
		Effluent	150.14	0.99996	0.9998	0.495	0.002	1	0.12	0.44
4	791, 21.05	Effluent	150.14	0.99996	0.9998	0.435	0.002	1	0.07	0.47
4b	791, -1.9	Effluent	150.14	0.99996	0.9994	0.34	0.001	1	0.03	0.48
5	769, 78.62	PH1	6.9	0.931	0.7414	0.36	0.062	0.69	0	0.48
		PH ₂ in	11.80	0.952	0.7888	0.43	-	-	-	-
		PH ₂ out	16.07	0.974	0.8532	0.42	0.155	0.76	0.03	0.47
		RL-2	34.18	0.9999	0.9853	0.594	-	-	-	-
		RL-6	61.91	0.99996	0.9976	0.48	-	-	-	-
		Effluent	150.14	0.99996	0.9997	0.42	0.002	1	0.16	0.38
6	769, 16.08	Effluent	150.14	0.99996	0.9989	0.385	0.001	0.958	0.12	0.40
6b	769, -3.43	Effluent	150.14	0.99996	0.9994	0.35	0.001	0.959	0.12	0.39
6c	769, -18.4	Effluent	150.14	0.99996	0.9965	0.26	0.013	0.939	0.106	0.39
7	742, 73.15	Effluent	150.14	0.99996	0.9983	0.425	0.002	0.862	0.13	0.40

Note: All mass balances adjusted for accuracy

3.5.2.3.2 Effect of temperature

Figures 3.21, 3.22 and 3.23 show the change in temperatures with residence time for all the experimental runs. It can be observed that steady state conditions were achieved during the experiments that were run at the same temperatures, but with different oxidant excess. Conditions very close to isothermal were achieved throughout almost all the 120 meters of reactor, from RL-2 to RL-17B.

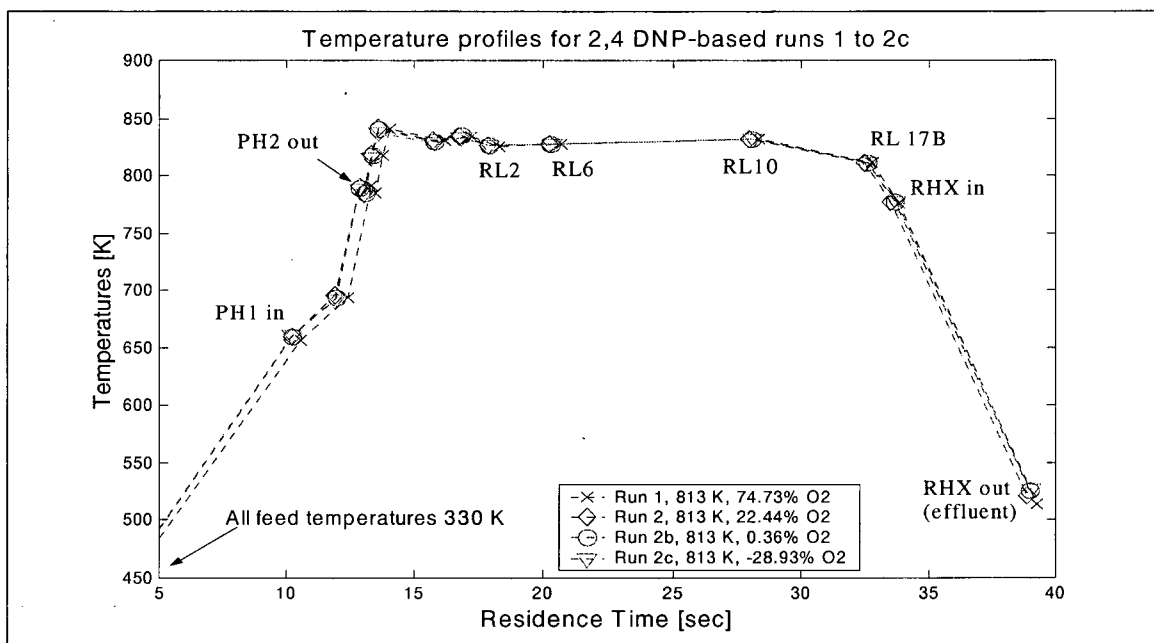


Figure 3.22 2,4 DNP and ammonia experiments. Temperature profiles runs 1-2c

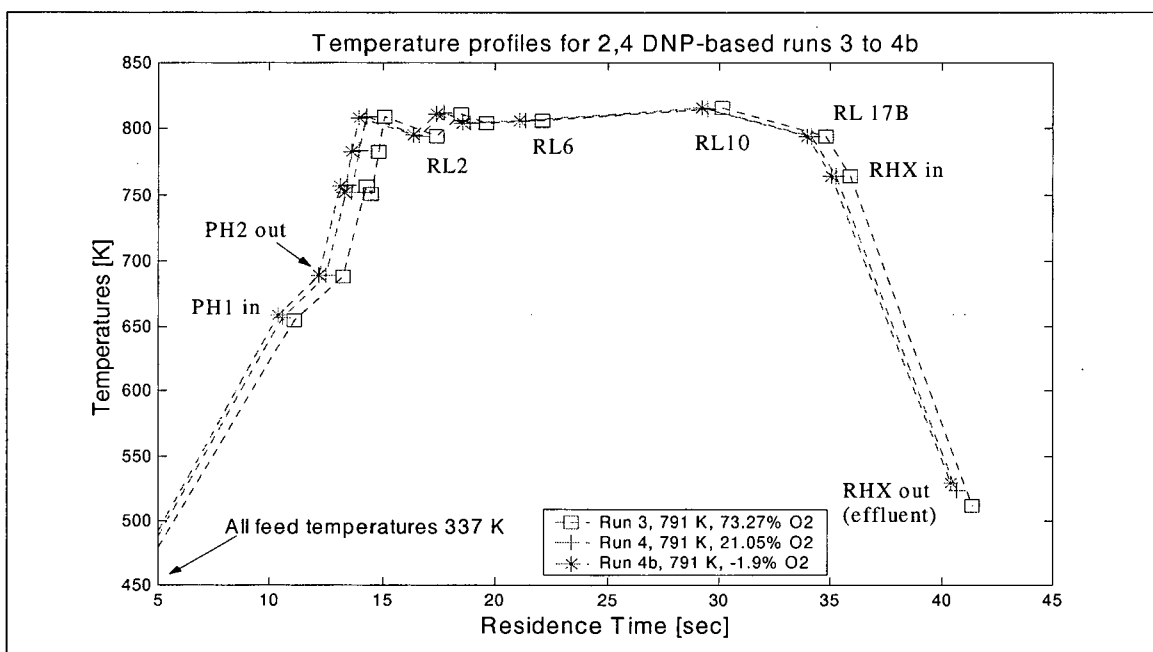


Figure 3.23 2,4 DNP and ammonia. temperature profiles runs 3-4b

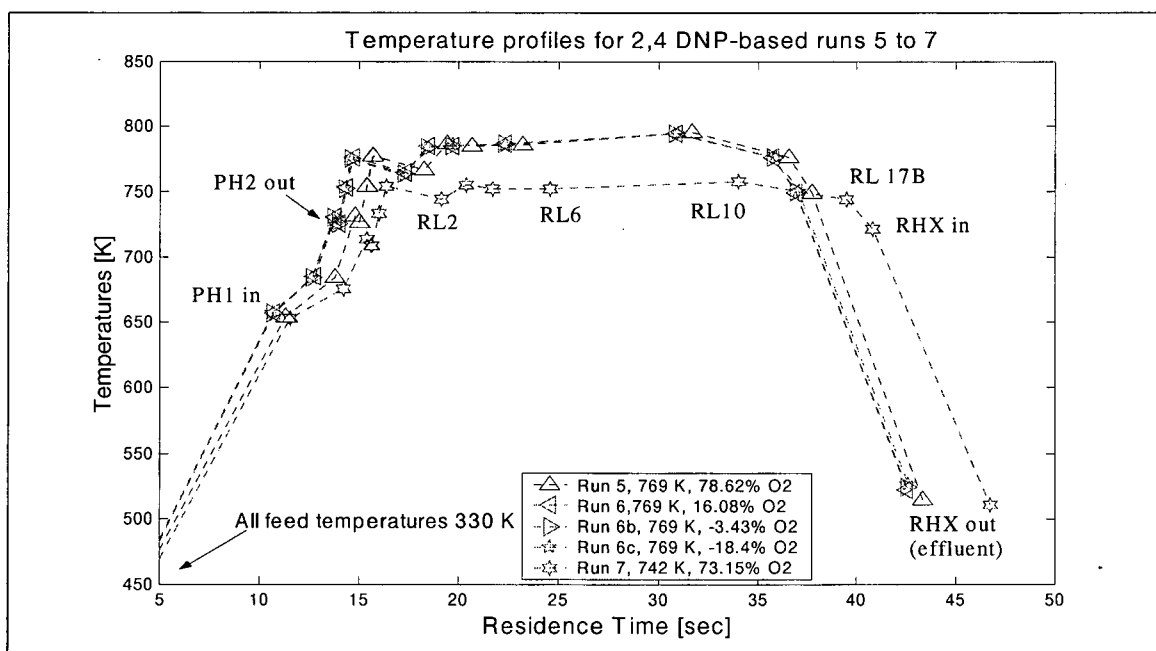


Figure 3.24 2,4 DNP and ammonia. Temperature profiles runs 5-7

Runs 1, 3, 5 and 7 represent experiments with high excess oxygen (approximately the same, between 73 and 78%) carried out at different temperatures (from 813 K to 742 K). The data in Table 3.11 show that the conversion of 2,4 DNP was not affected by lowering the temperature, always staying maximum. TOC conversions decreased slightly at the lower temperatures (769 K and 742 K), but always remained higher than 99%. This suggested that TOC destruction at temperatures lower than 742 K would have started to decrease. The ammonia destruction was always poor, but decreased slightly (within the error margins) at lower temperatures. The same was observed by Killilea et al.²⁹, who obtained very poor conversions using oxygen as the oxidizing agent, even at temperatures above 823 K. No CO was observed in any of these runs and the CO₂ yield slightly decreased at 742 K. N₂O yields tended to increase for lower temperatures, which was consistent with the findings of previous researchers.^{28, 29, 31} Runs 2, 4 and 6 were carried out at moderate oxygen excess (16 to 22%) and followed the same trend as the runs with high oxygen excess. No NO or NO₂ were observed in the gaseous effluent in any of the cases. This agreed with the results obtained in the experiments mentioned in section 3.2.2.1.1 at UBC.

Runs 2b and 6b corresponded to two different operation temperatures (813 K and 769 K respectively) at oxygen flows around the stoichiometric point. Similarly to the runs previously mentioned, 2,4 DNP destructions were maximum, and TOC conversion slightly decreased from 813 to 769 K. Ammonia conversions remained approximately constant (35 to 37%), but was lower than those of the previous runs. N₂O production increased at 769 K, and the CO₂ slightly decreased. No CO was detected at these conditions.

The influence of temperature at sub-stoichiometric levels was also investigated in runs 2c, 4b and 6c. Runs 2c and 6C were carried out at very sub-stoichiometric levels and 4b

slightly below the stoichiometric point. Even though 2,4 DNP was fully destroyed, TOC conversions decreased with decreasing the temperatures, but were always higher than 99%. N_2O production increased, and small amounts of CO were observed in the effluent gas from run 2c. In this run phenol was detected as part of the aqueous effluent stream. In general, temperatures did not have a strong effect in the effluent concentrations of nitrates or nitrites.

3.5.2.3.3 *Effect of residence time*

Figures 3.21 to 3.23, introduced in the previous section, (similar to the trends from Figures 3.8 and 3.9) show that the residence times for higher temperature runs were lower. Higher residence times were observed in sections of the system that were operated at lower temperatures, such as the preheaters and the regenerative heat exchanger.

The influence of residence time in the destruction of this waste was studied at different temperatures in runs in which intermediate samples were taken (1, 3, 5). Figures 3.24 to 3.29 present plots of change in the conversions and yields, and of the formation of intermediates with residence time for runs 1, 3, and 5.

In general, 2,4 DNP was completely destroyed early in the process (before the first sampling port in the reactor (RL-2)), while the highest TOC conversions were achieved by the end of the reactor. The organic intermediates detected were picric acid, 2-nitrophenol and 4-nitrophenol. Picric acid was found in runs 3 and 5, which were carried out at 791 and 769 K respectively, but it was not found in run 1, which was conducted at 813 K. Interestingly, runs 3 and 5 showed that 2-nitrophenol disappeared, but reappeared in small amounts, to be finally destroyed. Yet, more experiments and a detailed study of the intermediates would be

needed in order to reach conclusions on the sequence of formation and disappearance of these species. Ammonium carbamate (NH_2COO) and urea ($(\text{NH}_2)_2\text{CO}$) are some of the compounds that could have been formed during the oxidation process. However, no chemical analyses were performed in order to detect them. Phenol was not found as an intermediate at any stages, although it was part of the effluent stream of a very sub-stoichiometric run (run 2c, at -28.93% below the stoichiometric amount of oxygen). This was different from what has been observed by Martino and Savage^{36, 37} for the case of mono-nitrophenol oxidation in SCWO, where phenol was an important aqueous-phase product.

For the SCWO of m- and p- nitrophenols, Martino and Savage^{36, 37} observed two major parallel primary paths: one leading to phenol and the other one to ring-opening products and ultimately to CO and CO₂. In these experiments, it was observed that the decomposition of 2,4 DNP led to the formation of 2- and 4- nitrophenols, but the pathway leading to phenol formation was not observed, except in the case of run 2c, at 813 K and very sub-stoichiometric oxygen flows. There exists the possibility, however, that phenol had been a very reactive intermediate and that it was completely destroyed between sampling ports. In general, the intermediate products measured from the destruction of 2,4 DNP were 2-nitrophenol, 4-nitrophenol and picric acid. In all cases, these intermediates were completely destroyed.

Ammonia conversions were higher while there were large amounts of TOC in the system. The reduction in the TOC/NH₃ with the destruction of the organics clearly affected the ammonia destruction. Probably some carbonic inorganic salts were formed, which remained stable at the conditions explored. It could also be possible that large amounts of CO had been competing with the ammonia for the oxygen.

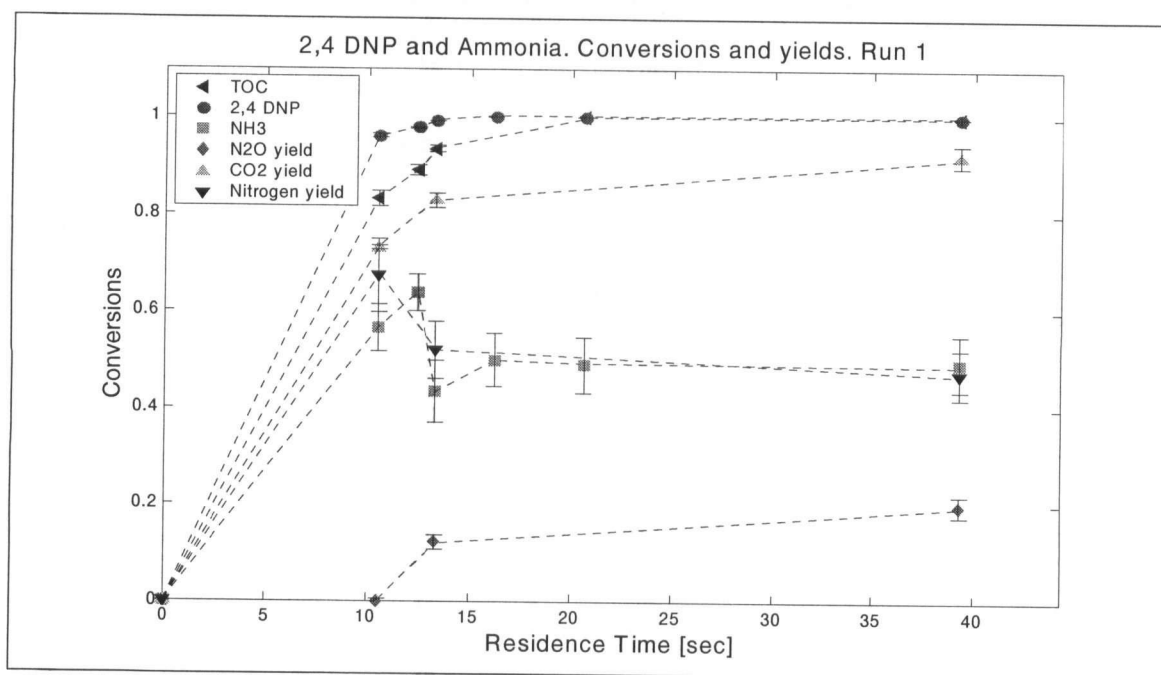


Figure 3.25 2,4 DNP and ammonia. Conversions and yields for Run1 (813 K, 74.7% O₂ excess)

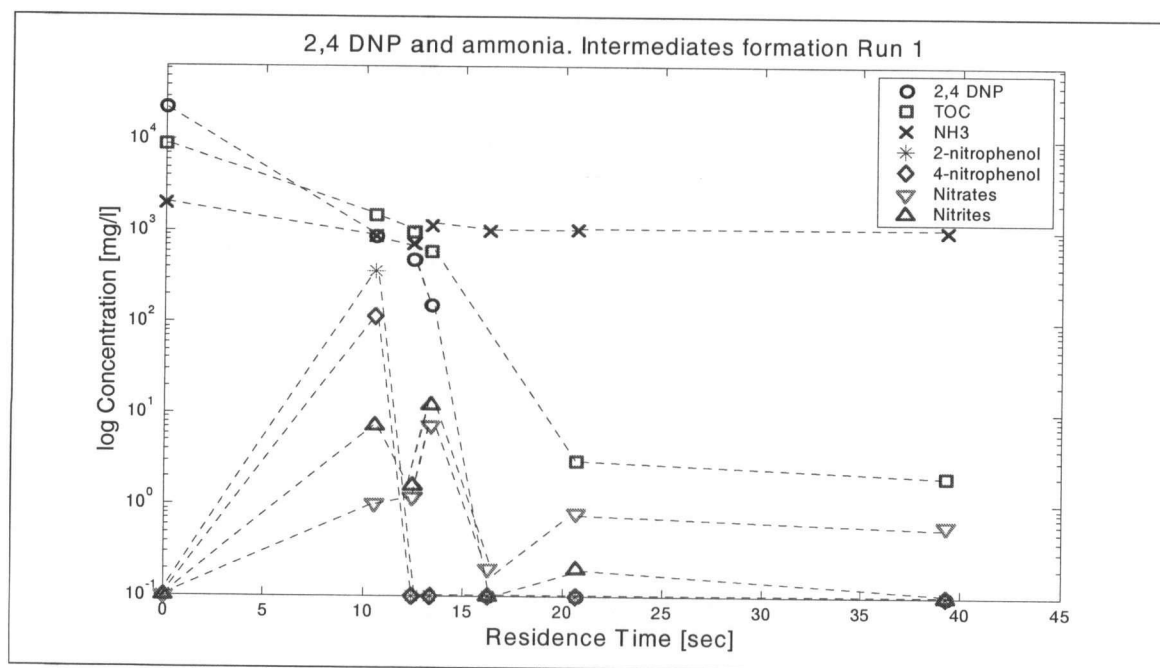


Figure 3.26 2,4 DNP and ammonia. Intermediates, TOC and ammonia destruction, Run 1

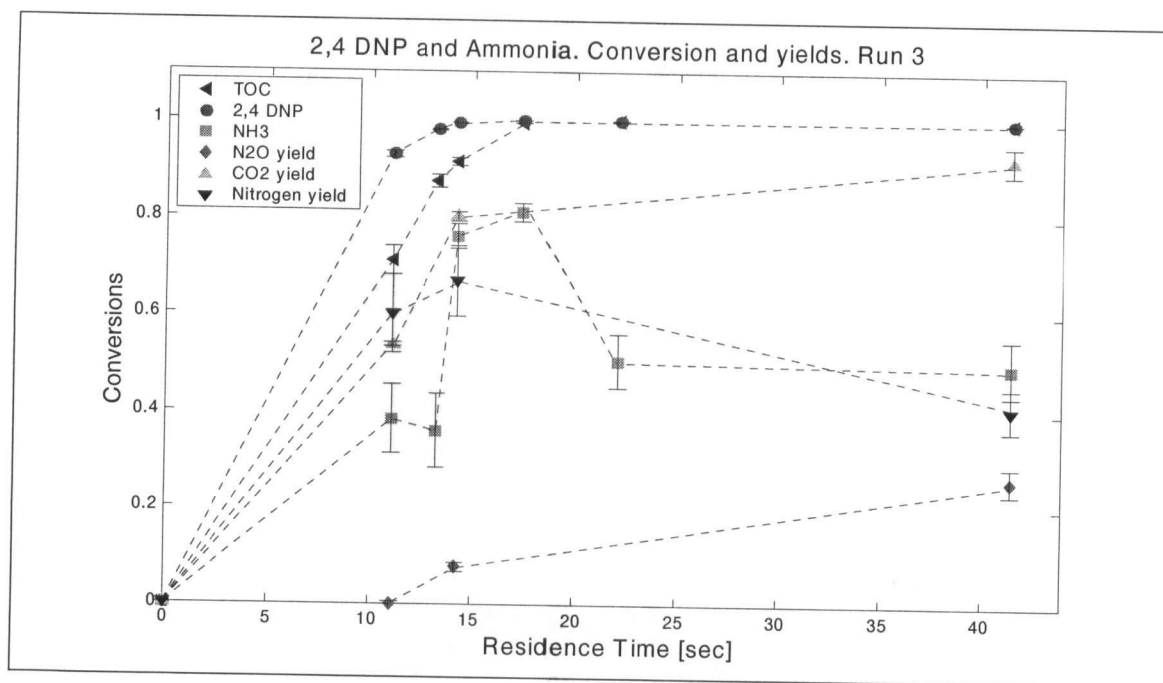


Figure 3.27 2,4 DNP and ammonia. Conversions and yields for Run 3 (791 K, 73.3% O₂ excess)

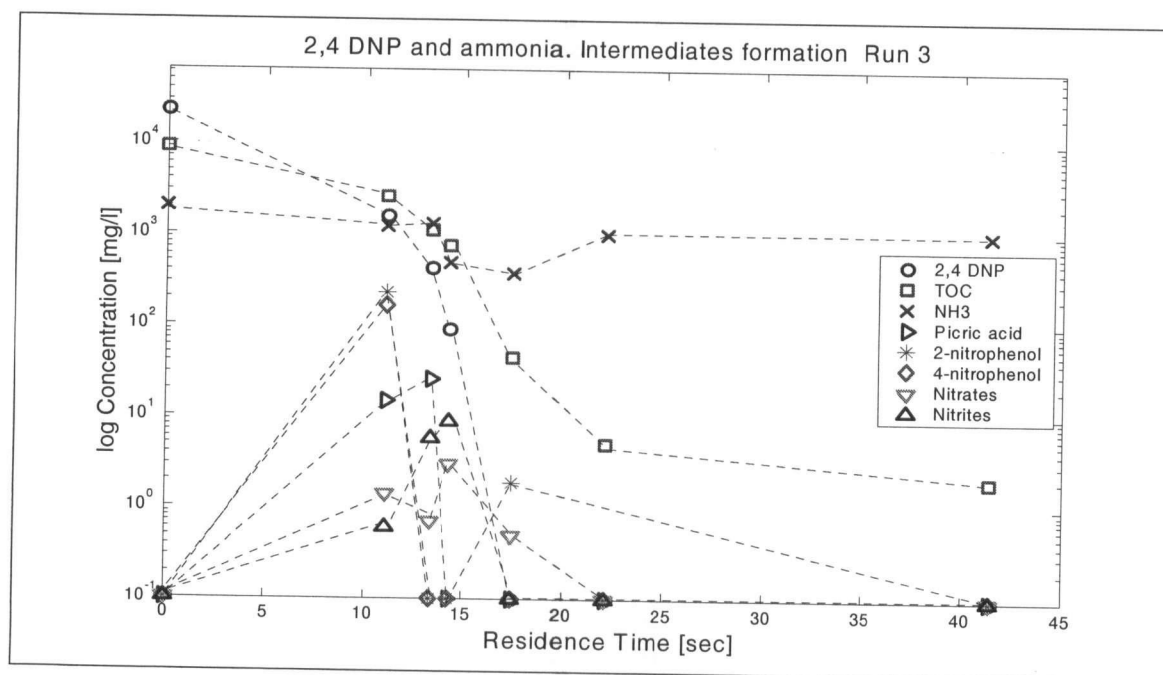


Figure 3.28 2,4 DNP and ammonia. Intermediates, TOC and ammonia destruction, Run 3

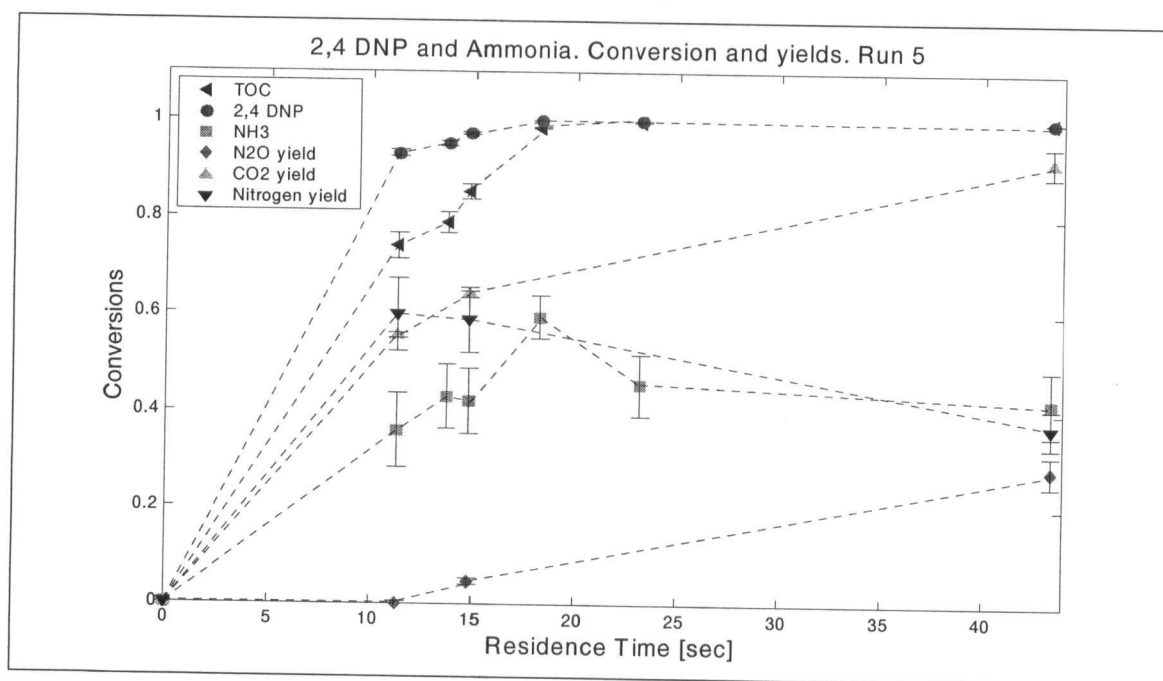


Figure 3.29 2,4 DNP and ammonia. Conversions and yields for Run 5 (769 K, 78.6% O₂ excess)

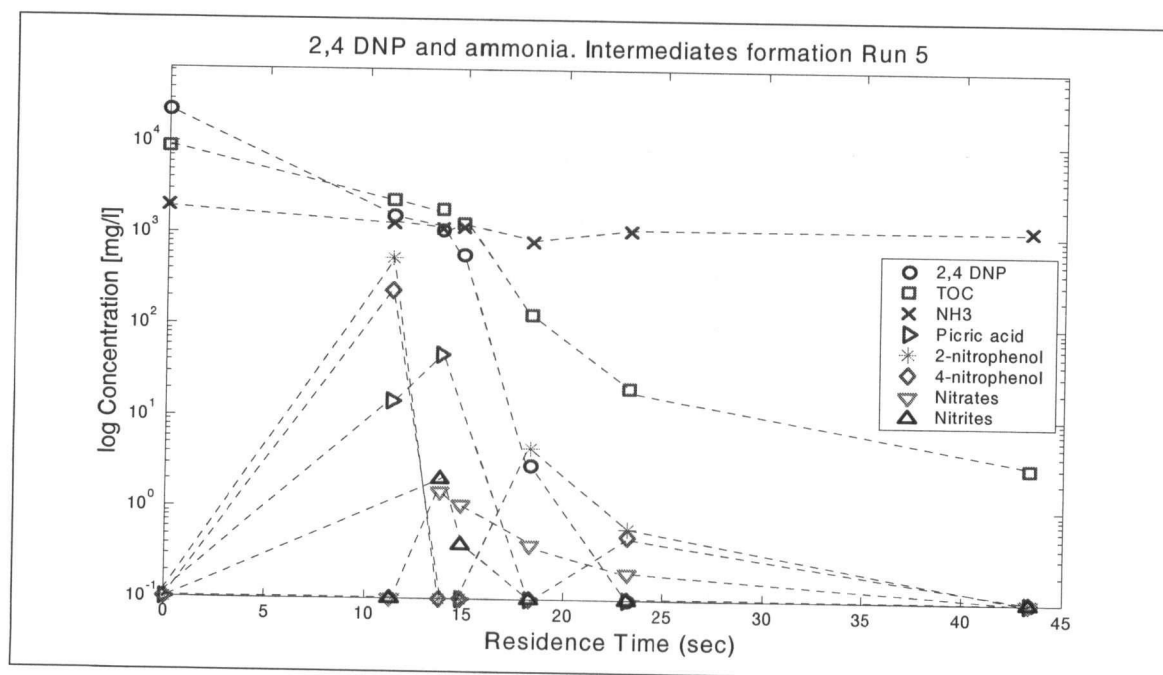


Figure 3.30 2,4 DNP and ammonia. Intermediates, TOC and ammonia destruction, Run 5

3.5.2.3.4 *Effect of oxidant excess*

The effect of changing the oxygen excess was explored at 813 K (runs 1, 2, 2b, and 2c), 791 K (runs 3, 4, 4b) and 769 K (runs 5, 6, 6b, 6c) and is shown in Figures 3.30 to 3.32. Generally the excess of oxygen did not have an effect on TOC and 2,4 DNP destruction, except when below stoichiometric, where TOC conversions and CO₂ yields decreased.

Higher oxygen excesses yielded better ammonia conversions, although destruction efficiencies never exceeded 50%, which suggested that indiscriminately increasing the oxygen excess would not be a suitable way to improve ammonia destruction. This agrees with Dell'Orco et al.²⁷, who found that in oxygen deficient environments, nitrates and nitrites were converted to ammonia by reaction with organic carbon. Nitrate concentrations in the aqueous effluent were always below 0.6 mg/L, but they were found to decrease with lowering the oxygen excess. Nitrites were most of the time below the detection limits (0.1 mg/L).

In all cases, bicarbonate production increased with lower oxygen excess, whereas the N₂O yields tended to slightly decrease for lower oxygen excesses. For example, from runs 1 to 2c, with the same reactor's temperatures but different oxygen excess, bicarbonate increased from 3480 mg/L in run 1 (74.73 % excess O₂) to 5940 mg/L in run 2c (-28.93 % excess O₂) (See Appendix H)

Traces of CO in the gas and of phenol in the aqueous stream were only obtained at a very sub-stoichiometric oxygen level, for run 2c (-28.93 % below the stoichiometric point).

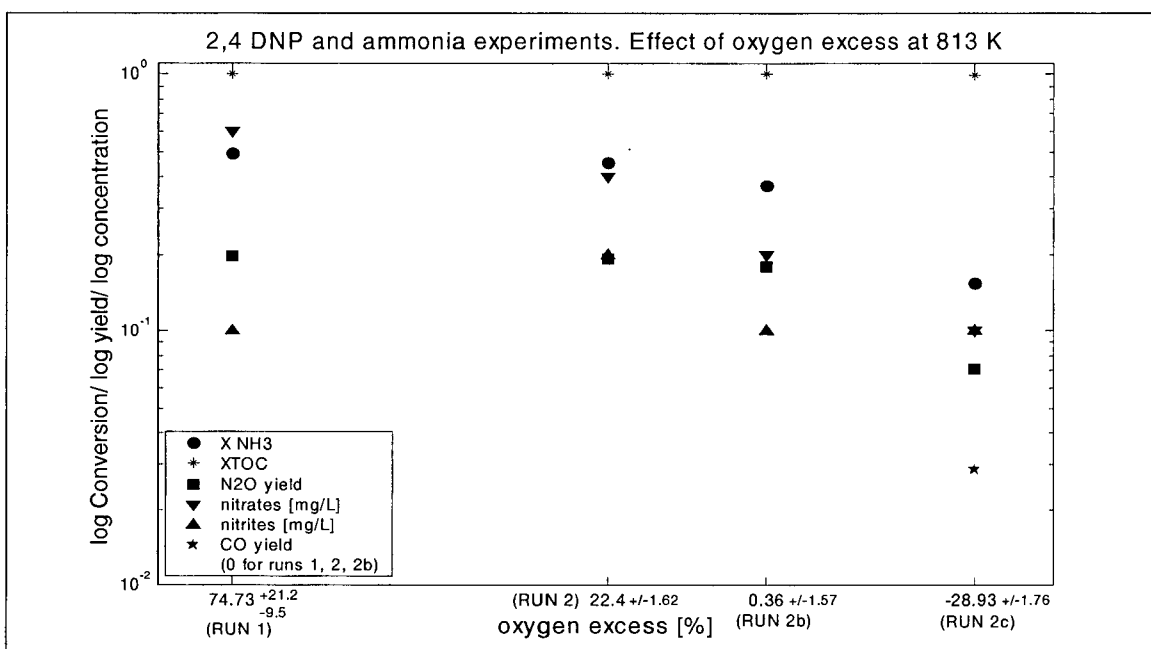


Figure 3.31 2,4 DNP and ammonia. Effect of oxygen excess at 813 K

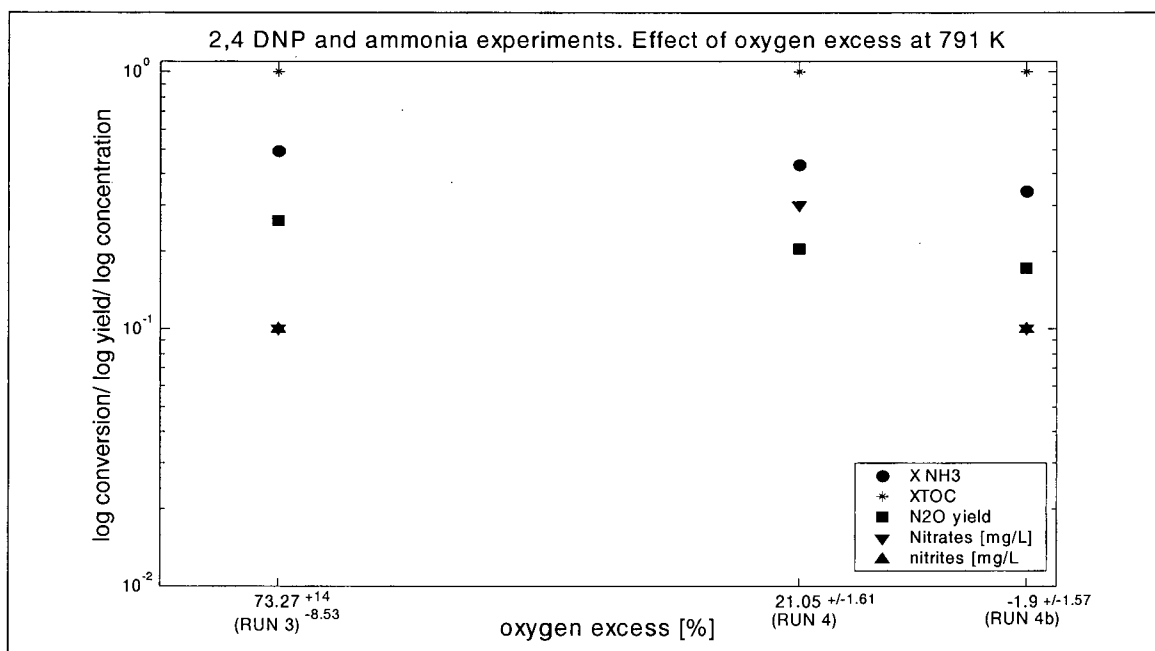


Figure 3.32 2,4 DNP and ammonia. Effect of oxygen excess at 791 K

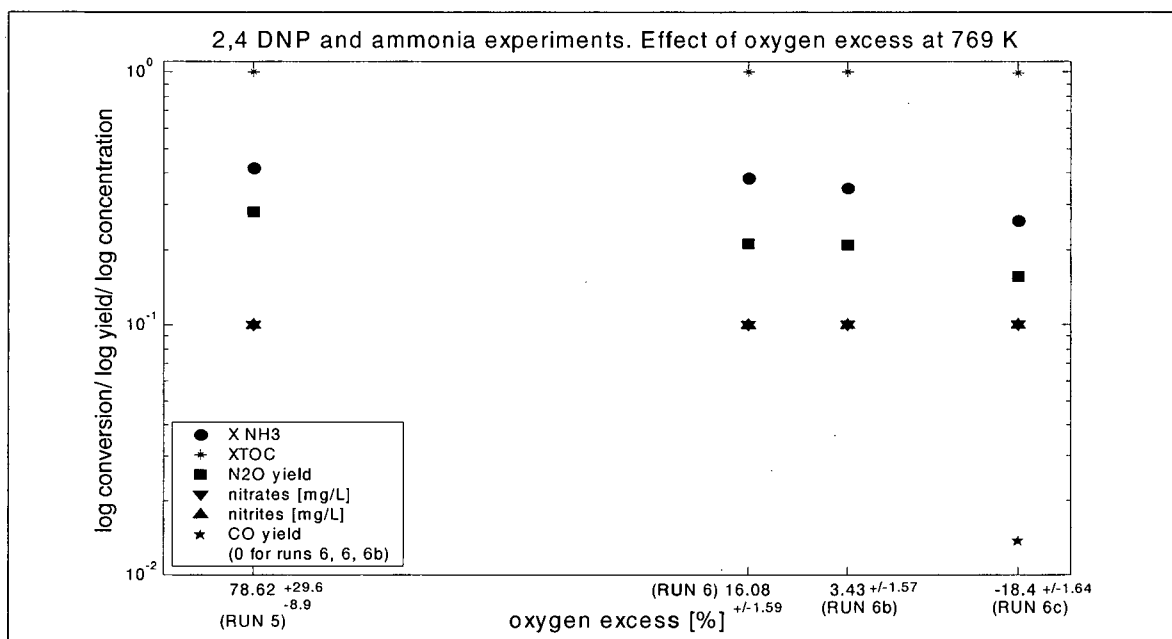


Figure 3.33 2,4 DNP and ammonia. Effect of oxygen excess at 769 K

3.6 Conclusions

The conclusions will be divided in two sections, corresponding to each group of tests:

1. Phenol

- High concentrations of phenol were successfully destroyed at 25 MPa, 666 –778 K and oxygen excesses from 0 to 39%. TOC and phenol DREs were in the range of 0.75 to 0.9977 and 0.95 to 0.9998 respectively
- As a general trend, higher DREs were obtained at higher temperatures, although not in all cases. More experiments would be needed in order to clarify this point.
- Moderate - but higher than stoichiometric- excess oxygen was needed in order to achieve high phenol and TOC conversions (e.g. between 10 and 39 %).
- The feed concentration did not have much effect in the phenol DREs. However, TOC conversions tended to be lower for lower feed concentrations.

- Reaction kinetics taken from the literature were used to predict phenol decompositions. The best were observed with the rate laws proposed by Krajnc and Levec, Gopalan and Savage, and Koo et al.

2. Wastes with 2,4 DNP

a. 2,4 DNP, ammonium sulphate and ammonia

- The waste containing 2,4 DNP, ammonia and ammonium sulphate was highly corrosive to the system.
- High concentrations of 2,4 DNP were fully destroyed and TOC DREs were of 99.92%. Due to the unclosed nitrogen balance, no conclusions on the destruction of ammonia could be made.

b. 2,4 DNP and ammonia

- High concentrations of 2,4DNP were fully destroyed, with TOC DREs of 0.9898 to 0.9998. Ammonia conversions, in contrast, were very poor, from 0.37 to 0.5.
- Maximum DREs of 2,4 DNP were obtained at temperatures as low as 742 K, with TOC conversions of 0.9983. NH_3 conversions decreased slightly at the lower temperatures.
- Even at sub stoichiometric oxygen flows, 2,4 DNP destruction was 99.996 %.
- Ammonia conversions were only slightly increased with oxygen concentration.
- 2- and 4-nitrophenol, and in some cases picric acid, were the intermediates detected. Analysis of intermediate samples lead to the belief that the destruction of 2,4 DNP followed a primary path to mononitrophenols. Destruction of 2- and 4-nitrophenol, apparently, didn't follow a path to CO_2 through phenol.

Chapter 4 Corrosion observed in the UBC-Noram SCWO facility

4.1 Previous experience

As noted in chapter 2, corrosion is one of the main challenges in SCWO systems and as such, has been given a lot attention. It has been found that the corrosion in SCWO of many materials depends on the physical properties of water.⁴⁵ As pointed out in section 2.1, at constant pressure, the density, dielectric constant and the ion product decrease drastically after the critical point. These properties affect the dissociation of the aggressive, corrosive species and the stability of the protective oxide layers in a way that makes corrosion most severe at high temperatures where the water density remains high.^{4 45} In general, corrosion rates tend to increase with temperature, reach a maximum, and decrease with further increase in temperature.⁴ However, the generalization that supercritical water is less corrosive is only valid for water at low density.⁴⁵ Increasing the pressure at supercritical temperatures, for example, will increase the density, the dielectric constant and the ionic product, subsequently favouring corrosion. The initial increase of corrosion with temperature has been justified by the effect of temperature on the rate constant of the reactions responsible for corrosion.⁴ Figure 4.1 sketches the rate of corrosion at 25 MPa found by Mitton et al.⁴⁶ in different portions of their tubular system, which was comprised of a preheater, a reactor and a cool-down heat exchanger. In the preheater, corrosion increased in the region from high subcritical to critical temperatures. Low corrosion was observed in the outlet of the preheater or inlet of the cool-down heat exchanger, portions of the system that operated at supercritical conditions. A peak in corrosion was again observed in the cool-down heat exchanger, at high subcritical temperatures. Even though corrosion in the reactor was not explored, degradation was suspected to be insignificant compared to that of the preheater and cool-down heat

exchanger, which failed several times in a period of time, while the reactor continued to work without apparent problems.

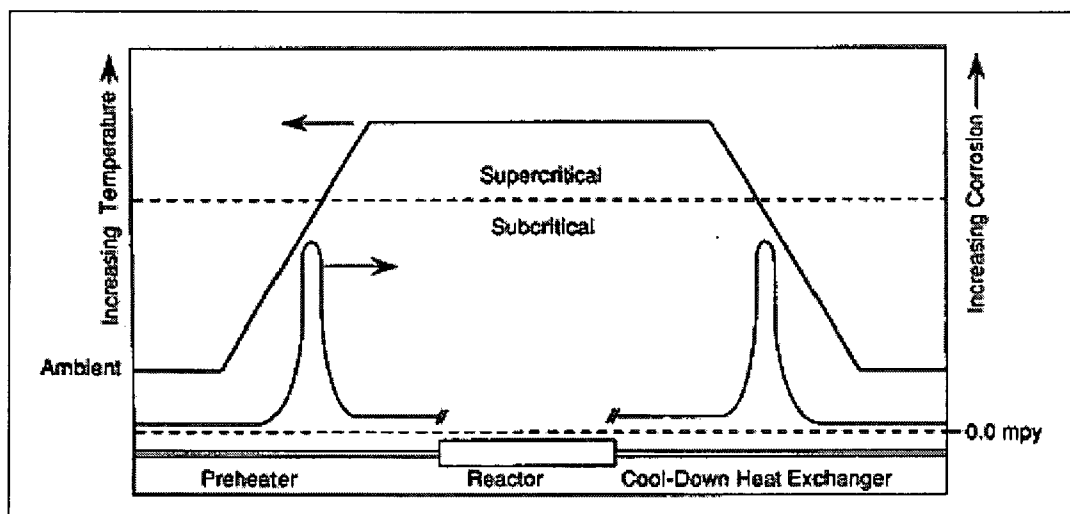


Figure 4.1 Corrosion as a function of temperature in preheater and heat exchanger. ⁴⁶

Kritzer and Dinjus⁴⁷ studied the corrosion of alloy 625 in high-temperature, high-pressure sulphate solutions. They found no corrosion in solutions containing H_2SO_4 and O_2 at low temperatures (between 150 and 200 °C), but observed that at higher temperatures, high densities favoured corrosion. In contrast, corrosion decreased considerably in low-density regions. In the corroded sections, solid, black products were found, mainly consisting of chromium, molybdenum and niobium, and smaller amounts of nickel. Solutions of NaHSO_4 and O_2 had been observed to display similar trends. No corrosion was detected in oxygenated Na_2SO_4 solutions up to 350 °C, while deoxygenated H_2SO_4 caused severe corrosion at low temperatures (200 °C). However, these rates became lower at higher temperatures.

Facing the problem of materials degradation in SCWO, a number of methods for reducing corrosion damages have been proposed, commonly addressing 3 different areas:^{48, 4}

- Corrosion resistant liners and coatings
- Feed modification
- Reactor design

Titanium and platinum have been suggested because of their good corrosion resistance. However, they are expensive. Elements in the feed that cause aggressive corrosion can also be diluted and/or somehow extracted from the waste prior treatment by SCWO. Another way to handle corrosion has been the development of novel reactors. The most common designs are the transpiring wall reactor⁴⁹ and down-flow vertical vessels.⁴⁸ On the basis of Figure 4.1, for example, two approaches could be used to manage corrosion in a system like this: a) incorporate easily replaceable, inexpensive sections at the two locations most prone to corrosion⁴⁶, or b) use more expensive, corrosion resistant materials in these sections.

4.2 Corrosion in the UBC-Noram pilot plant

As noted in section 3.4.2.1, the 2,4 DNP and ammonium sulphate solution treated in our SCWO pilot plant was highly corrosive to the system. During the experiment, no failures occurred. However, during the start-up of the next tests with water, the first preheater failed, when temperatures reached only 300 °C. The failure occurred at 1.72 m from its inlet. On a later cold static pressure test at 517 bars, the inner tube from the regenerative heat exchanger (RHX) also burst. The RHX failed where the hot stream coming from the reactor (outer tube) impinged on it. Figure 4.2 shows the burst tube from the preheater 1.

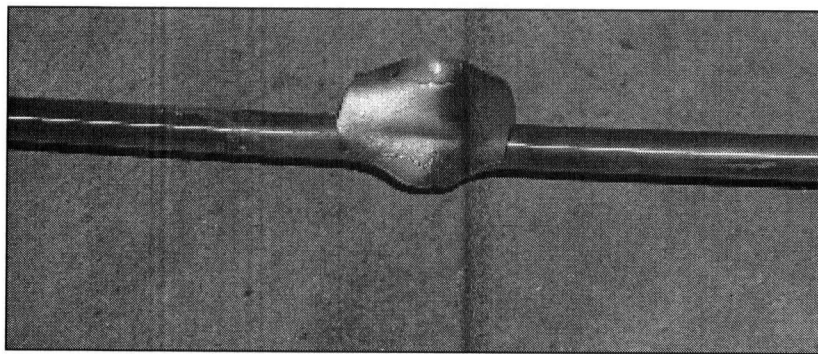


Figure 4.2 Tube failure due to corrosion in the first preheater (PH 1)

Only 58 litres of 2,4 DNP and ammonium sulphate solution were treated, under the conditions described in section 3.5.2.1. The metals analyses, for which results can be seen in Appendix G, yielded high concentrations of molybdenum, nickel, chromium and sulphur in the effluent, the latter most probably caused by sulphur salts deposited in the system. The metals analyses from the separate sampling ports showed that practically all of the molybdenum, nickel and chromium released from the system came from the port located in the inlet of the preheater 2 (PH 2 in). At the time the experiments were run, this port was the closest to the first preheater. Lower amounts of metals were detected in the samples from the other ports, but it was suspected that they had been carried by the flow to other points of the system and had remained there.

Samples from the previous tests with phenol were analyzed looking for traces of metals, in order to clarify whether the corrosion had been gradual, or if it had occurred only during the 2,4 DNP and ammonium sulphate test. These analyses showed that no metal had been lost during the phenol experiments. However, corrosion from previous tests could not be ruled out.

The total amount of metals lost in the system was calculated based on the analyses of the effluent stream, the composition of alloy 625 under normal (no corrosion) conditions, and the

fact that only 58 litres of solution had been treated (See Appendix I). The calculations indicate that a total of approximately 18 g of metals (Ni, Cr, and Mo) were lost during the test, enough to weaken the tubes and to cause them to fail.

The analysis of the corroded tube is summarized below.

Wall thickness measurements

The thickness of the preheater 1 and regenerative heat exchanger's tube walls were measured with a thickness probe at locations where no corrosion was observed as well as in the corroded areas. Measurements were made every one inch at four different points of the tube's cross sectional area, separated by 90°. Figures 4.3 and 4.4 show the thickness and bulk temperature profiles in the corroded sections of PH1 and RHX respectively. As pointed out in section 3.4.2, temperature profiles were calculated using only water properties. Since these experiments also contained high excess oxygen (198%), real bulk temperatures would be expected to be few degrees lower than those presented in these figures. The results in Figures 4.3 and 4.4 show a considerable decrease in the thickness in both the preheater 1 and the regenerative heat exchanger. Note that the areas most affected by corrosion were in the vicinity of the critical point for the experiment's pressure (24.9 MPa). Most of the metallic losses in the inner tube of the RHX came from its top, internal surface, on the impinging point of the hot fluid coming from the reactor.

Thickness measurements were also taken in the test section to look for signs of corrosion. However, these tubes were found to be in good condition.

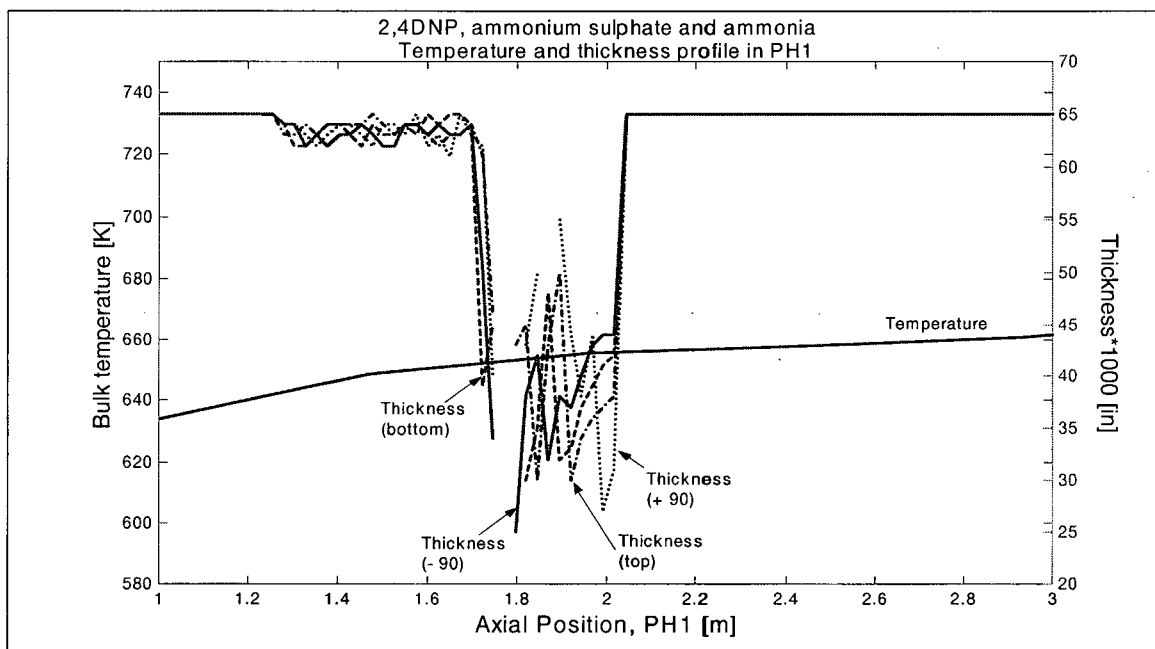


Figure 4.3 Temperature and thickness profiles, PH 1.

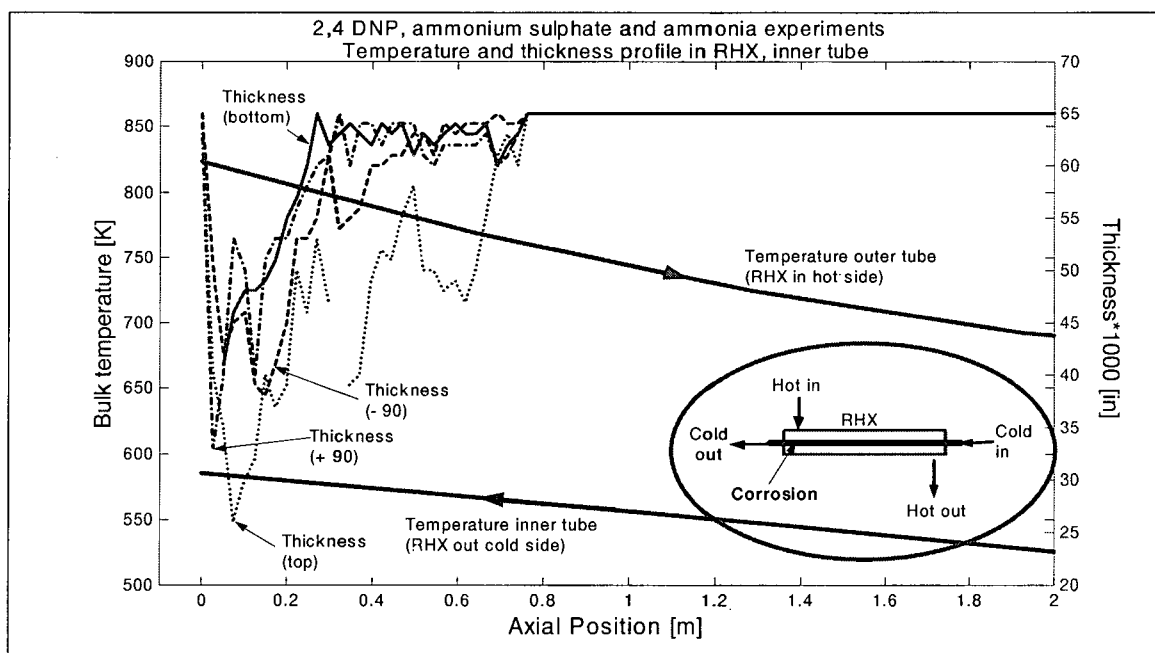


Figure 4.4 Temperature and thickness profiles, RHX

The next three tests have not yielded any definite conclusions yet, leaving some work to be done.

Optical Microscope

An optical microscope was used to visualize the main changes on the exposed surface of the samples of corroded and non-corroded sections of the tubes. The samples were chemically prepared (etched) by the Pulp and Paper Research Institute of Canada (PAPRICAN) and analyzed under an optical microscope, with resolution of up to 400X. The graphic images (see Appendix I for graphic results) showed major irregularities in the shape of the surfaces of the corroded sections.

Scanning Electron Microscopy/ Energy Dispersive Spectroscopy (SEM/EDS)

SEM and EDS were used to examine the cross section of the tubes, determine the features of the corroded surface, and obtain an elemental analysis of any adherent deposits.

The SEM is one of the major tools in the failure analysis process. After initial visual examination of the specimen, the sequence of procedures for a SEM examination in a typical project might go as follows⁵⁰:

- Failure area viewed at low magnification -secondary electrons show an overall picture of the area.
- Magnification increased to about 300X- secondary electron view highlights details with excellent depth of field.
- Magnification increased to 3000X- backscatter electrons used to examine grain structure.

- EDS system identifies the elements present and their percentages in the materials examined.

The tests were conducted in the Metals and Materials Department at UBC. Their analysis is still in progress.

Auger electron spectroscopy/ X-ray photoelectron spectroscopy (AES/XPS)

AES/XPS were used to examine the longitudinal section of the tubes. Both techniques provide quantitative analysis of elements. XPS can also identify the chemical state of an element. For example, a metal can be differentiated from its oxide or carbide. AES, which uses an electron beam for excitation, can be used to produce an elemental map of the surface and analyze small features such as particles and corrosion pits. Both techniques can produce a depth profile that gives the distribution of elements in the surface layers.

In this case, only one longitudinal sample from the failed part of the preheater 1 (PH1) was analyzed, looking for any enrichment or depletion in the alloy elements at the corroded surface and the chemical composition of any adherent deposit or corrosion products in the surface of the tube. Their analysis is still in progress.

4.3 Conclusions

Even though this corrosion study is ongoing and no definite conclusions have been reached regarding the causes of such severe degradation in the system, some preliminary conclusions can be drawn:

- The 2.4% by wt. 2,4 DNP waste containing 2.1% by wt. of ammonium sulphate and 6.67% by wt. of ammonia was clearly corrosive to the system. While the possibility of some prior corrosion should not be completely rejected, this solution obviously caused enough damage to provoke the failure of PH 1 and RHX.
- The corrosion profiles in the system agree with the observations made by Kritzer and Dinjus⁴⁵ and Mitton et al.⁴⁶ that highest corrosion rates are observed at high temperature and high density points, that is in the high temperature subcritical area when operating the SCWO system at 25 MPa.
- More research needs to be done with the 2,4 DNP-ammonium sulphate-ammonia waste, but this first experimental trial suggested that sulphates elimination/reduction would be needed in order to treat the waste by SCWO.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

Phenol experiments

- High concentrations of phenol were successfully destroyed at 25 MPa, 666 –778 K and oxygen excesses from 0 to 39%. TOC and phenol DREs were in the range of 0.75 to 0.9977 and 0.95 to 0.9998 respectively
- As a general trend, higher DREs were obtained at higher temperatures, although not in all cases. More experiments would be needed in order to clarify this point.
- Moderate - but higher than stoichiometric- excess oxygen was needed in order to achieve high phenol and TOC conversions
- The feed concentration did not have much effect in the phenol DREs. However, TOC conversions tended to be lower for lower feed concentrations.
- Reaction kinetics taken from the literature was used to predict phenol decompositions. The best agreements were observed with the rate laws proposed by Krajnc and Levec, Gopalan and Savage, and Koo et al.

Wastes with 2,4 DNP

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- More research needs to be done with the 2,4 DNP-ammonium sulphate-ammonia waste, but this first experimental trial suggested that sulphates elimination/reduction would be needed in order to treat the waste by SCWO.
- High concentrations of 2,4 DNP were fully destroyed and TOC DREs were of 99.92%. Due to the unclosed nitrogen balance, no conclusions on the destruction of ammonia could be made at this point.

b. 2,4 DNP and ammonia

- High concentrations of 2,4DNP were fully destroyed, with TOC DREs of 0.9898 to 0.9998. Ammonia conversions, in contrast, were very poor, from 0.37 to 0.5.
- Maximum DREs of 2,4 DNP were obtained at temperatures as low as 742 K, with TOC conversions of 0.9983. NH₃ conversions decreased slightly at the lower temperatures.
- Even at sub stoichiometric oxygen flows, 2,4 DNP destruction was 99.996 %.
- Ammonia conversions were only slightly increased with oxygen concentration.
- 2- and 4-nitrophenol, and in some cases picric acid, were the intermediates detected. Analysis of intermediate samples lead to believe that the destruction of 2,4 DNP followed a primary path to mononitrophenols. Destruction of 2- and 4-nitrophenol, apparently, didn't follow a path to CO₂ through phenol.

5.2 Recommendations

Even though high concentrations of 2,4 DNP wastes can be fully destroyed by SCWO, using low oxygen excess and moderate temperatures, ammonia conversion during these experiments was very poor. According to other researchers^{28,31,33,34}, using nitrates as co-oxidant agents can solve this problem. Another possibility is to treat feed streams with higher TOC concentration.

The possibility of treating even higher feed concentrations of 2,4 DNP calls for a better way of keeping the feed in solution. This could be solved by containing the aqueous 2,4 DNP solution in a slightly pressurized container at a temperature below the saturation point, but high enough to keep the nitrophenols into solution.

It is important that the gas samples are not contaminated with atmospheric air. In the future, gas samples from the effluent could be taken from the outlet of the effluent tank's gas-liquid separator. This would not require major changes to the system. For the case of the intermediate sampling ports, it would be necessary to make sure that all the air is evacuated from the vial before collecting the gaseous sample.

Bench top experiments should be carried out to shed more light on the corrosion caused by the sulphate containing 2,4 DNP waste. This would lead to conclusions on the feasibility of treating nitration wastewaters with sulphates. The use of liners or corrosion-resistant materials in the parts of the reactor that are more prone to corrosion could be considered.

References

- ¹ <http://cisat.isciii.es/bt/atsdr/profiles/Nitroben.pdf>
- ² Boyd, D. A., Gairns, S. A., Guenkel, A. A., US Patent 6288289, 2001, "Integrated Effluent Treatment for Nitroaromatic Manufacture".
- ³ Freeman, H. M., 1989, *Standard Handbook of Hazardous Waste Treatment and Disposal*, US Environmental Protection Agency, McGraw Hill, New York, Chap. 9.
- ⁴ Chang, H. O., 2001, *Hazardous and Radioactive Waste Treatment Technologies Handbook*, Idaho National Engineering and Environmental Lab, Idaho, USA, Chap. 5.
- ⁵ Esplugas, S., Gimenez, J., Contreras, S., Pascual, E., and Rodriguez, M., 2002, "Comparison of Different Advanced Oxidation Processes for Phenol Degradation", *Water Research*, **36**(4), pp. 1034-1042.
- ⁶ Gloyna, E., F., Li, L., and McBrayer, R., N., 1994, "Engineering Aspects of Supercritical Water Oxidation", *Water Sci. Tech.*, **30**(9), pp. 1-10.
- ⁷ Savage, P.E., 1999, "Organic Chemical Reactions in Supercritical Water", *Chem. Rev.*, **99**(2), pp.603-621.
- ⁸ McDonald, D. D., and Kriksunov, L. B., 2001, "Probing the Chemical and Electrochemical Properties of SCWO Systems", *Electrochimica Acta*, **47**(5), pp. 775-790.
- ⁹ Griffith, J. W., and Raymond, D. H., 2002, "The First Commercial Supercritical Water Oxidation Sludge Processing Plant", *Waste Management*, **22**(4), pp. 453-459.
- ¹⁰ Modell, M., US Patent 4543190, 1985, "Processing Methods for the Oxidation of Organics in Supercritical Water".
- ¹¹ Thomason, T.B., and Modell, M., 1984, "Supercritical Water Destruction of Aqueous Wastes", *Hazardous Waste*, **1**, pp. 453-264.
- ¹² Staszak, C.N., Malinowski, K.C., and Killilea, W. R., 1987, "The Pilot-Scale Demonstration of the Modar Oxidation Process for the Destruction of Hazardous Organic Waste Materials", *Environ. Progress*, **6**, pp. 39-43.
- ¹³ McBrayer, R.N., and Griffith, J.W., 1996, "Turn Off the Heat", *Industrial Wastewater*, July/August pp. 43-48.
- ¹⁴ Matsumura, Y., Nunuora, T., Uruse, T., and Yamamoto, K., 2000, " Supercritical Water Oxidation of High Concentrations of Phenol", *J. Haz. Materials*, **73**(3), pp. 245-254.

- ¹⁵ Li, L., Chen, P., and Gloyna, E.F., 1994. , "Chemical Oxidation: Technology for the Nineties", *Proceedings of the Third International Symposium, Chemical Oxidation: Technology for the Nineties*, Eckenfelder, W, Bowers, A., and. Roth, J., Eds, Vanderbilt University, Nashville, TN.
- ¹⁶ Thornton, T.D., and Savage, P. E., 1992, "Kinetics of Phenol Oxidation in Supercritical Water", *AIChE J.*, **38** pp. 321-327.
- ¹⁷ Gopalan, S., and Savage, P. E., 1995, "A Reaction Network Model for Phenol Oxidation in Supercritical Water", *AIChE. J.*, **41**, pp. 1864- 1873.
- ¹⁸ Krajnc, M., and Levec, J., 1996, "On the Kinetics of Phenol Oxidation in Supercritical Water", *AIChE J.*, **42**, pp. 1977-1984.
- ¹⁹ Eckert, C. A., Leman, G. M., and Yang, H. H., 1990, "Homogeneous Catalysis for Wet Oxidation: Design and Economic Feasibility of a Mobile Detoxification Unit", *Haz. Mat. Control*, 3(20).
- ²⁰ Rogak, S. N., Khan, M. S., and Vera Pérez, I., 2002, "Thermal Design of Supercritical Water Oxidation Reactors", *Proceedings of IMECE2002 ASME International Mechanical Engineering Congress & Exposition*, IMECE 2002-33853, New Orleans, USA.
- ²¹ Koo, M., Lee, W.K., and Lee, C.H., 1997, "New Reactor System for SCWO and its Application on Phenol Destruction", *Chem. Eng. Sci.* **52**, pp. 1201-1214.
- ²² Oshima, Y., Hori, K., Toda, M., Chommanad, T., and Koda, S., 1998, "Phenol Oxidation Kinetics in Supercritical Water", *J. Supercrit. Fluids*, **13**, pp. 241-246.
- ²³ Portela J.R., Nebot E., and de la Ossa E.M., 2001, "Kinetic Comparison Between Subcritical and Supercritical Water Oxidation of Phenol", *Chem. Eng. J.*, **81** (1-3) pp. 287-299.
- ²⁴ Kolaczowski, S.T., Beltran, F.J., McLurgh, D.B, and Rivas, F.J., 1997, "Wet Air Oxidation of Phenol: Factors that may Influence Global Kinetics", *Trans. IchemE*, **75** (B) pp. 257-265.
- ²⁵ Harradine, D. M., Buelow, S. J., Delll'Orco, R. B., Foy, B. R., and Robinson, J. M., 1993, "Oxidation Chemistry of Energetic Materials in Supercritical Water", *Hazardous Waste and Hazardous Materials*, **10**(2), pp. 233-245.
- ²⁶ Li, L., Gloyna, E.F., and Sawicki, J.E., 1993, "Treatability of DNT Process Wastewater by Supercritical Water Oxidation", *Water Environment Research*, **53**(3), pp250-257.
- ²⁷ Dell'Orco, P., Luan, L., Proesmans, P., and Wilmanns, E, 1995, "Reaction Chemistry of Nitrogen Species in Hydrothermal Systems: simple Reactions, Waste Simulants, and Actual Wastes", *First International Workshop on Supercritical Water Oxidation*, Florida, USA.
- ²⁸ Proesmans, P.I., Luan, L., and Buelow, S., 1997, "Hydrothermal Oxidation of Organic Wastes Using Ammonium Nitrate", *Ind. Eng, Chem. Res.* **36** (5), pp. 1559-1566.

- ²⁹ Cocero, M. J., Alonso, E., Torío, R., Vallelado, D. and Fdez-Polanco, F., 2000, "Supercritical Water Oxidation in a Pilot Plant of Nitrogenous Compounds: 2-propanol Mixtures in the Temperature Range 500-700 °C", *Ind. Eng. Chem. Res.*, **39** (10), pp. 1784-1791.
- ³⁰ Killilea, W. R., Swallow, K. C., and Hong, G. T., 1992, "The Fate of Nitrogen in Supercritical Water Oxidation", *The Journal of Supercritical Fluids*, **5**, pp. 72-78.
- ³¹ Gidner, A., Stenmark, L., Abrahamson, J., and Carlsson, K., 1999, "The Chematur Engineering SCWO Pilot Plant. Treatability Studies", *6th meeting of Supercritical Fluids, Nottingham, England*.
- ³² Luan, L., Proesmans, P.I., and Buelow, S., 1997, "Hydrothermal Oxidation of Ammonia/Organic Mixtures", *The 4th Symposium on Supercritical Fluids, Sendai, Japan*.
- ³³ Aymonier, C., Beslin, P., Jolival, C., and Cansell, F., 2000, "Hydrothermal Oxidation of a Nitrogen-Containing Compound: The Fenuron", *The Journal of Supercritical Fluids*, **17**, pp. 45-54.
- ³⁴ Lee, D. S., Park, K. S., Nam, Y.W., Kim, Y-C, and Lee, C. H., 1997, "Hydrothermal Decomposition and Oxidation of p-Nitroaniline in Supercritical Water", *Journal of Hazardous Materials*, **56**(3), pp. 247-256.
- ³⁵ Ding, Z., Y., Li, L., Wade, D., and Gloyna, E.F., 1998, "Supercritical Water Oxidation of NH₃ Over a MnO₂/CeO₂ Catalyst", *Ind. Eng. Chem. Res.*, **37**(5), pp. 1707-1716.
- ³⁶ Martino, C.J., and Savage, P.E., 1997, "Thermal Decomposition of Substituted Phenols in Supercritical Water", *Ind. Eng. Chem. Res.*, **36** (5), pp.1385-1390.
- ³⁷ Martino, C.J., and Savage, P.E., 1999, "Oxidation and Thermolysis of Methoxy-, Nitro-, and Hydroxy-Substituted Phenols in Supercritical Water", *Ind. Eng. Chem. Res.*, **38** (5), pp. 1784-1791.
- ³⁸ Boyd, D. A., Gairns, S. A., and Guenkel, A.A., U.S. Patent # 6,288,289,2001, "Integrated Effluent Treatment Process for Nitroaromatic manufacture".
- ³⁹ Wagner, W. and Pruß, A., 2002, "The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use", *J. Phys. Chem. Ref. Data*, **31**(2), pp. 387-535.
- ⁴⁰ Martino, C.J., and Savage, P.E., 1999, "Total Organic Carbon Disappearance Kinetics for the Supercritical Water Oxidation of Monosubstituted Phenols", *Environ. Sci. Technol*, **33**(11), pp. 1911-1915.
- ⁴¹ Holman, J. P., 2001, *Experimental Methods for Engineers*, McGraw Hill, Boston, Chap. 3.
- ⁴² Rice, S. F., and Steeper, R. R., 1998, "Oxidation Rates of Common Organic Compounds in Supercritical Water", *Journal of Hazardous Materials*, **59**(2-3), pp. 261-278.

- ⁴³ Li, R., Thornton, T. D., and Savage, P. E., 1992, "Kinetics of CO₂ Formation from the Oxidation of Phenols in Supercritical Water", *Environ. Sci. Technol.*, **26**(12), pp. 2388-2395.
- ⁴⁴ Martino, C.J., and Savage, P.E., 1999, "Supercritical Water Oxidation Kinetics and Pathways for Ethylphenols, Hydroxyacetophenones, and Other Monosubstituted Phenols", *Ind. Eng. Chem. Res.*, **38**(5), pp. 1775-1783.
- ⁴⁵ Kritzer, P., Boukis, N., and Dinjus, E., 1999, "Factors Controlling Corrosion in High-Temperature Aqueous Solutions: A Contribution of the Dissociation and Solubility Data influencing Corrosion Processes", *The Journal of Supercritical Fluids*, **15**(3), pp. 205-227.
- ⁴⁶ Mitton, D.B., Han, E. -H., Zhang, S. -H., Hautanen, K. E., and Latanision, R. M., 1997, "Degradation of Supercritical Water Oxidation Systems", *ACS Symposium series 670. Supercritical Fluids Extraction and Pollution Prevention*, Amer. Chem. Soc., USA, Chap. 17, pp. 243-253.
- ⁴⁷ Kritzer, P., Boukis, N., and Dinjus, E., 1998, "Corrosion of Alloy 625 in High-temperature, High-Pressure Sulphate Solutions", *Corrosion*, **54**(9), pp. 689-698.
- ⁴⁸ Mitton, D. B., Eliaz, N., Cline, J. A., and Latanision, R. M., 2001, "An Overview of the Current Understanding of Corrosion in SCWO Systems for the Destruction of Hazardous Waste Products", *Materials Technology*, **16**(1), pp. 44-53.
- ⁴⁹ Mueggenburg, H. H., Rousar, D. C., and Young, M. F., US Patent 5,387,398, 1995, "Supercritical Water Oxidation Reactor with Wall Conduits for Boundary Flow Control".
- ⁵⁰ www.engelmet.com, Engel Metallurgical Ltd., Minnesota, USA.
- ⁵¹ Younlove, B., 1982, *Journal of Physical and Chemical Reference Data*, Amer. Chem. Soc.; New York, **Vol. 11** (Supplement no.1).
- ⁵² Gibson, N., BCRI, personal communication.

Appendix A Oxygen flow meter calibration

1. Objectives:

To calibrate the oxygen flow measurements with the new pressure transmitter (Foxboro IDP10) and an orifice meter 1.14 mm in diameter. This pressure transmitter was installed in order to improve the system's flow control. The previous one was used during the first experiments with phenol detailed in Chapter 3 of this work, and its calibration relation was the following:

$$\dot{m} = 4.16 * (V - V_0)^{1/2} \quad [A.1]$$

Where \dot{m} was the oxygen mass flow in kg/h, V the voltage reading from the data acquisition system, and V_0 the zero offset of the transmitter.

2. Experimental set up and test description

The Foxboro transmitter and the orifice were used to measure the oxygen flow coming from the O₂ booster and the differential pressure across the orifice. The output from the transmitter, which is read by the data acquisition system (channel 24), was 2 to 10 V, depending on the oxygen flow. A 24-volt power supply was used to feed the transmitter.

The calibration of the pressure transmitter was performed on two occasions; on the first one it was observed that the temperatures on the high-pressure side of the system were not constant and that they tended to be higher after the booster became warmer from operating. Changes in the system were made for the second set of calibrations, and the previous pulsation damper was used as a container to absorb both pressure and temperature pulsations (please refer to Figures A.1 and A.2 for the first and second system's layouts). The second

calibration was used for interpretation of all experiments and the first calibration is given here only for completeness.

The pressure of the oxygen coming from the booster is set to the desired value by a pressure regulator, and then the fluid flows through the orifice meter (Figures A.1 and A.2). Its temperature is measured by a thermocouple (T_{HP}) and registered by the SCWO data acquisition system, and the pressure is read by a pressure gauge. When oxygen flows through the orifice, the transmitter records the differential pressure, which on its screen is measured in inches of water, and in volts by the SCWO data acquisition system (channel 24 on the computer). The oxygen flow rate is controlled by a needle valve, and a bulb thermometer (TLP) measures its temperature at atmospheric pressure. A flow meter, model Equimeter RC-M-415, then measures the volumetric flow. A pressure indicator (DP1 601) is used to measure the pressure in the inlet of the flow meter (P_{LP}).

Oxygen properties were obtained from a Matlab lookup table generated from the Journal of Physical and Chemical Reference Data ⁵¹.

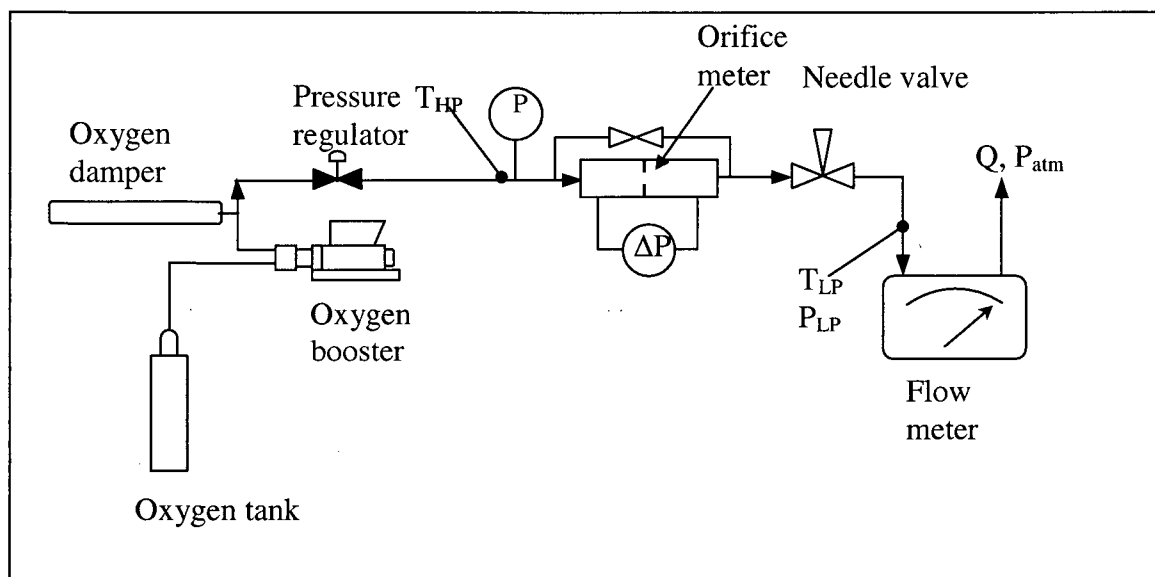


Figure A.1 Schematic of the oxygen set up for the first set of calibrations

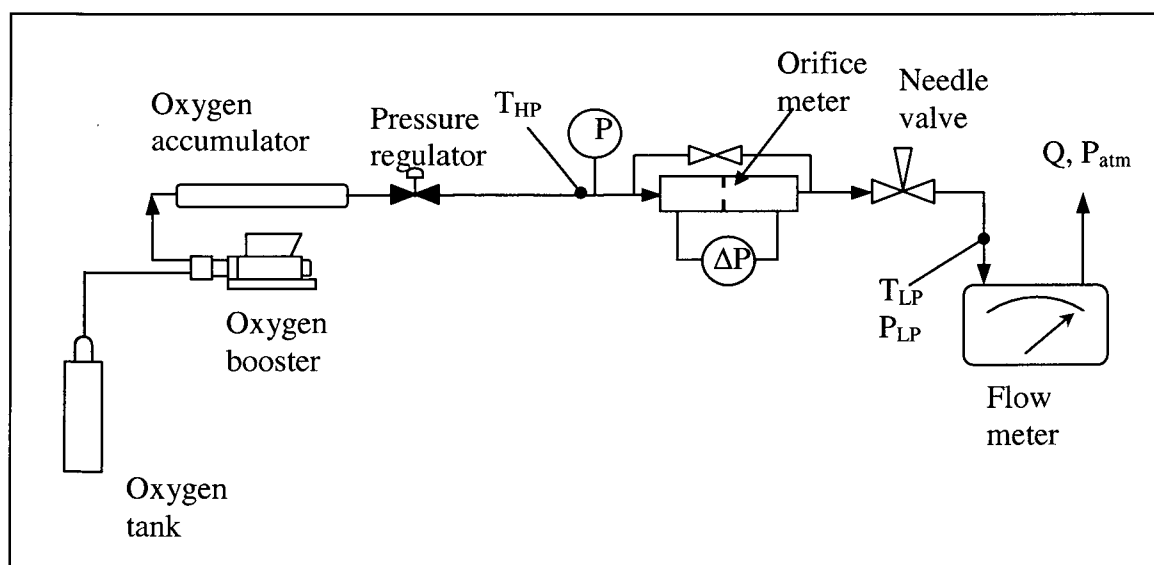


Figure A.2 Schematic of the oxygen set up for the second set of calibrations

3. Calculations

From Bernoulli's Law:

$$\frac{\dot{m}^2}{\rho} = K\Delta P \quad [A.2]$$

And since the change in pressure (ΔP) is linear to the output voltage signal:

$$\frac{\dot{m}^2}{\rho} = k'(V - V_0) \quad [A.3]$$

Where V_0 is the zero offset in voltage ($V_0=1.999$), V is the voltage read at each flow conditions, and k' is a factor that can be found by fitting the data to the correlation.

First calibration test

The transmitter was calibrated at 3900 psi and 4200 psi.

Calibration data for both 3900 psi and 4200 psi can be seen in Table A.1, and in Figures A.3, A.4 and A.5.

At 3900 psi, the mass flow rate obtained as a function of the voltage difference was:

$$\dot{m} = 0.197 * \rho^{1/2} * (V - V_0)^{1/2} \quad [A.4]$$

Where:

\dot{m} : Mass flow rate in kg/h,

ρ : Average density at 3900 psi and the temperatures that appear in Table A.1 (341 kg/m^3),

V : Output voltage (V)

V_0 : Zero offset of the transmitter (V)

At 4200 psi, the mass flow rate obtained was:

$$\dot{m} = 0.214 * \rho^{1/2} * (V - V_0)^{1/2} \quad [A.5]$$

Where the average density is $\rho = 352.37 \text{ kg/m}^3$

As it was stated before, it was observed that the temperatures were quite unstable, and increasing with time. This could have been one of the reasons for not having a single coefficient k' which was not dependent on the pressure.

Second calibration test

For this test, the pulsation damper (10 feet long by 2 inches in diameter, 316 SS) was used as an oxygen accumulator to absorb all the temperature and pressure fluctuations when the system was operating, changes can be observed by comparing Figures A.1 and A.2.

The procedure followed for the calculations was the same as the one explained above, and the calibration was performed for 3600, 3900 and 4200 psi. The calibration data at all pressures can be seen in Table A.2 and Figures A.6, A.7 and A.8.

For all cases, the obtained relations were a function of the same coefficient k' . In this case \dot{m} yielded the following result:

$$\dot{m} = 0.23 * \rho^{1/2} * (V - V_0)^{1/2} \quad [A.6]$$

Where ρ was the average density for each pressure:

$$\rho_{(3600 \text{ psi})} = 339.07 \text{ kg/m}^3$$

$$\rho_{(3900 \text{ psi})} = 364.34 \text{ kg/m}^3$$

$$\rho_{(4000 \text{ psi})} = 372.94 \text{ kg/m}^3$$

Error analysis

The uncertainty in the oxygen mass flow rate was calculated on the basis of the uncertainties in the primary measurements. The uncertainties in the thermocouples and volume flow meter were neglected, being considered much smaller than that of the high-pressure side manometer, which directly influences the mass flow.

The pressure gauge used had a precision of 50 psi, which introduced different densities uncertainties, depending on the pressure. This was because the density did not change linearly with the pressure.

The calculation of any possible error in the density was performed for some of the pressures most commonly used, which were: 3800 ± 50 psi, 3900 ± 50 psi, and 4150 ± 50 psi. Densities at these pressures, and at their corresponding average temperatures on the high-pressure were obtained from the lookup table. The yielded errors were the following:

$$\rho_{(3800 \text{ psi})} = 355.49 \pm 1.2 \%$$

$$\rho_{(3900 \text{ psi})} = 364.64 \pm 1.26 \%$$

$$\rho_{(4150 \text{ psi})} = 384.75 \pm 1.14 \%$$

The contribution of the constant factor (0.23) to the error in the flow was also calculated. From Figure 7 it can be observed that the exact value of the constant oscillated from 0.228 to 0.232, 0.23 being the mean value.

The unbiased standard deviation was calculated according to equation [A.7],⁴¹ where $n=3$.

$$\Gamma = \left[\frac{1}{n-1} * \sum_{i=1}^n (X_i - X_m)^2 \right]^{1/2} \quad [\text{A.7}]$$

The result yielded $\Gamma=0.002$ and the uncertainty in the equation's constant was $\pm 0.87\%$.

To obtain the contribution of the voltage to the oxygen flow rate equation, several cases of oxidation experiments were considered. During these experiments, the system pressure and oxygen flows were considered to be stable. No samples were taken from the intermediate ports; hence no external actions to upset the system's stability existed. The analysed runs were Run 2, 2b, 2c, 4, 4b, 6, 6b, 6c, and 7 of the 2,4 dinitrophenol-based experiments. To calculate the voltages uncertainty, the average of the voltages reading of all the runs were taken, as well as their corresponding maximum and minimum deviations, in percent. The unbiased standard deviation was calculated according to equation [A.7], and the Chauvenet's criterion for rejecting a reading ⁴¹ was applied. This resulted in a voltage uncertainty of 0.04% (see Table A.3 for calculations). The uncertainty in the zero offset was assumed to be negligible. Finally, the expected uncertainty in the oxygen mass flow rate formula (which is a product function of the type $R=y_1^{a1} * y_2^{a2} * \dots y_n^{an}$) can be expressed by general equation [A.8] ⁴¹, or by the simplified case for product type functions [A.9]:

$$wR = \left[\left(\frac{\partial R}{\partial y_1} * w_1 \right)^2 + \left(\frac{\partial R}{\partial y_2} * w_2 \right)^2 + \dots \left(\frac{\partial R}{\partial y_n} * w_n \right)^2 \right]^{1/2} \quad [A.8]$$

$$wR = R * \left[\sum \left(\frac{a_i * w_i}{y_i} \right)^2 \right]^{1/2} \quad [A.9]$$

Where wR is the uncertainty in the oxygen mass flow, and w_i are the uncertainties in the independent variables. The values of the uncertainties depended on the pressures at which the oxygen system was operated, and the target voltages. Table A.4 shows their values for runs 2, 2b, 2c, 4, 4b, 6, 6b, 6c and 7 of the 2,4 DNP and ammonia experiments.

4. Conclusions

The oxygen flowmeter Forboro IDP10 was calibrated, and mass flow rate relations were obtained.

The second set of calibrations was considered to be more accurate, due to the uniformity in the temperatures on the high-pressure side, and the stability in the oxygen flow and pressure at all times. An error analyses was performed, yielding that the uncertainty on the equation's constant was $\pm 0.87\%$, the voltage's uncertainty was 0.04% and the error in the density depended on the pressure at which the oxygen system was being operated.

For subsequent calibrations, the relation mass flow rate- voltage will be the following:
[A.6], (considering the calculated uncertainties)

$$\dot{m} = 0.23 * \rho^{1/2} * (V - V_0)^{1/2}$$

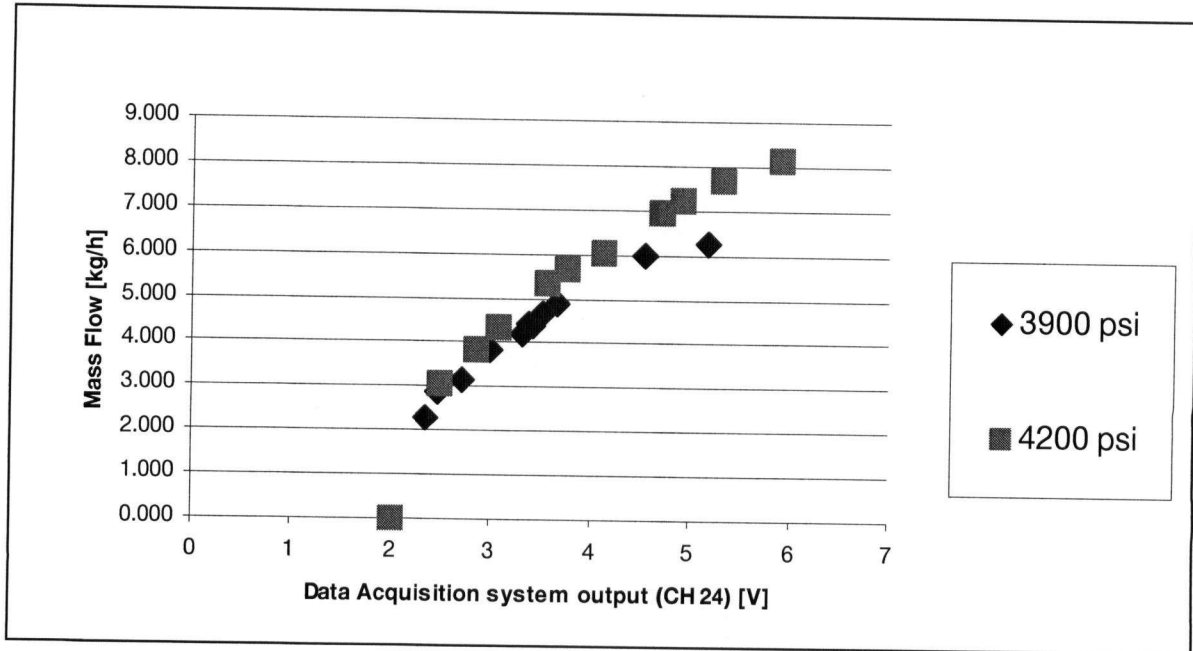


Figure A.3 First set of calibrations. Mass flow rate vs. voltage.

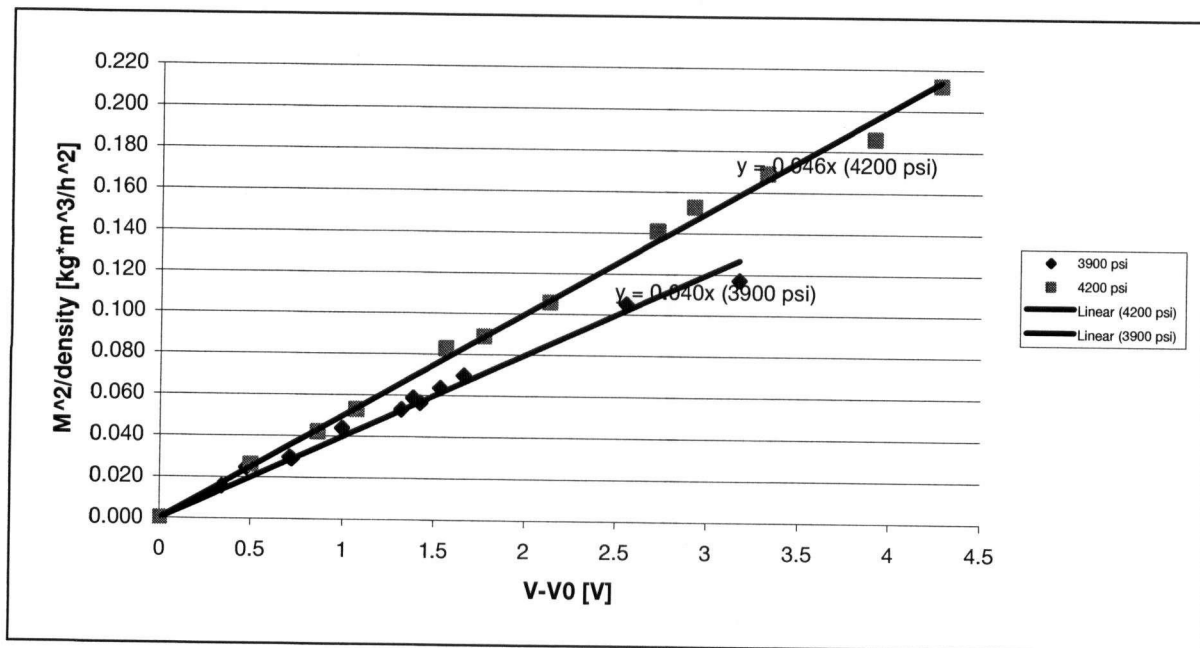


Figure A.4 First set of calibrations. $m^2/\text{density}$ vs. voltage difference.

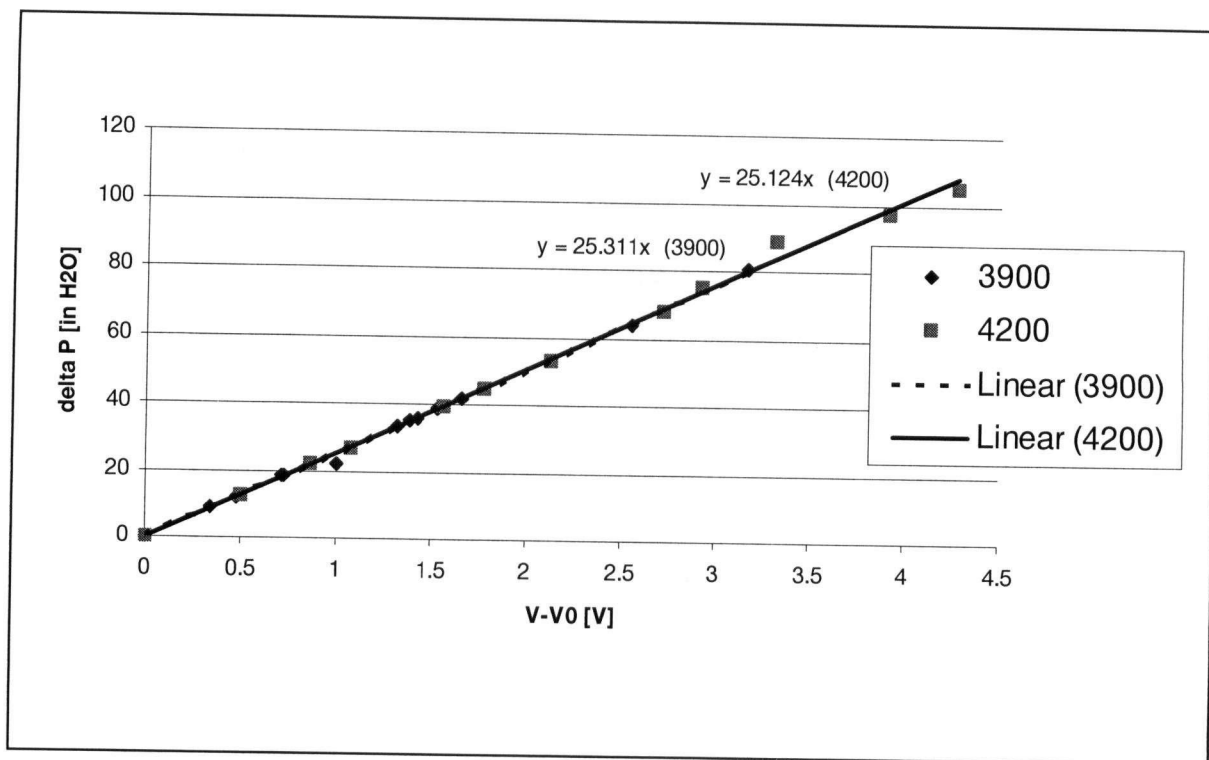


Figure A.5 First set of calibrations. Transmitter reading vs. voltage difference.

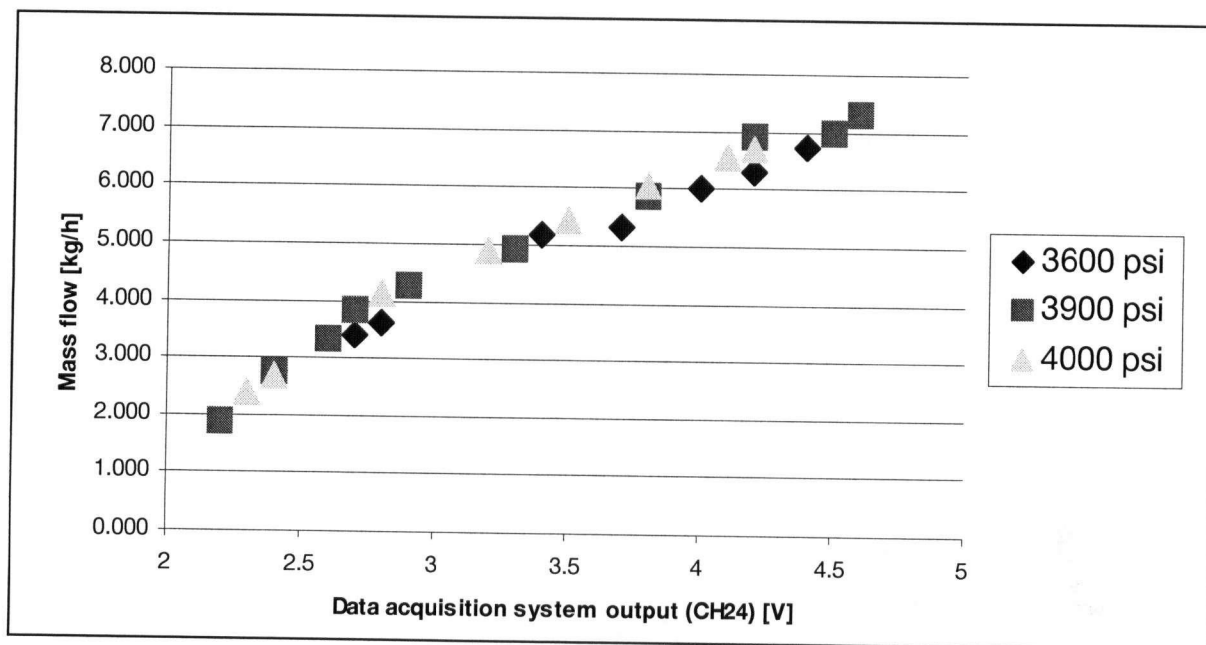


Figure A.6 Second set of calibrations. Mass flow rate vs. voltage.

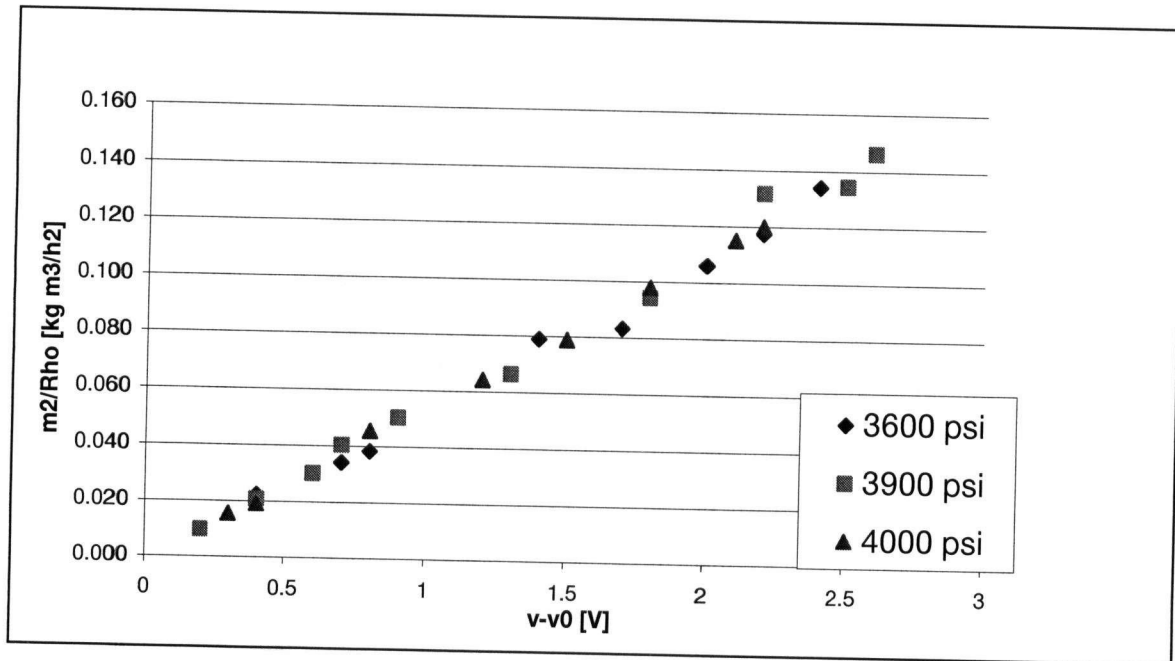


Figure A.7 Second set of calibrations. $m^2/\text{density}$ vs. voltage difference.

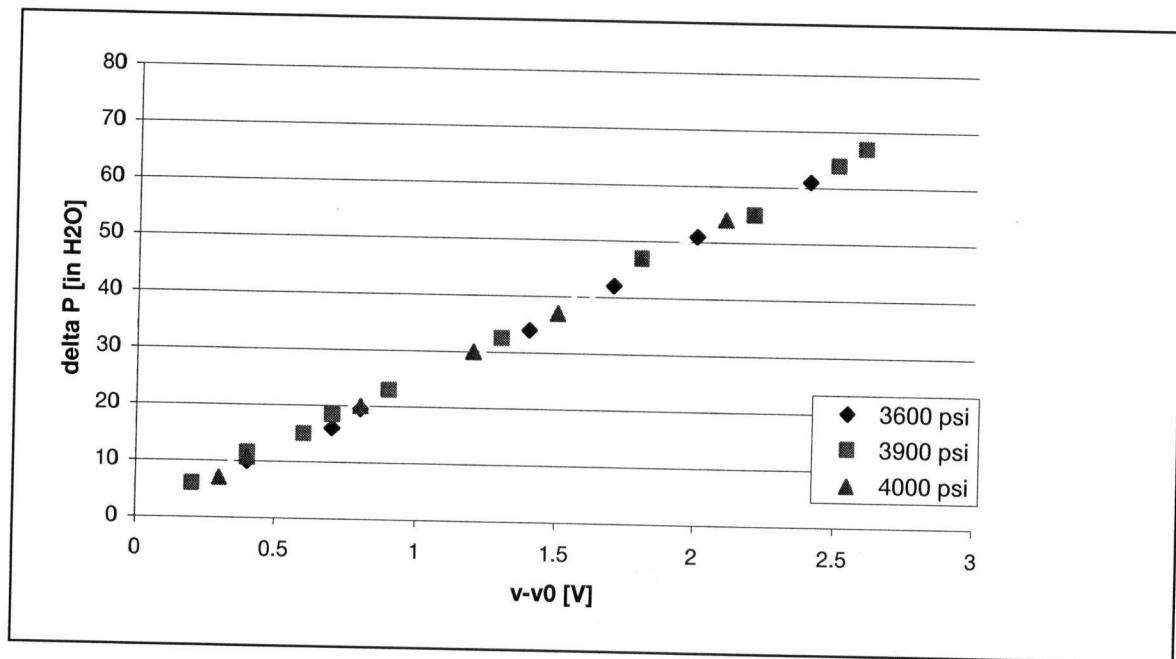


Figure A.8 Second set of calibrations. Transmitter reading vs. voltage difference.

Table A.1 First set of calibrations data at 3900 and 4200 psi

CALIBRATION AT 3900 PSI

System Pressure [psia]	Temperature side [C]	Density @ high pressure [kg/m ³]	Flow meter [l/min]	Temperature at Flow meter outlet [C]	Pressure at Flow meter inlet [psia]	Absolute Pressure at Flow meter inlet [psia]	Density @ low pressure (Flow meter inlet) [kg/m ³]	Mass Flow [kg/h]	CH ₂ 4 [V]	V-V0	m ² /Rho	delta P Foxboro [in. H ₂ O]	m ² /Rho/ (V-V0)	delta P Foxboro/ (V-V0)
3914.5	30	347.7	0.00	19.3	0.00	14.50	1.10	0.00	1.9976	0	0	0.02	0	0
3914.5	37.4	336.26	28.85	15.3	0.00	14.50	1.32	2.29	2.34	0.34	0.016	8.75	0.046	25.55
3914.5	35.6	339	35.50	17.3	0.35	14.85	1.36	2.89	2.48	0.48	0.025	12.03	0.052	25.20
3914.5	36	338.38	38.10	15.1	0.55	15.05	1.39	3.17	2.71	0.71	0.030	18.25	0.042	25.62
3914.5	34.3	341.03	38.10	17.1	0.55	15.05	1.38	3.15	2.72	0.72	0.029	18.41	0.040	25.48
3914.5	37.9	335.56	44.88	16.5	1.06	15.56	1.43	3.84	2.99	1.00	0.044	22.05	0.044	22.14
3914.5	38.8	334.28	48.12	14.5	1.31	15.81	1.46	4.22	3.32	1.32	0.053	33.51	0.040	25.44
3914.5	37.3	336.4	50.51	16.5	1.49	15.99	1.47	4.39	3.38	1.38	0.059	35.21	0.042	25.47
3914.5	34.6	340.56	49.75	14.7	1.43	15.93	1.47	4.44	3.42	1.42	0.056	36.07	0.040	25.39
3914.5	35.7	338.85	52.17	15.4	1.62	16.12	1.48	4.65	3.53	1.53	0.064	39.02	0.042	25.46
3914.5	33.9	341.65	54.40	16.2	1.79	16.29	1.50	4.88	3.66	1.66	0.070	42	0.042	25.26
3914.5	35.7	338.85	63.36	14.0	2.47	16.97	1.57	5.97	4.55	2.55	0.105	63.59	0.041	24.91
3914.5	38.3	334.99	65.79	14.1	2.65	17.15	1.59	6.26	5.17	3.17	0.117	80.64	0.037	25.42
average		338.73											0.039	

CALIBRATION AT 4200 PSI

System Pressure [psia]	Temperature side [C]	Density @ high pressure [kg/m ³]	Flow meter [l/min]	Temperature at Flow meter outlet [C]	Pressure at Flow meter inlet [psia]	Absolute Pressure at Flow meter inlet [psia]	Density @ low pressure (Flow meter inlet) [kg/m ³]	Mass Flow [kg/h]	CH ₂ 4 [V]	V-V0	m ² /Rho	delta P Foxboro [in. H ₂ O]	m ² /Rho/ (V-V0)	delta P Foxboro/ (V-V0)
4214.5	37	360.33	36.65	13.9	0.56	15.06	1.39	3.06	2.50	0.50	0.026	12.5	0.052	24.98
4214.5	46.3	346.34	44.68	14.3	0.92	15.42	1.43	3.82	2.86	0.86	0.042	21.91	0.049	25.41
4214.5	37.8	359.13	50.00	13.7	1.21	15.71	1.45	4.36	3.07	1.07	0.053	27.14	0.049	25.31
4214.5	48	343.94	59.64	14.1	1.63	16.13	1.49	5.34	3.56	1.56	0.083	39.53	0.053	25.30
4214.5	37	360.33	62.57	13.9	1.79	16.29	1.51	5.66	3.77	1.77	0.089	44.9	0.050	25.33
4214.5	49.2	342.30	65.50	14.0	2.04	16.54	1.53	6.02	4.13	2.13	0.106	53.36	0.050	25.02
4214.5	49.5	341.90	72.99	14.3	2.64	17.14	1.58	6.94	4.72	2.72	0.141	67.91	0.052	24.94
4214.5	48.4	343.39	75.00	14.5	2.91	17.41	1.61	7.24	4.92	2.92	0.153	75.12	0.052	25.70
4214.5	45.1	348.15	77.98	15.1	3.28	17.78	1.64	7.67	5.32	3.32	0.169	88.73	0.051	26.71
4214.5	40.5	355.07	80.43	15.3	3.78	18.28	1.68	8.13	5.91	3.91	0.186	97.5	0.048	24.92
4214.5	39	357.32	84.99	16.1	4.07	18.57	1.71	8.70	6.27	4.27	0.212	105.2	0.050	24.62
average		350.75		13.3									0.046	

Table A.2 Second set of calibrations, data at 3600, 3900 and 4000 psi

CALIBRATION AT 3600 PSI														
System Pressure [Psi]	T surface high Pressure side [C]	Density @ high g/m ³	Flow meter [l/min]	Temperature @ Flow meter outlet [C]	Pressure at Flow meter inlet [Psi]	Absolute Pressure at Flow meter inlet [Psi]	Density @ low (Flow meter inlet) [kg/m ³]	Mass Flow [kg/h]	CH24 [V]	V-V0	m ² /Rho	delta P Foxboro [in. H ₂ O]	m ² /Rho/ (V-V0)	delta P Foxboro/ (V-V0)
3614.5	20.7	339.28	34.46	18.0	0.11	14.61	1.33	2.76	2.4	0.40	0.022	10	0.056	24.94
3614.5	20.8	339.11	42.31	18.0	0.19	14.69	1.34	3.40	2.7	0.70	0.034	16	0.049	22.82
3614.5	20.9	339.11	44.74	18.0	0.22	14.72	1.34	3.60	2.8	0.80	0.038	19.5	0.048	24.34
3614.5	20.9	338.95	63.42	17.5	0.38	14.88	1.36	5.17	3.4	1.40	0.079	34	0.056	24.27
3614.5	20.9	338.95	64.86	17.5	0.44	14.94	1.37	5.31	3.7	1.70	0.083	42	0.049	24.69
3614.5	20.9	338.95	72.73	17.5	0.53	15.03	1.37	5.99	4	2.00	0.106	51	0.053	25.49
3614.5	20.9	338.95	76.53	17.5	0.54	15.04	1.37	6.31	4.2	2.20	0.117	55	0.053	24.99
3614.5	20.7	339.28	81.30	17.5	0.64	15.14	1.38	6.75	4.4	2.40	0.134	61	0.056	25.41
average	20.8	339.07		17.7									0.052	

CALIBRATION AT 3900 PSI														
System Pressure [Psi]	T surface high Pressure side [C]	Density @ high g/m ³	Flow meter [l/min]	Temperature @ Flow meter outlet [C]	Pressure at Flow meter inlet [Psi]	Absolute Pressure at Flow meter inlet [Psi]	Density @ low (Flow meter inlet) [kg/m ³]	Mass Flow [kg/h]	CH24 [V]	V-V0	m ² /Rho	delta P Foxboro [in. H ₂ O]	m ² /Rho/ (V-V0)	delta P Foxboro/ (V-V0)
3914.5	20.9	364.20	23.58	18.5	0.06	14.56	1.33	1.88	2.2	0.20	0.01	6	0.048	29.85
3914.5	20.9	364.20	34.46	18.5	0.12	14.62	1.33	2.75	2.4	0.40	0.02	11.6	0.052	28.93
3914.5	20.7	364.55	41.38	18.5	0.17	14.67	1.34	3.32	2.6	0.60	0.03	15	0.050	24.96
3914.5	20.7	364.55	46.69	18.5	0.52	15.02	1.37	3.83	2.7	0.70	0.04	18.5	0.057	26.39
3914.5	20.9	364.20	53.05	18.5	0.27	14.77	1.34	4.28	2.9	0.90	0.05	23	0.056	25.53
3914.5	20.8	364.37	60.54	18.5	0.36	14.86	1.35	4.92	3.3	1.30	0.07	32.5	0.051	24.98
3914.5	20.9	364.20	71.34	18.0	0.51	15.01	1.37	5.86	3.8	1.80	0.09	47	0.052	26.10
3914.5	20.8	364.37	83.92	18.0	0.59	15.09	1.38	6.93	4.2	2.20	0.13	55	0.060	24.99
3914.5	20.9	364.20	84.27	18.0	0.68	15.18	1.38	7.00	4.5	2.50	0.13	64	0.054	25.59
3914.5	20.7	364.55	88.89	19.0	0.56	15.06	1.37	7.30	4.6	2.60	0.15	67	0.056	25.76
average	20.8	364.34		18.4									0.054	

CALIBRATION AT 4000 PSI														
System Pressure [Psi]	T surface high Pressure side [C]	Density @ high g/m ³	Flow meter [l/min]	Temperature @ Flow meter outlet [C]	Pressure at Flow meter inlet [Psi]	Absolute Pressure at Flow meter inlet [Psi]	Density @ low (Flow meter inlet) [kg/m ³]	Mass Flow [kg/h]	CH24 [V]	V-V0	m ² /Rho	delta P Foxboro [in. H ₂ O]	m ² /Rho/ (V-V0)	delta P Foxboro/ (V-V0)
4014.5	20.8	372.91	30.23	17.50	0.01	14.51	1.33	2.40	2.3	0.301	0.02	7	0.051	23.26
4014.5	20.7	373.09	33.56	18.00	0.07	14.57	1.33	2.68	2.4	0.401	0.02	10.7	0.048	26.68
4014.5	20.7	373.09	51.19	17.50	0.18	14.68	1.34	4.12	2.8	0.801	0.05	20	0.057	24.97
4014.5	20.8	372.91	60.36	17.50	0.29	14.79	1.35	4.89	3.2	1.201	0.06	30	0.053	24.98
4014.5	20.8	372.91	66.45	17.50	0.39	14.89	1.36	5.42	3.5	1.501	0.08	37	0.053	24.65
4014.5	20.9	372.74	73.62	18.00	0.50	15	1.37	6.04	3.8	1.801	0.10	47	0.054	26.10
4014.5	20.8	372.91	79.37	18.00	0.58	15.08	1.38	6.55	4.1	2.101	0.12	54	0.055	25.70
4014.5	20.8	372.91	81.08	17.50	0.55	15.05	1.38	6.69	4.2	2.201	0.12	55	0.055	24.99
average	20.8	372.94		17.7									0.053	

Table A.3 Uncertainty in voltage, 2,4 DNP and ammonium sulphate experiments

RUN		Deviation from the voltages [%]	Deviation from the mean (y- y _m)	Deviation^2	Deviation/USD (used to apply Chauvenet's criterion)	New deviation	Deviation^2
2	max	0.07335	-0.00222	4.948E-06	-6.017E-02	0.00522	2.7288E-05
	min	0.07738	0.00180	3.256E-06	4.882E-02	0.00925	8.5612E-05
2b	max	0.06356	-0.01202	1.445E-04	-3.252E-01	-0.00457	2.0922E-05
	min	0.08848	0.01290	1.665E-04	3.490E-01	0.02035	4.1415E-04
2c	max	0.07146	-0.00412	1.698E-05	-1.115E-01	0.00333	1.1074E-05
	min	0.01761	-0.05797	3.361E-03	-1.568E+00	-0.05052	2.5527E-03
4	max	0.13178	0.05621	3.159E-03	1.521E+00	0.06366	4.0521E-03
	min	0.15527	0.07969	6.350E-03	2.156E+00	0.08714	7.5927E-03
4b	max	0.06872	-0.00686	4.709E-05	-1.856E-01	0.00059	3.4322E-07
	min	0.00982	-0.06576	4.324E-03	-1.779E+00	-0.05831	3.4004E-03
6	max	0.05025	-0.02532	6.413E-04	-6.851E-01	-0.01788	3.1957E-04
	min	0.04238	-0.03320	1.102E-03	-8.981E-01	-0.02575	6.6316E-04
6b	max	0.01776	-0.05782	3.343E-03	-1.564E+00	-0.05037	2.5372E-03
	min	0.06062	-0.01495	2.236E-04	-4.045E-01	-0.00750	5.6313E-05
6c	max	0.06887	-0.00671	4.501E-05	-1.815E-01	0.00074	5.4687E-07
	min	0.06928	-0.00630	3.966E-05	-1.704E-01	0.00115	1.3240E-06
7	max	0.09162	0.01604	2.574E-04	4.340E-01	0.02349	5.5182E-04
	min	0.20220	0.12662	1.603E-02	3.425E+00	0	0
	mean:	0.07558	U.S.D:	3.697E-02	New mean:	0.06813	
						USD:	3.7322E-02
					Voltage uncertainty = V± 0.04%		

Table A.4 Uncertainty in mass flow. 2,4 DNP and ammonium sulphate experiments

RUN	2	2b	2c	4	4b	6	6b	6c	7
Oxygen Flow [kg/h]	1.02	0.83	0.59	1.00	0.81	0.96	0.86	0.68	1.44
Stoichiometric oxygen [kg/h]	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Voltage [V]	2.0566	2.039	2.0211	2.0554	2.0374	2.0512	2.0412	2.03	2.11
$wR = R * \left[\sum \left(\frac{a_i * w_i}{y_i} \right)^2 \right]^{1/2}$	$\dot{m} = 0.23 * \rho^{1/2} * (V - V_0)^{1/2}$								
a1	1	1	1	1	1	1	1	1	1
y1	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
w1	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
a2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
y2	364.34	364.34	364.34	364.34	364.34	364.34	364.34	364.34	364.34
w2	4.58	4.58	4.58	4.58	4.58	4.58	4.58	4.58	4.58
a3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
y3	0.0536	0.036	0.0181	0.0524	0.0344	0.0482	0.0382	0.0238	0.1072
w3 (0.04% of V)	8.23E-04	8.16E-04	8.08E-04	8.22E-04	8.15E-04	8.20E-04	8.16E-04	8.11E-04	8.44E-04
Wf	0.0134	0.013	0.0146	0.0134	0.013	0.0132	0.013	0.0136	0.0164
Oxygen excess with average flow [%]	12.92	-7.45	-34.46	11.64	-9.53	7.06	-4.62	-24.74	59.68
Oxygen excess with average flow+Wf [%]	14.411	-6.004	-32.83	13.123	-8.084	8.5222	-3.173	-23.23	61.504
Oxygen excess uncertainty [%]	1.49	1.44	1.63	1.48	1.45	1.47	1.44	1.51	1.83

Appendix B Gas flow meter calibration report

1. Objectives:

To calibrate the measurements obtained with the SCWO gas flow meter (AL 425 Canadian Meter Company Limited), by using an Equimeter RC-M-415 as a standard.

2. Set up:

We located both flow meters in series; the standard preceding the SCWO one, (Figure B.1). The gas source consisted of a compressed air tank with a pressure regulator, which allowed us to change the air's outlet pressure, and the flow entering the flow meters. We assumed that there was no pressure drop inside the flow meters, which was corroborated by measuring the differential pressure between inlet and outlet of the device (less than 1 psi for all measurements).

Additionally, it was assumed that there was no pressure drop between both flow meters.

3. Procedure:

- a) Set the pressure regulator to 10 psi, and check for leaks on both flow meters, and their connecting lines.

⇒ No leaks were detected

- b) Set the pressure regulator to different pressures and take measurements with both flow meters.

The standard flow meter reads the measurement in clockwise cycles of 0.01 m^3 .

The SCWO flow meter measured 1 cubic foot per revolution

- c) Develop a corrections table for the SCWO flow meter, based on the measurements from the standard flow meter

4. Error analysis

The precision of the instrument was of 5% or 0.05 ft^3 , taken from its minimum division divided by 2.

5. Conclusions

⇒ The SCWO gas flow meter was calibrated against a standard flow meter

⇒ A correction chart was developed, which should be consulted whenever measurements with the object flow meters are taken.

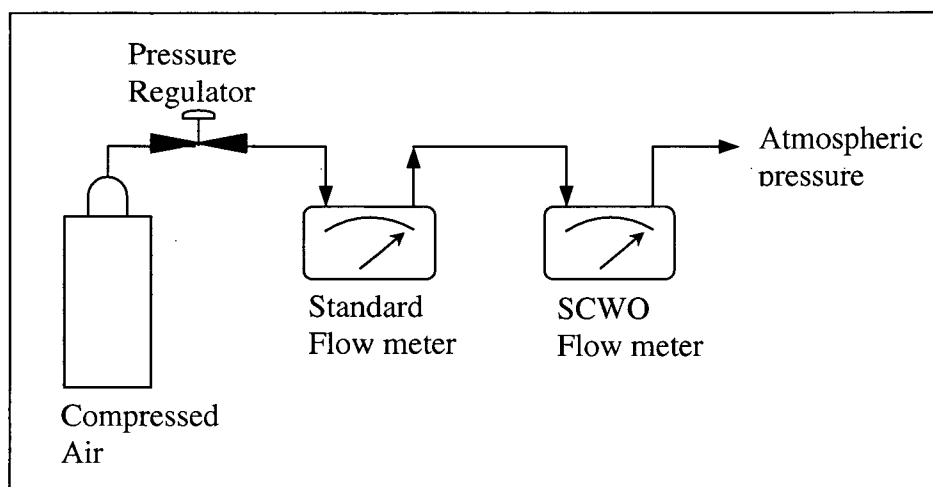


Figure B.1 Schematic of the calibration setup

Table B.1 Gas Flow measurements. Corrections table

MEASURED FLOW [FT ^3/SEC] (SCWO flow meter)	MEASURED FLOW [L/SEC] (SCWO flow meter)	CORRECT FLOW [L/SEC] (Standard flow meter)	MEASURED FLOW [FT ^3/SEC] (SCWO flow meter)	MEASURED FLOW [L/SEC] (SCWO flow meter)	CORRECT FLOW [L/SEC] (Standard flow meter)
0.00353	0.1	0.158	0.02154	0.61	0.530
0.00388	0.11	0.162	0.02189	0.62	0.537
0.00424	0.12	0.166	0.02225	0.63	0.543
0.00459	0.13	0.170	0.02260	0.64	0.550
0.00494	0.14	0.175	0.02295	0.65	0.557
0.00530	0.15	0.180	0.02331	0.66	0.563
0.00565	0.16	0.186	0.02366	0.67	0.569
0.00600	0.17	0.191	0.02401	0.68	0.575
0.00636	0.18	0.197	0.02436	0.69	0.582
0.00671	0.19	0.204	0.02472	0.7	0.588
0.00706	0.2	0.210	0.02507	0.71	0.594
0.00742	0.21	0.217	0.02542	0.72	0.599
0.00777	0.22	0.224	0.02578	0.73	0.605
0.00812	0.23	0.231	0.02613	0.74	0.611
0.00847	0.24	0.238	0.02648	0.75	0.617
0.00883	0.25	0.246	0.02684	0.76	0.623
0.00918	0.26	0.253	0.02719	0.77	0.628
0.00953	0.27	0.261	0.02754	0.78	0.634
0.00989	0.28	0.269	0.02790	0.79	0.639
0.01024	0.29	0.277	0.02825	0.8	0.645
0.01059	0.3	0.285	0.02860	0.81	0.650
0.01095	0.31	0.293	0.02895	0.82	0.656
0.01130	0.32	0.301	0.02931	0.83	0.662
0.01165	0.33	0.310	0.02966	0.84	0.667
0.01201	0.34	0.318	0.03001	0.85	0.673
0.01236	0.35	0.326	0.03037	0.86	0.678
0.01271	0.36	0.335	0.03072	0.87	0.684
0.01306	0.37	0.343	0.03107	0.88	0.690
0.01342	0.38	0.351	0.03143	0.89	0.696
0.01377	0.39	0.360	0.03178	0.9	0.701
0.01412	0.4	0.368	0.03213	0.91	0.707
0.01448	0.41	0.376	0.03249	0.92	0.714
0.01483	0.42	0.385	0.03284	0.93	0.720
0.01518	0.43	0.393	0.03319	0.94	0.726
0.01554	0.44	0.401	0.03355	0.95	0.733
0.01589	0.45	0.409	0.03390	0.96	0.739
0.01624	0.46	0.418	0.03425	0.97	0.746
0.01660	0.47	0.426	0.03460	0.98	0.753
0.01695	0.48	0.434	0.03496	0.99	0.760
0.01730	0.49	0.442	0.03531	1	0.768
0.01766	0.5	0.449	0.03566	1.01	0.775
0.01801	0.51	0.457	0.03602	1.02	0.783
0.01836	0.52	0.465	0.03637	1.03	0.792
0.01871	0.53	0.473	0.03672	1.04	0.800
0.01907	0.54	0.480	0.03708	1.05	0.809
0.01942	0.55	0.487	0.03743	1.06	0.818
0.01977	0.56	0.495	0.03778	1.07	0.828
0.02013	0.57	0.502	0.03814	1.08	0.838
0.02048	0.58	0.509	0.03849	1.09	0.848
0.02083	0.59	0.516	0.03884	1.1	0.858
0.02119	0.6	0.523			

Appendix C Thermocouples location with system's length

The inlet of the cold side of the regenerative heat exchanger (RHX) has been taken as zero (the feed) and the outlet of its cold side as the effluent.

Table C.1 Thermocouples location in the SCWO pilot plant

Thermocouple	Type	Location in the system	Distance from feed [m]
RHX in (cold side)			0.00
PH1 in	Bulk	Preheater 1	6.90
PH2 in	Bulk	Preheater 2	11.80
PH2 out	Bulk	Preheater 2	16.07
B2	Bulk	Test Section	17.08
S10	Surface (bottom)	Test Section	17.14
S4	Surface (bottom)	Test Section	17.18
SB9	Surface (top)	Test Section	17.23
S9	Surface (bottom)	Test Section	17.33
SB8	Surface (top)	Test Section	17.42
S8	Surface (bottom)	Test Section	17.52
SB7	Surface (top)	Test Section	17.60
S7	Surface (bottom)	Test Section	17.69
SB6	Surface (top)	Test Section	17.76
S6	Surface (bottom)	Test Section	17.83
SB5	Surface (top)	Test Section	17.89
S5	Surface (bottom)	Test Section	17.92
SB4	Surface (top)	Test Section	17.98
SB3	Surface (top)	Test Section	18.11
S3	Surface (bottom)	Test Section	18.19
SB2	Surface (top)	Test Section	18.26
S2	Surface (bottom)	Test Section	18.34
SB1	Surface (top)	Test Section	18.41
S1	Surface (bottom)	Test Section	18.48
B3	Bulk	Test Section	18.55
S11	Surface (bottom)	Test Section	18.66
S12	Surface (bottom)	Test Section	18.82
S13	Surface (bottom)	Test Section	19.00
S14	Surface (bottom)	Test Section	19.18
S15	Surface (bottom)	Test Section	19.30
S16	Surface (bottom)	Test Section	19.38
S17	Surface (bottom)	Test Section	19.52
S18	Surface (bottom)	Test Section	19.65
S19	Surface (bottom)	Test Section	19.79
S20	Surface (bottom)	Test Section	19.95

Thermocouple	Type	Location in the system	Distance from feed [m]
B4	Bulk	Test Section	20.44
R1B	Surface	Reactor	27.32
R1A	Surface	Reactor	33.54
RL2	Bulk	Reactor	34.18
R2A	Surface	Reactor	34.21
R2B	Surface	Reactor	40.43
R3b	Surface	Reactor	41.04
R3a	Surface	Reactor	47.26
R4A	Surface	Reactor	47.90
R4B	Surface	Reactor	54.11
R5B	Surface	Reactor	54.76
R5A	Surface	Reactor	61.00
RL6	Bulk	Reactor	61.91
R6A	Surface	Reactor	61.94
R6B	Surface	Reactor	68.16
R7B	Surface	Reactor	68.80
R7A	Surface	Reactor	75.02
R8A	Surface	Reactor	75.66
R8B	Surface	Reactor	81.88
R9B	Surface	Reactor	82.51
R9A	Surface	Reactor	88.73
RL10	Bulk	Reactor	89.64
R10A	Surface	Reactor	89.67
R10B	Surface	Reactor	95.88
R11B	Surface	Reactor	96.52
R11A	Surface	Reactor	102.74
R12A	Surface	Reactor	103.40
R12B	Surface	Reactor	109.60
R13B	Surface	Reactor	110.21
R13A	Surface	Reactor	116.50
R14A	Surface	Reactor	117.10
R14B	Surface	Reactor	123.32
R15B	Surface	Reactor	123.96
R15A	Surface	Reactor	130.18
R16A	Surface	Reactor	130.81
R16B	Surface	Reactor	137.03
R17B	Surface	Reactor	137.64
RHX in (hot side)	Surface	RHX	143.71
RHX out (hot side)	Surface	RHX	150.14

continued

Appendix D Sample coolers validation

Temperature test for sample coolers

To test how fast the samples were cooled we proceeded as following:

- A 1/16" inconel thermocouple was inserted in the 1/4" sampling tube 2.5 cm downstream from the centre of the reactor's tube (see Figure 3.5 in Chapter 3). In the case of preheater 1 (PH 1), the selected thermocouple was 3/16" and the tube 3/8" (to avoid plugging of possible tarry material in this point)
- The system was warmed up and the reactor's temperature elevated up to 500 °C
- The cooling water valves were opened
- The needle sampling valves were opened to allow a flow of approximately 0.1 mL/sec pass through them, and
- The temperature measured by the thermocouples was registered by the data acquisition system.

The registered temperatures were always in the range of 200-250 °C, so the quenching of the samples was considered to be good enough to prevent reaction from occurring in the sampling ports.

Equation D.1 was used to know how long it took the hot fluid to travel from its location in the reactor to the tip of the thermocouple. A was the total area of the tube, considering the inserted thermocouple, L was the length between the reactor and the tip of the thermocouple (always 2.5 cm), and \dot{m} was the sample flow, approximately 0.1 mL/sec. The resulting time was 3.1 sec for PH 1 and 1.5 sec for the rest of the sampling ports (PH 2 in, PH 2 out, RL-2, RL-6, and RL-10).

$$t = \frac{A \cdot L}{\dot{m}} \quad [\text{D.1}]$$

Calculation of necessary rinsing times

The same principle of Equation D.1 was used to calculate the total necessary rinsing time for each sampling port, considering the total length of tube from the reactor to the sampling valve (see Figure D. 1). Both the portion of the sampling tubes containing the inserted thermocouple, and the free portions were considered. Equation D.1 was then varied as:

$$t_{\text{total}} = t_{\text{portion with thermocouple}} + t_{\text{portion without thermocouple}} \quad [\text{D.2}]$$

It resulted that the PH 1 had to be rinsed for at least 325 seconds (5.4 minutes) and the rest of the ports for at least 90 seconds (1.5 minutes) in order to evacuate at least one residence time.

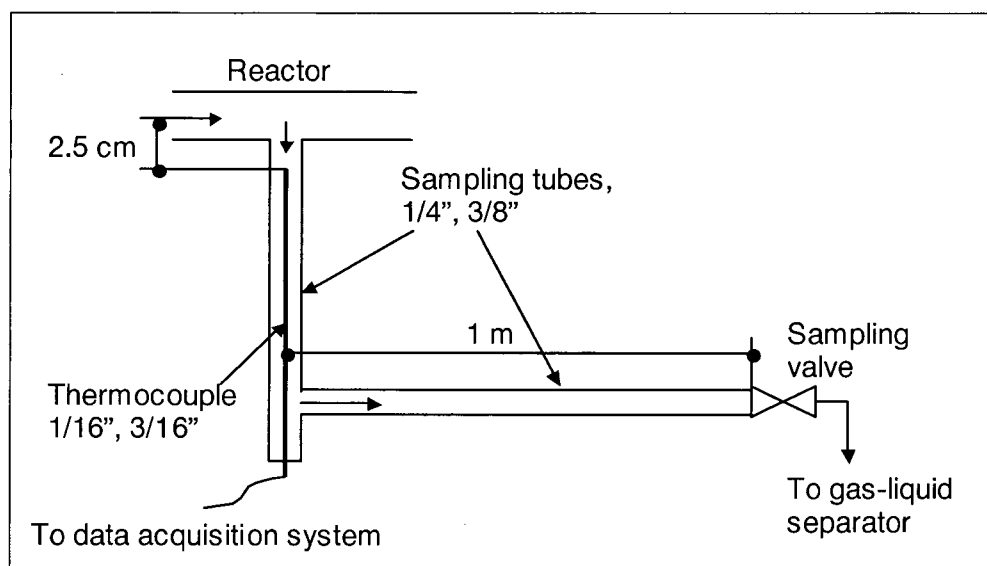


Figure D.1 Sampling ports (Cooling jacket not shown)

Appendix E Preparation for 2,4 DNP, ammonium sulphate and ammonia

The solubility of 2,4 DNP depends both on both the pH (fixed at around 9 for the wastes treated in this thesis) and the temperature of the solution. Table E.1 shows temperature-solubility relations for 2,4 DNP at different pHs, in both ammonium sulphate and ammonium hydroxide solutions. This table was used as a reference when setting the solubility temperatures for the feeds. The procedures followed to prepare both types of 2,4 DNP-based solutions were the following:

1. To prepare the 4% wt 2,4 DNP and 2% wt ammonium sulphate solution, the 200 L feed tank was filled with 100 litres of distilled water, then 4 kg of wet solid 2,4 dinitrophenol were added. Since the solubility of 2,4 DNP in ammonium sulphate solution is very low (see Table D.1); 2,4 DNP was first dissolved in a high pH solution with ammonium hydroxide, and 3130 mL of 99% purity sulphuric acid was added afterwards to achieve the desired sulphates concentration and pH. After this, the tank was filled up with more distilled water to reach 200 L. To dissolve all the 2,4 DNP solids, the solution was heated up to 85 °C, by means of a steam coil, and stirred with a mechanical stirrer and by bubbling in low-pressure nitrogen. During the process, the person preparing the solution wore a self-contained breathing apparatus that allowed them to perform the job safely.

When feed samples were taken from the feed tank, it was observed that not all the dinitrophenols had dissolved, and that only a 2.4% wt as 2,4 DNP solution was obtained. Additionally, the final concentration of ammonium sulphate was considerably lower than expected (only 0.39% wt), and the total ammonia concentration in the feed was much higher

than desired (6.67% wt). For this reason, the procedure to prepare the solution for the test without sulphates was changed, in order to try to dissolve the dinitrophenol in small batches.

2. The 2% DNP and ammonia solution was prepared as a set of 8 batches. The 2,4 dinitrophenol was purchased as 4, 1kg bottles of wet solid. 20L of deionised water was poured into a large stockpot equipped with a heating tape on the outside. As the water was heating, one half of a 2,4 DNP bottle was added. To this mixture was added 1200 ml of a 30% ammonia solution. Sufficient water was added to obtain an approximate volume of 25L. An overhead mixer was used to agitate the solids at the bottom of the pot until dissolved. Typically, dissolution occurred between 40-45°C. Each batch of 25L was transferred to a plastic container for transportation. Once in the laboratory, the 8, 25 litre containers were poured into the feed tank.

Table E.1 Solubility of 2,4 DNP solutions with temperature and pH⁵²

pH of solution	Solution	Temperature [C]	Solubility [% wt]
5	Ammonium sulphate	20	0.042
		40	0.081
		64	0.257
9	Ammonium hydroxide	20	0.12
		51.7	0.61
		75.3	1.11
11	Ammonium hydroxide	20	0.704
		40	1.785
		68	5.516

Appendix F Phenol experiments. Results and mass balances

Channel configuration for the Data Acquisition System

Table F.1 Channel configuration. Phenol experiments

Channel	Port	Position
1	PH2-in	PH2-in
2	PH2-out	PH2-out
3	E-2	B2
4	E-11	B3
5	E-25	B4
6	RL2-in	RL2-in
7	RL6-in	RL6-in
8	RL10-in	RL10-in
9	E-5	S7
10	E-11	SB8
11	E-4	S10
12	E-22	S19
13	E-24	S20
14	E-23	SB20
15	R1-B	R1B
16	R3-B	R3B
17	R8-A	R8A
18	R15-A	R15A
19	R15-B	R15-B
20	R11-A	R11-A
21		PIC 431
22		PT431
23		-
24		O ₂

Temperatures entered in text files for Matlab programs

Text files: run1.txt, run2.txt, run3.txt... and run9.txt

Matlab files: ratelawsanalysis.m, convephenol.m, temprofiles2.m and temprofiles4.m

Table F.2 Temperatures for text files. Phenol experiments

Distance from the feed [m]	Registered temperature	Observations
0	Feed	Ambient temperature
6.90	PH1 in RHX out, (cold side)	Calculated with MATLAB (RHEX.m) using TE 123 (obtained from Fortran program), and assuming no losses.
11.80	PH2 in	Measured (CH 1)
16.07	PH2 out	Measured (CH 2)
17.08	B2	Measured (CH3)
18.76	B3	Measured (CH4)
20.44	B4	Measured (CH5)
34.18	RL-2	Measured (CH6)
61.91	RL-6	Measured (CH7)
89.64	RL-10	Measured (CH8)
137.64	Reactor End	Measured (CH 18)
143.71	RHX in (Hot side)	Assumed = to Reactor's end
150.137	RHX out, TE 123	Calculated by Fortran program

PHENOL RUN 1

Date of test: Run 1.July11/01
 Data File jul11-1a.txt
 Feed Phenol
 Feed concentration 4.036 %wt as Phenol
 Feed Flow rate 0.780 litres/min
 O2 flow rate 5.026 kg/h 83.7667 g/min 10 % Excess
 Stoichiometric O2 flow rate 4.57 kg/h 76.1667 g/min
 Vent Gas Flow rate 75.51 litres/min at about 300K, 1 atm
 = 3.0675 gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2_in	RL6_in	Effluent
Total Organic Carbon (µgC/g)	32000	21500	16300	11020	8180	5920.0
Phenol (µg/g)	40357		13360			795.0

Gaseous Stream Analysis

Sample Location	Effluent	PH2out
Oxygen (%)	36.87	75.35
Carbon Monoxide (%)	8.26	2.3
Carbon Dioxide (%)	53.33	19.03
Hydrogen (%)	1.2	0
water vapor [%] (ambient temperature =26	0.34	3.32

Abbreviation

Sample Location

Feed Feed prior to test
 Effluent Final effluent
 PH2_in Preheater 2 Inlet
 PH2_out Preheater 2 Outlet
 RL2_in Reactor Section 2 Inlet
 RL6_in Reactor Section 6 Inlet
 RL10_in Reactor Section 10 Inlet
 gaseous stream Vent gas (gas from gas-liquid

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
		1	12.011	15.9994	1	% of infl.	% of infl.
Component	M.W.		g/min	g/min			
Feed							
TOC	n/a		in PhOH	0		0	0
Phenol (C6H6O)	94.11		24.105	5.352		100.0%	6.0%
Oxygen (O2)	32.00		0	83.767		0.0%	94.0%
Total Influent			24.105	89.118			
Liquid Effluent							
Total Carbon less TOC (assume CO3)			not measured				
TOC (assume CHx)	12.011		4.618	0.000		19.2%	0
Phenol (C6H6O)	94.11		0.475	0.105		2.0%	0.1%
Vent Gas							
Oxygen (O2)	32.00			36.1904			40.6%
Carbon Monoxide (CO)	28.01		3.0405	4.0540		12.6%	4.5%
Carbon Dioxide (CO2)	44.01		19.6309	52.3490		81.4%	58.7%
Hydrogen (H2)	2.016	0.0742					
Total Effluents		0.074	27.764	92.699			
Recovery (effluent/influent)x100	%		115	104			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion/ yield
TOC	32000	5920.0	0.815
Phenol	40357	795.0	0.98
CO yield			0.121815822
CO2 yield			0.786493678

PHENOL RUN 2

Date of test: Run 2.July11/01
 Data File jul11-1b.txt
 Feed Phenol
 Feed concentration 4.036 %wt as Phenol
 Feed Flow rate 0.780 litres/min
 O2 flow rate 6.130 kg/h 102.1667 g/min 34 % Excess
 Stoichiometric O2 flow rate 4.57 kg/h
 Vent Gas Flow rate 73.10 litres/min at about 300K, 1 atm
 = 2.9696 gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2_in	RL6_in	Effluent
Total Organic Carbon (µgC/g)	32000					6920.0
Phenol (µg/g)	40357					2042.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	52.22
Carbon Monoxide (%)	6.58
Carbon Dioxide (%)	38.57
Hydrogen (%)	0.76

Abbreviation

Sample Location

Feed Feed prior to test
 Effluent Final effluent
 PH2_in Preheater 2 Inlet
 PH2_out Preheater 2 Outlet
 RL2_in Reactor Section 2 Inlet
 RL6_in Reactor Section 6 Inlet
 RL10_in Reactor Section 10 Inlet
 gaseous stream Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
		1	12.011	15.9994	1	% of infl.	% of infl.
Component	M.W.		g/min	g/min			
Feed							
TOC	n/a		in PhOH	0		0	0
Phenol (C6H6O)	94.11		24.105	5.352		100.0%	5.0%
Oxygen (O2)	32.00		0	102.167		0.0%	95.0%
Total Influent			24.105	107.518			
LIQUID EFFLUENT							
Total Carbon less TOC (assume			not measured				
TOC (assume CHx)	12.011		5.398	0.000		22.4%	0
Phenol (C6H6O)	94.11		1.220	0.271		5.1%	0.3%
Vent Gas							
Oxygen (O2)	32.00			49.6216			46.2%
Carbon Monoxide (CO)	28.01		2.3448	3.1264		9.7%	2.9%
Carbon Dioxide (CO2)	44.01		13.7446	36.6522		57.0%	34.1%
Hydrogen (H2)	2.016	0.0455					
Total Effluents		0.045	22.707	89.671			
Recovery (effluent/influent)x100 %			94	83			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion/yield
TOC	32000	6920.0	0.78
Phenol	40357	2042.0	0.95
CO yield			0.093942573
CO2 yield			0.550663382

PHENOL RUN 3

Date of test: Run 3.July11/01
 Data File jul11-2b.txt
 Feed Phenol
 Feed concentration 4.036 %wt as Phenol
 Feed Flow rate 0.780 litres/min
 O2 flow rate 6.360 kg/h 106 g/min 39 % Excess
 Stoichiometric O2 flow rate 4.57 kg/h
 Vent Gas Flow rate NOT MEASURED litres/min at about 300K, 1 atm
 = gmol/min

Aqueous Stream Analysis

RL6_IN E

Sample Location	Feed	PH2 in	PH2 out	RL2_in	RL6_in	Effluent
Total Organic Carbon (µgC/g)	32000					73.0
Phenol (µg/g)	40357					8.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	
Carbon Monoxide (%)	
Carbon Dioxide (%)	
Hydrogen (%)	

Abbreviation

Sample Location

Feed Feed prior to test
 Effluent Final effluent
 PH2_in Preheater 2 Inlet
 PH2_out Preheater 2 Outlet
 RL2_in Reactor Section 2 Inlet
 RL6_in Reactor Section 6 Inlet
 RL10_in Reactor Section 10 Inlet
 gaseous stream Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
		1	12.011	15.9994	1	% of infl.	% of infl.
Component	M.W.		g/min	g/min			
Feed							
TOC	n/a		in PhOH	0		0	0
Phenol (C6H6O)	94.11		24.105	5.352		100.0%	4.8%
Oxygen (O2)	32.00		0	106.000		0.0%	95.2%
Total Influent			24.105	111.352			
LIQUID EFFLUENT							
Total Carbon less TOC (assume			not measured				
TOC (assume CHx)	12.011		0.057	0.000		0.2%	0
Phenol (C6H6O)	94.11		0.005	0.001		0.0%	0.0%
Vent Gas							
Oxygen (O2)	32.00			0.0000			0.0%
Carbon Monoxide (CO)	28.01		0.0000	0.0000		0.0%	0.0%
Carbon Dioxide (CO2)	44.01		0.0000	0.0000		0.0%	0.0%
Hydrogen (H2)	2.016	0.0000					
Total Effluents		0.000	0.062	0.001			
Recovery (effluent/influent)x100 %			0	0			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion/yield
TOC	32000	73.0	0.99771875
Phenol	40357	8.0	0.9998
CO yield			0
CO2 yield			0

PHENOL RUN 4

Date of test: Run 4.July11/01
 Data File jul11-2b.txt
 Feed Phenol
 Feed concentration 4.036 %wt as Phenol
 Feed Flow rate 0.780 litres/min
 O₂ flow rate 6.130 kg/h 102.1667 g/min 34 % Excess
 Stoichiometric O₂ flow rate 4.57 kg/h
 Vent Gas Flow rate NOT MEASURED litres/min at about 300K, 1 atm
 = gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2_in	RL6_in	Effluent
Total Organic Carbon (µgC/g)	32000					4540.0
Phenol (µg/g)	40357					932.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	50.1
Carbon Monoxide (%)	8.09
Carbon Dioxide (%)	39.65
Hydrogen (%)	0.92

Abbreviation

Sample Location

Feed Feed prior to test
 Effluent Final effluent
 PH2_in Preheater 2 Inlet
 PH2_out Preheater 2 Outlet
 RL2_in Reactor Section 2 Inlet
 RL6_in Reactor Section 6 Inlet
 RL10_in Reactor Section 10 Inlet
 gaseous stream Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
Component	M.W.	1	12.011	15.9994	1	% of infl.	% of infl.
Feed							
TOC	n/a		in PhOH	0		0	0
Phenol (C ₆ H ₆ O)	94.11		24.105	5.352		100.0%	5.0%
Oxygen (O ₂)	32.00		0	102.167		0.0%	95.0%
Total Influent			24.105	107.518			
LIQUID EFFLUENT							
Total Carbon less TOC (assume C)			not measured				
TOC (assume CH _x)	12.011		3.541	0.000		14.7%	0
Phenol (C ₆ H ₆ O)	94.11		0.557	0.124		2.3%	0.1%
Vent Gas							
Oxygen (O ₂)	32.00			0.0000			0.0%
Carbon Monoxide (CO)	28.01		0.0000	0.0000		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		0.0000	0.0000		0.0%	0.0%
Hydrogen (H ₂)	2.016	0.0000					
Total Effluents		0.000	4.098	0.124			
Recovery (effluent/influent)x100	%		17	0			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion
TOC	32000	4540.0	0.86
Phenol	40357	932.0	0.98
CO yield			0
CO ₂ yield			0

PHENOL RUN 5

Date of test: Run 5.July19/01
 Data File: jul19-1a.txt
 Feed: Phenol
 Feed concentration: 2.700 %wt as Phenol
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 4.180 kg/h 69.66667 g/min 34 % Excess
 Stoichiometric O₂ flow rate: 3.13 kg/h 52.16667
 Vent Gas Flow rate: 31.63 litres/min at about 300K, 1 atm
 = 1.2849 gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2 in	RL6 in	Effluent
Total Organic Carbon (µgC/g)	21550	15100	11440	8860	7480	4430.0
Phenol (µg/g)	27127	16026	11798	9372	5737	704.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	46.27
Carbon Monoxide (%)	8.91
Carbon Dioxide (%)	43.85
Hydrogen (%)	0.97

88.24
 0
 11.76
 0

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
RL10_in	Reactor Section 10 Inlet
gaseous stream	Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
		1	12.011	15.9994	1	% of infl.	% of infl.
Component	M.W.		g/min	g/min			
Feed							
TOC	n/a		in PhOH	0		0	0
Phenol (C ₆ H ₆ O)	94.11		16.203	3.597		100.0%	4.9%
Oxygen (O ₂)	32.00		0	69.667		0.0%	95.1%
Total Influent			16.203	73.264			
LIQUID EFFLUENT							
Total Carbon less TOC (assume CO ₃)			not measured				
TOC (assume CH _x)	12.011		3.455	0.000		21.3%	0
Phenol (C ₆ H ₆ O)	94.11		0.420	0.093		2.6%	0.1%
Vent Gas							
Oxygen (O ₂)	32.00			19.0246			26.0%
Carbon Monoxide (CO)	28.01		1.3739	1.8318		8.5%	2.5%
Carbon Dioxide (CO ₂)	44.01		6.7613	18.0302		41.7%	24.6%
Hydrogen (H ₂)	2.016	0.0251					
Total Effluents		0.025	12.011	38.980			
Recovery (effluent/influent)x100	%		74	53			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion
TOC	21550	4430.0	0.79
Phenol	27127	704.0	0.97
CO yield			0.081733252
CO ₂ yield			0.402245019

PHENOL RUN 6

Date of test: Run 6.July19/01
 Data File: jul19-1b.txt
 Feed: Phenol
 Feed concentration: 2.700 %wt as Phenol
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 3.100 kg/h 51.66667 g/min -1 % Excess
 Stoichiometric O2 flow rate: 3.13 kg/h
 Vent Gas Flow rate: 71.90 litres/min at about 300K, 1 atm
 = 2.9209 gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2_in	RL6_in	Effluent
Total Organic Carbon (µgC/g)	21550	16310	13230	12280	8480	5420.0
Phenol (µg/g)	27127	20434	16270	10505	6655	1531.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	52.66
Carbon Monoxide (%)	8.15
Carbon Dioxide (%)	38.42
Hydrogen (%)	0.77

Abbreviation

Sample Location

Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
RL10_in	Reactor Section 10 Inlet
gaseous stream	Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
		1	12.011	15.9994	1	% of infl.	% of infl.
Component	M.W.		g/min	g/min			
Feed							
TOC	n/a		in PhOH	0		0	0
Phenol (C6H6O)	94.11		16.203	3.597		100.0%	6.5%
Oxygen (O2)	32.00		0	51.667		0.0%	93.5%
Total Influent			16.203	55.264			
LIQUID EFFLUENT							
Total Carbon less TOC (assume CO)				not measured			
TOC (assume CHx)	12.011		4.228	0.000		26.1%	0
Phenol (C6H6O)	94.11		0.914	0.203		5.6%	0.4%
Vent Gas							
Oxygen (O2)	32.00			49.2182			89.1%
Carbon Monoxide (CO)	28.01		2.8566	3.8088		17.6%	6.9%
Carbon Dioxide (CO2)	44.01		13.4664	35.9103		83.1%	65.0%
Hydrogen (H2)	2.016	0.0453					
Total Effluents		0.045	21.465	89.140			
Recovery (effluent/influent)x100	%		132	161			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion
TOC	21550	5420.0	0.75
Phenol	27127	1531.0	0.94
CO yield			0.169944997
CO2 yield			0.801139484

PHENOL RUN 7

Date of test: Run 7.July25/01
 Data File jul25-2a
 Feed Phenol
 Feed concentration 2.700 %wt as Phenol
 Feed Flow rate 0.780 litres/min
 O2 flow rate 3.780 kg/h 63 g/min 21 % Excess
 Stoichiometric O2 flow rate 3.13 kg/h
 Vent Gas Flow rate 36.61 litres/min at about 300K, 1 atm
 = 1.4872 gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2 in	RL6 in	Effluent
Total Organic Carbon (µgC/g)	21700	15100	11200	8960	7010	4120.0
Phenol (µg/g)	27436	13133	10766	7488	5383	2750.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	46.53
Carbon Monoxide (%)	9.16
Carbon Dioxide (%)	43.4
Hydrogen (%)	0.91

77.95
 2.58
 19.08
 0.38

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
RL10_in	Reactor Section 10 Inlet
gaseous stream	Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
		1	12.011	15.9994	1	% of infl.	% of infl.
Component	M.W.		g/min	g/min			
Feed							
TOC	n/a		in PhOH	0		0	0
Phenol (C6H6O)	94.11		16.387	3.638		100.0%	5.5%
Oxygen (O2)	32.00		0	63.000		0.0%	94.5%
Total Influent			16.387	66.638			
LIQUID EFFLUENT							
Total Carbon less TOC (assume C)			not measured				
TOC (assume CHx)	12.011		3.214	0.000		19.6%	0
Phenol (C6H6O)	94.11		1.643	0.365		10.0%	0.5%
Vent Gas							
Oxygen (O2)	32.00			22.1436			33.2%
Carbon Monoxide (CO)	28.01		1.6348	2.1797		10.0%	3.3%
Carbon Dioxide (CO2)	44.01		7.7456	20.6548		47.3%	31.0%
Hydrogen (H2)	2.016	0.0273					
Total Effluents		0.027	14.237	45.343			
Recovery (effluent/influent)x100	%		87	68			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion
TOC	21700	4120.0	0.81
Phenol	27436		1.00
CO yield			0.096583876
CO2 yield			0.45761356

PHENOL RUN 8

Date of test: Run 8.July25/01
 Data File: jul25-2b
 Feed: Phenol
 Feed concentration: 2.700 %wt as Phenol
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 3.740 kg/h 62.33333 g/min 19 % Excess
 Stoichiometric O₂ flow rate: 3.13 kg/h
 Vent Gas Flow rate: 30.74 litres/min at about 300K, 1 atm
 = 1.2488 gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2 in	RL6 in	Effluent
Total Organic Carbon (µgC/g)	21700					1240.0
Phenol (µg/g)	27436					672.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	
Carbon Monoxide (%)	
Carbon Dioxide (%)	
Hydrogen (%)	

Abbreviation

Sample Location

Feed: Feed prior to test
 Effluent: Final effluent
 PH2_in: Preheater 2 Inlet
 PH2_out: Preheater 2 Outlet
 RL2_in: Reactor Section 2 Inlet
 RL6_in: Reactor Section 6 Inlet
 RL10_in: Reactor Section 10 Inlet
 gaseous stream: Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
Component	M.W.	1	12.011	15.9994	1	% of infl.	% of infl.
Feed			g/min	g/min			
TOC	n/a		in PhOH	0		0	0
Phenol (C ₆ H ₆ O)	94.11		16.387	3.638		100.0%	5.5%
Oxygen (O ₂)	32.00		0	62.333		0.0%	94.5%
Total Influent			16.387	65.972			
LIQUID EFFLUENT							
Total Carbon less TOC (assume CO ₃)			not measured				
TOC (assume CH _x)	12.011		0.967	0.000		5.9%	0
Phenol (C ₆ H ₆ O)	94.11		0.401	0.089		2.4%	0.1%
Vent Gas							
Oxygen (O ₂)	32.00			0.0000			0.0%
Carbon Monoxide (CO)	28.01		0.0000	0.0000		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		0.0000	0.0000		0.0%	0.0%
Hydrogen (H ₂)	2.016	0.0000					
Total Effluents		0.000	1.369	0.089			
Recovery (effluent/influent)x100	%		8	0			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion
TOC	21700	1240.0	0.94
Phenol	27436	672.0	0.98
CO yield			n.m
CO ₂ yield			n.m

PHENOL RUN 9

Date of test: Run 9.July25/01
 Data File: jul25-2b
 Feed: Phenol
 Feed concentration: 2.700 %wt as Phenol
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 3.740 kg/h 62.33333 g/min 19 % Excess
 Stoichiometric O2 flow rate: 3.13 kg/h
 Vent Gas Flow rate: 30.74 litres/min at about 300K, 1 atm
 = 1.2488 gmol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2 in	PH2 out	RL2_in	RL6_in	Effluent
Total Organic Carbon (µgC/g)	21700					2290.0
Phenol (µg/g)	27436					179.0

Gaseous Stream Analysis

Sample Location	GLS
Oxygen (%)	27.07
Carbon Monoxide (%)	3.63
Carbon Dioxide (%)	68.85
Hydrogen (%)	0.45

Sample Location

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
RL10_in	Reactor Section 10 Inlet
gaseous stream	Vent gas (gas from gas-liquid separator)

Mass Balance		Hydrogen	Carbon	Oxygen	Hydrogen	Carbon	Oxygen
Component	M.W.	1	12.011	15.9994	1	% of infl.	% of infl.
Feed			g/min	g/min			
TOC	n/a		in PhOH	0		0	0
Phenol (C6H6O)	94.11		16.387	3.638		100.0%	5.5%
Oxygen (O2)	32.00		0	62.333		0.0%	94.5%
Total Influent			16.387	65.972			
LIQUID EFFLUENT							
Total Carbon less TOC (assume CO3)				not measured			
TOC (assume CHx)	12.011		1.786	0.000		10.9%	0
Phenol (C6H6O)	94.11		0.107	0.024		0.7%	0.0%
Vent Gas							
Oxygen (O2)	32.00			10.8170			16.4%
Carbon Monoxide (CO)	28.01		0.5440	0.7253		3.3%	1.1%
Carbon Dioxide (CO2)	44.01		10.3174	27.5131		63.0%	41.7%
Hydrogen (H2)	2.016	0.0113					
Total Effluents		0.011	12.755	39.079			
Recovery (effluent/influent)x100	%		78	59			

Destruction Efficiencies	in(mg/l)	out(mg/l)	Conversion
TOC	21700	2290.0	0.89
Phenol	27436	179.0	0.99
CO yield			0.032138079
CO2 yield			0.609561086

Deviations in oxygen excesses per runs

Parameter	Run	1	2	3	4	5	6	7	8	9
O2 flow [V]	Average	3.46	4.17	4.33	4.17	3.02	2.62	2.81	2.81	2.81
	Max	3.61	4.45	4.59	4.34	4.20	3.75	3.24	2.91	2.91
	Min	3.33	3.92	4.07	3.99	2.57	1.96	2.68	2.75	2.75
O2 flow [kg/h]	Average	5.04	6.13	6.36	6.13	4.20	3.11	3.74	3.74	3.74
	Max	5.29	6.51	6.70	6.36	6.18	5.60	4.63	3.97	3.97
	Min	4.82	5.77	5.98	5.86	3.14	0.59	3.43	3.60	3.60
O2 excess [%]	Average	10	34	39	34	34	-1	21	19	19
	Max	15.85	42.49	46.53	39.22	97.31	78.93	48.03	26.98	26.98
	Min	5.46	26.25	30.89	28.31	0.29	-81.25	9.59	14.87	14.87
O2 excess (deviation from the mean) [%]	Max	5.52	8.36	7.41	5.10	63.07	79.69	28.68	7.65	7.65
	Min	-4.87	-7.87	-8.22	-5.82	-33.95	-80.49	-9.76	-4.46	-4.46
O2 excess, average deviation [%]		5	8	8	5	34*	80	10*	6	6

* In the case of runs with very high deviations above the average, values close to the minimum deviation were used.

Other comparisons with other studies (runs 2, 3, 4, 8, 9)

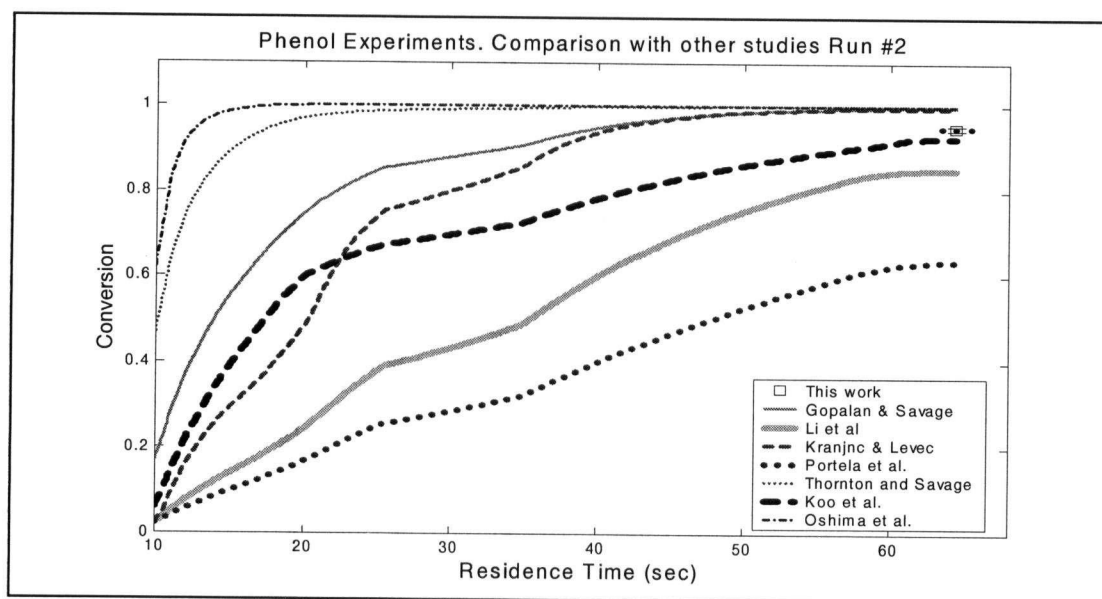


Figure F.1 Phenol Experiments. Agreement study. Run 2

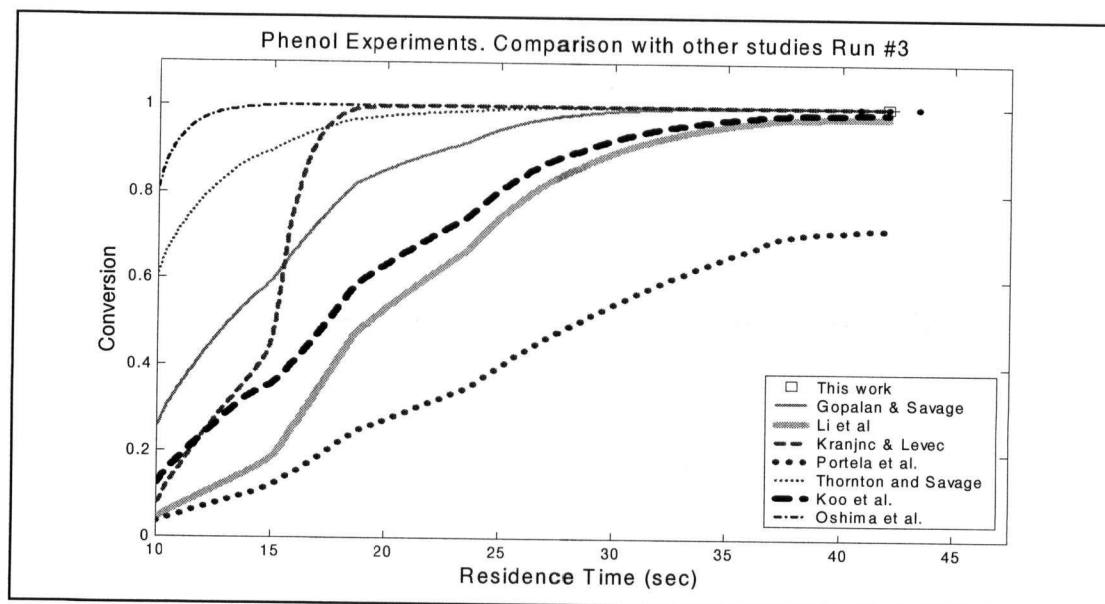


Figure F.2 Phenol Experiments. Agreement study. Run 3

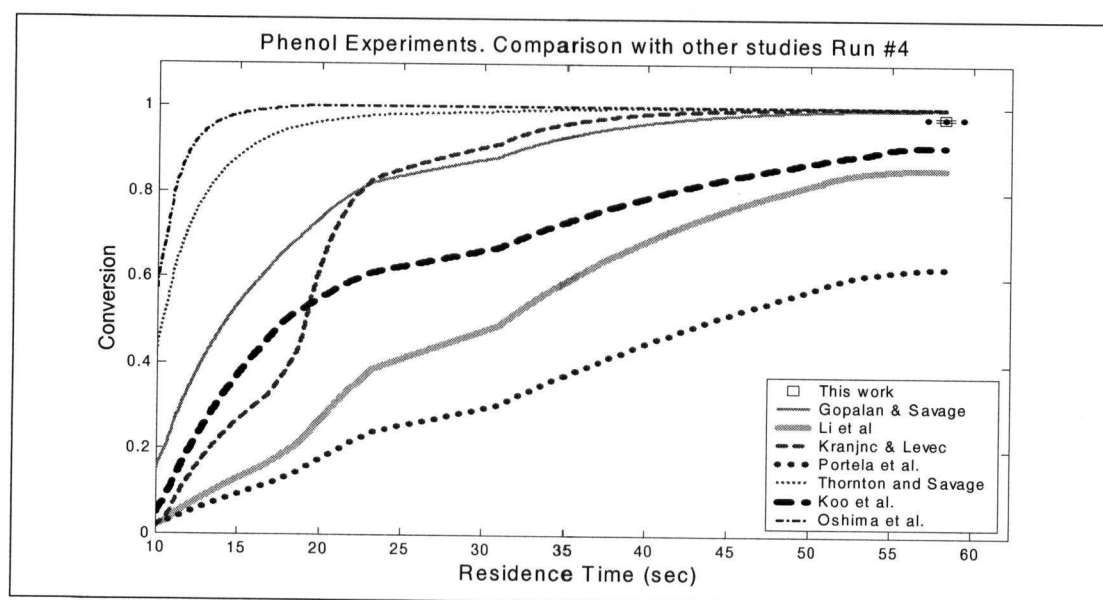


Figure F.3 Phenol Experiments. Agreement study. Run 4

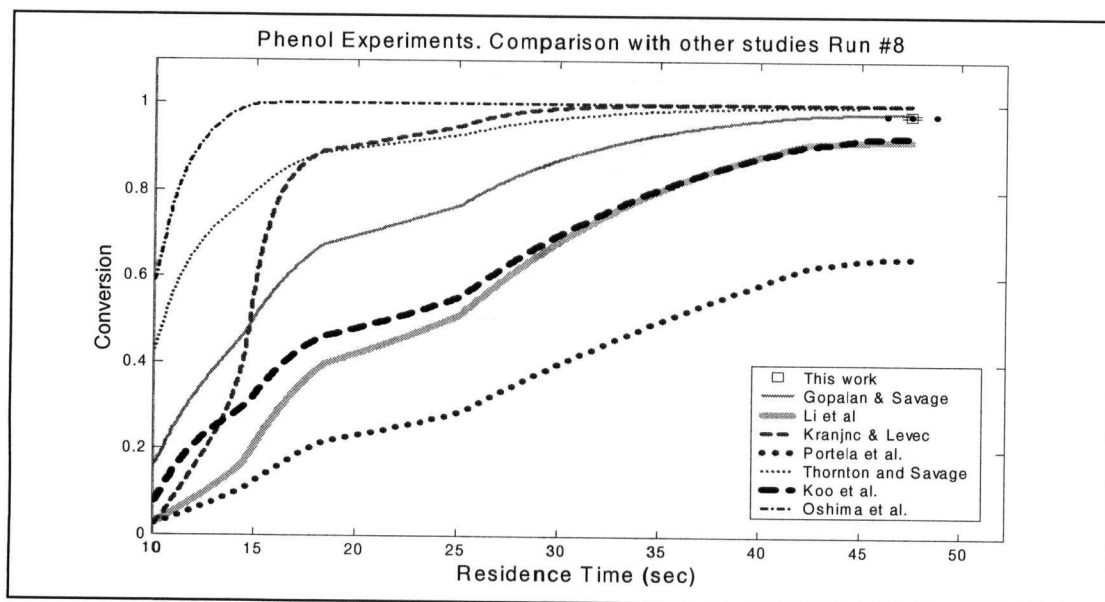


Figure F.4 Phenol Experiments. Agreement study. Run 8

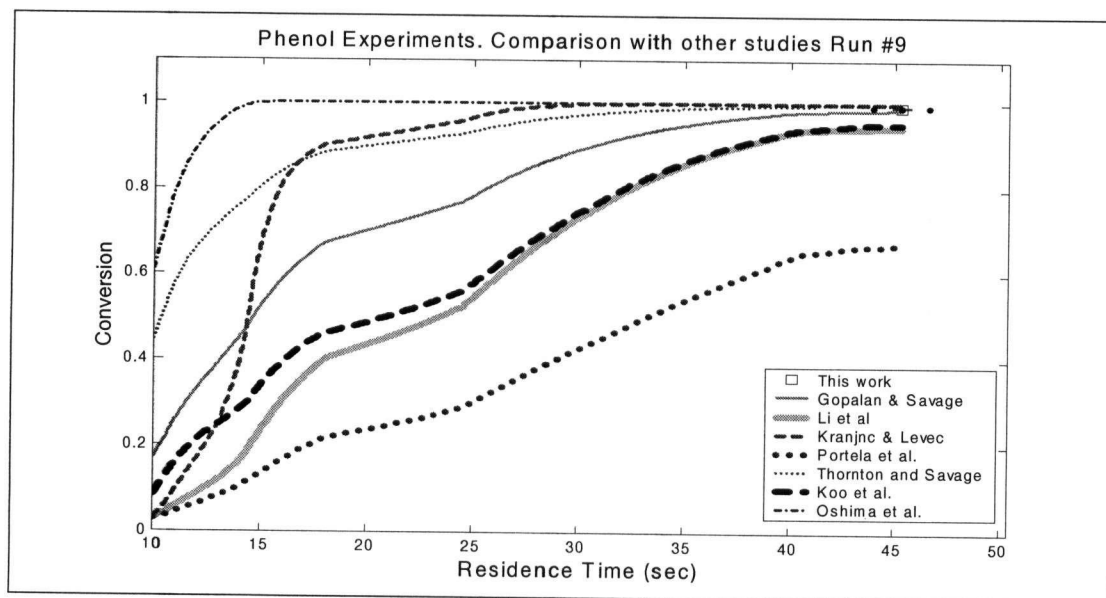


Figure F.5 Phenol Experiments. Agreement study. Run 9

Appendix G 2,4 DNP, ammonia and ammonium sulphate experiments

Channel configuration for the Data Acquisition System

Table G.1 Channel configuration. 2,4 DNP, ammonium sulphate and ammonia

Channel	Port	Position
1	PH2-in	PH2-in
2	PH2-out	PH2-out
3	E-2	B2
4	E-11	B3
5	E-25	B4
6	RL2-in	RL2-in
7	RL6-in	RL6-in
8	RL10-in	RL10-in
9	E-19	S2
10	E-14	SB2
11	E-17	S4
12	E-18	SB4
13	E-5	S7
14	E-4	SB7
15	E-23	S20
16	R3-B	R3B
17	R8-A	R8A
18	R15-A	R15A
19	Feed tank	Feed tank
20	R11-A	R11-A
21		PIC 431
22		PT431
23		-
24		O ₂

Temperatures entered in text files for Matlab programs

Text files: wastel.txt, Matlab files: dnpwastel.m

Table G.2 Temperatures for text files. 2,4 DNP; ammonium sulphate and ammonia

Distance from the feed [m]	Registered temperature	Observations
0	Feed	Measured, CH 19
6.9	PH1 in RHX out, (cold side)	Calculated by in Matlab, assuming no losses
11.8	PH2 in	Measured, CH 1
16.07	PH2 out	Measured, CH 2
17.08	B2	Measured, CH 3
18.76	B3	Measured, CH 4
20.44	B4	Measured, CH 5
34.18	RL-2	Measured, CH 6
61.91	RL-6	Measured, CH 7
89.64	RL-10	Measured, CH 8
130.18	Reactor End	Measured (close to the end), CH18
143.71	RHX in (hot side)	Temperature loss was of approximately 8 °C *
150.137	RHX out, TE 123	Measured (TE 123)

*** Calculation of temperature loss from the end of the reactor to RHX**

1. Enthalpy loss (Δh) in another non-heated portion of the reactor (RL-10 to RL-11A) was calculated. Knowing the temperatures at RL-10 (848 K) and RL-11A (839 K), the heat loss \dot{q} was represented as in equation G.1, with L as the distance between the two. (13.1 m). Δh was calculated from the water properties table³⁹, yielding that $\Delta h = -2.4808 \text{ e4 J/kg}$

$$\frac{\dot{q}}{L} = \Delta h \quad \text{G.1}$$

2. Knowing the temperature close to the end of the reactor (831 K) and the distance from this point to the beginning of the RXH (also 13.1 m), the heat loss \dot{q}_2 was obtained as:

$$\dot{q}_2 = \frac{831 \text{ K}}{848 \text{ K}} \dot{q} = -2.4281 \text{ e4 J/kg}$$

3. Finally, the temperature in the inlet of the RHX was obtained from the heat lost in the portion from the end of the reactor, yielding that $T_{\text{RHX, in}} = 823 \text{ K}$.

2.4 DNP, Ammonia and Ammonium Sulphate Run 0

Date of test: November 26th/01
 Data file: nov2601.txt, nov26b01.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.400 wt% as Dinitrophenol
 Feed total ammonia: 6.670 wt% as NH₃
 Feed ammonium sulphate: 2.108 wt% as (NH₄)₂SO₄
 Feed Flow rate: 0.800 litres/min
 O₂ flow rate: 2.820 kg/h 47 g/min 197 % Excess
 Stoichiometric O₂ flow rate: 0.95 kg/h
 Vent Gas Flow rate: 26.10 litres/min at about 300K, 1 atm
 = 1.0603 g/mol/min

Aqueous Stream Analysis

Sample Location	Feed	PH2in	PH2out	RL2 in	RL6 in	Effluent
Total Ammonia (as N) (µgN/g)	55800					810
Total Ammonia (µgN/g)	67757.1429					983.571429
Total Carbon (µgC/g)						
Total Organic Carbon (µgC/g)	9425	1410		644	218	8.0
Total Sulfate as (as S) (µgN/g)	5110					1304.0
Total Sulfate as SO ₄ (µgN/g)	15330					3912
ratio NH ₃ /TOC (mole/mole)	5.07464949					
pH	8.9					7.4
2,4-Dinitrophenol (µg/g)	24088	81.2	16.5	1.6	0.7	1.0
2-Nitrophenol (µg/g)	0	84.4	70.5	40	0	1.0
4-Nitrophenol (µg/g)	0	196	146	51.2	2.2	1.0
Phenol (µg/g)	0	0	0	0	0	1.0
Nitrate (NO ₃) (as N) (µg/g)	0.03					0.3
Nitrate (NO ₃) (µg/g)	0.13285714					1.32857143
Nitrite (NO ₂) (as N)(µg/g)	0.06					2.04
Nitrite (NO ₂) (µg/g)	0.19714286					6.70285714
Carbonate(CO ₃)	0					12600
Bicarbonate(HCO ₃)	0					1810
Metals						
Calcium (µg/g)	<2	8	11	2	4	1
Cobalt	<0.05	13	8.3	3.8	13.2	0.23
Chromium (µg/g)	<0.05	2640	891	437	836	4.71
Copper (µg/g)	<0.1	219	137	67.6	186	5.5
Iron (µg/g)	<0.2	1020	351	134	1190	<2
Potassium (µg/g)	<5	<20	<6	<3	<4	<5
Molybdenum (µg/g)	<1	1400	800	344	1120	231
Sodium (µg/g)	1.4	-	-	-	-	2.2
Nickel (µg/g)	<0.05	9520	4710	2230	5350	81.1
Zinc	<2	105	54.7	38	87.3	3.1

Gaseous Stream Analysis

Sample Location	PH2out	EFFLUENT
Oxygen (%)	45.4	8.2
Nitrogen (%)	32	63.4
Nitrous Oxide N ₂ O(%)	0.6	<5
Nitrogen dioxide (NO ₂)(%)	nd	nd
Carbon Monoxide (%)	3.6	<1
Carbon Dioxide (%)	19.1	32.1
Hydrogen (%)	0.6	<1

Abbreviation

Feed: Feed prior to test
 Effluent: Final effluent
 PH2_in: Preheater 2 Inlet
 PH2_out: Preheater 2 Outlet
 RL2_in: Reactor Section 2 Inlet
 RL6_in: Reactor Section 6 Inlet
 RL10_in: Reactor Section 10 Inlet

gaseous stream PH2 out: Vent gas (gas from gas-liquid separator) PH2 out

gaseous stream effluent: Vent gas (gas from gas-liquid separator) effluent

2,4 DNP, Ammonia and Ammonium Sulphate Run 0

Mass Balance		Nitrogen	Carbon	Oxygen	Sulfur	Nitrogen	Carbon	Oxygen	sulfur
		14.0067	12.011	15.9994	32.06	% of infl.	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min	g/min				
Feed									
Total Ammonia (as NH3)	17.031	44.640				93.8%			
Total Carbon less TOC	n/a		in 2.4dnp						
TOC	n/a		in 2.4dnp						
Total Sulfate as SO4 (µgN/g)	96			8.1756934	4.088			12.9%	100.0%
								0.0%	
2,4-Dinitrophenol (C6H4N2O5)	184.11	2.932	7.543	8.373		6.2%	100.0%	13.2%	
2-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.000		0.0%	0.0%	0.0%	
4-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.000		0.0%	0.0%	0.0%	
Phenol (C6H6O)	94.11		0.000	0.000		0.0%	0.0%	0.0%	
Nitrate (NO3)	61.99	0.000		0.000		0.0%		0.0%	
Nitrite (NO2)	45.99	0.000		0.001		0.0%		0.0010%	
Carbonate (CO3)	60.00		0.00000	0.00000			0.0%	0.0%	
Bicarbonate (HCO3)	61.00		0	0.00000			0.0%	0.0%	
Oxygen (O2)	32.00			47.000				74.0%	
Total Influent		47.572	7.543	63.550	4.088				
Liquid Effluent									
Total Ammonia (as NH3)	17.031	0.648				1.4%			
Total Carbon less TOC (assume CO3)	60.009					not measured			
TOC (assume CHx)	12.011		0.006				0.1%		
Total Sulfate as SO4 (µgN/g)	96.00			2.086	1.043				
2,4-Dinitrophenol (C6H4N2O5)	184.11	0.000	0.000	0.000		0.0%	0.0%	0.0%	
2-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.001		0.0%	0.0%	0.0%	
4-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.001		0.0%	0.0%	0.0%	
Phenol (C6H6O)	94.11	0.000	0.001	0.001		0.0%	0.0%	0.0%	
Nitrate (NO3)	61.99	0.00024		0.001			0.0%	0.0%	
Nitrite (NO2)	45.99	0.00163		0.00373		0.0%		0.0%	
Carbonate (CO3)	60.00		2.01785	8.06370		0.0%		12.7%	
Bicarbonate (HCO3)	61.00		0.28987	1.15836				1.8%	
Vent Gas									
Oxygen (O2)	32.00			2.7821				4.4%	
Nitrogen (N2)	28.01	18.8312				39.6%		0.0%	
Nitrous Oxide (N2O)	44.01	0.1485		0.1696		0.3%		0.3%	
Carbon Monoxide (CO)	28.01		0.1274	0.1696			1.7%	0.3%	
Carbon Dioxide (CO2)	44.01		4.0880	10.8569			54.2%	17.1%	
Hydrogen (H2)	2.016						0.0%		
Total Effluents		19.630	6.531	25.293	1.043				
Recovery (effluent/influent)x100	%	41.26	86.59	39.80	25.52				

Destruction Efficiencies	%	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	98.55%	Residual present as NH4HCO3 in effluent
TOC	99.92%	
CO yield	0.01687458	
CO2 yield	0.54167396	
N2O	0.00083132	
N2 yield	0.10541105	

Oxygen excess uncertainty		
Parameter		
O2 flow [V]	Average	2.40
	Max	2.46
	Min	2.35
O2 flow [kg/h]	Average	2.82
	Max	3.03
	Min	2.66
O2 excess [%]	Average	197
	Max	218.86
	Min	179.51
O2 excess (deviation from the mean) [%]	Max	21.65
	Min	-17.90

Appendix H 2,4 and ammonia experiments. Reports and mass balances

Discrepancies in ammonia analyses

Duplicates of samples were taken to measure ammonia in two different laboratories: BC Research Institute and UBC Civil engineering Environmental Lab. The BCRI laboratory gave consistently lower results. The reason for this is that the samples were not analyzed immediately, and were not properly prepared (acidified) before refrigerated. Unfortunately, the feed samples were only analyzed in the BCRI laboratory, (obviously yielding results that were lower than expected). The feed concentration was given by the amount of ammonia solution fed into the system, 2,000 mg/L (see Appendix E), under the assumption of perfect mixing. Table H.1 shows the results given by BCRI and by UBC.

Table H.1 Discrepancies in ammonia measurements

Laboratory	UBC	BCRI
Description	Ammonia mgN/L	Ammonia mgN/L
Bucket	12	-
feed		1851.33
Run 1 PH1	868	505.00
Run 1 PH2 in	723	602
Run 1 PH2 out	1130	927
Run 1 RL-2	1000	602
Run 1 RL-6	1020	927
Run 1 Effluent	1010	736
Run 2	1090	804
Run 2b	1260	1098
Run 2c	1690	1234
Run 3 PH1	1230	1065
Run 3 PH2 In	479	384
Run 3 PH2 out	1280	885
Run 3 RL-2	380	286
Run 3 RL-6	989	750
Run 3 Effluent	1010	810
Run 4 Effluent	1130	933
Run 4b Effluent	1320	936
Run 5 PH 1	1280	1095
Run 5 PH 2 in	1140	996
Run 5 PH 2 out	1160	963
Run 5 RL-2	812	678
Run 5 RL-6	1090	723
Run 5 RL 6 2nd	1040	687
Run 5 Effluent	1160	600
Run 6 Effluent	1230	873
Run 6b Effluent	1300	1050
Run 6c Effluent	1480	1380
Run 7	1150	606

Channel configuration for the Data Acquisition System

Table H.2 Channel configuration. 2,4 DNP and ammonia experiments

Channel	Port	Position
1	PH1 in	PH1 in
2	PH2-in	PH2-in
3	PH2-out	PH2-out
4	E-2	B2
5	E-11	B3
6	E-25	B4
7	RL2-in	RL2-in
8	RL6-in	RL6-in
9	TER-10	TER-10
10	E-19	PH1 (weak point)*
11	E-14	S7
12	E-17	S20
13	R2-B	R2-B
14	R3-A	R3-A
15	R6-A	R6-A
16	R11-A	R11-A
17	R13-A	R13-A
18	R17-A	R17-A
19	RHX in	RHX in
20	Feed tank	Feed tank
21	-	-
22		PT431
23	-	-
24		O ₂

*Close to the corrosion failure from the 2,4 DNP, ammonium sulphate and ammonia experiments. The burst part of the tube was replaced, along with the thinnest portion. However, the thickness in this point was slightly less than that of a non-corroded 3/8" tube

Temperatures entered in text files for Matlab programs

Text files: waste2.txt

Matlab files: dnpwaste2.m

Table H.3 Temperatures for text files. 2,4 DNP and ammonia experiments

Distance from the feed [m]	Registered temperature	Observations
0.00	Feed	Measured, CH 20
6.90	PH1 in	Measured, CH 1
11.80	PH2 IN	Measured, CH 2
16.07	PH2 OUT	Measured, CH 3
17.08	TS IN	Measured, CH 4
18.76	TS MID	Measured, CH 5
20.44	TS OUT	Measured, CH 6
34.18	RL-2	Measured, CH 7
40.40	R2-B	Measured, CH 13
47.26	R3-A	Measured, CH 14
61.91	R6-A	Measured, CH 15
110.21	R13-B	Measured, CH 17
137.64	R17-B	Measured, CH 18
143.71	RHX in	Measured, CH 19
150.14	RHX out	Measured, TE 123

Sample calculation for accounting for air contamination (from section 3.5.2.3.1)

Run 2c, effluent

In:

$$\dot{n}_{2,4DNP} = 0.096 \text{ mol/min (See Equation [14])}$$

$$\dot{n}_{O_2} = 0.307 \text{ mol/min}$$

$$\dot{n}_{NH_3} = 0.111 \text{ mol/min (See Equation [14])}$$

$$\dot{n}_{TOC} = 0.576 \text{ mol/min (See Equation [14])}$$

Out:

$$X_{2,4DNP} = 0.99996 (\approx 1)$$

$$X_{NH_3} = 0.155$$

$$X_{\text{TOC}} = 0.9898$$

$$N_2O/CO_2 \text{ (BCRI)} = 0.041$$

$$CO/CO_2 \text{ (BCRI)} = 0.051$$

$$C_{\text{liquid}} = 0.228 \text{ mol/min (CO}_3\text{)}$$

Solving:

- Equation [38]: $\dot{n}_{CO_2_{out}} = 0.325 \text{ mol/min}$
- Equation [39]: $\dot{n}_{CO_{out}} = 0.017 \text{ mol/min}$
- Equation [40]: $\dot{n}_{N_2O_{out}} = 0.0135 \text{ mol/min}$
- Equation [41]: $\dot{n}_{N_2_{out}} = 0.091 \text{ mol/min}$
- Equation [33]: $\dot{n}_{O_2_{out}} = -0.195 \text{ mol/min} = 0$
- Equation [43]: $\dot{n}_{\text{gas total}} = 0.461 \text{ mol/min}$
- Equations [44], [45], [46], trial and error: $x_a = 0.64$ (see Appendix H)
- Equation [47]: $\%_{N_2} = 71.87$
- Equation [48]: $\%_{O_2} = 13.86$
- Equation [49]: $\%_{CO_2} = 10.03$
- Equation [50]: $\%_{CO} = 0.51$
- Equation [51]: $\%_{N_2O} = 0.42$

Table H.4 2,4 DNP and ammonia experiments. Molar balances

MOLAR BALANCES																			
Run	Location	X NH3	X 2,4DNP	X TOC	O ₂ in [mol/min]*	x O ₂	CO ₂ liquid [mol/min]*	CO/CO ₂ (BCRI)	CO ₂ gas [mol/min]	CO gas [mol/min]	N ₂ O/CO ₂ (BCRI)	N ₂ O gas [mol/min]	NO ₂ and NO ₂ liquid [mol/min]*	N ₂ gas [mol/min]	O ₂ , out [mol/min]	O ₂ gas [mol/min]	Total gas flow rate [mol/min]	Total gas flow rate (with water vapour) [mol/min]	Total gas flow [L/min] (with water vapour)
1	PH 1 in	0.566	0.961	0.832	0.755	3.367	0.026	0.029	0.419	0.012	0.000	0.000	0.000	0.123	0.304	0.304	0.858	0.886	21.812
	PH 2 out	0.435	0.993	0.934	0.755	3.367	0.044	0.028	0.477	0.013	0.047	0.023	0.001	0.096	0.279	0.279	0.888	0.917	22.571
	Effluent	0.495	1	1	0.755	3.367	0.045	0.000	0.530	0.000	0.069	0.036	0.000	0.087	0.281	0.281	0.935	0.966	23.776
2	Effluent	0.455	1	1	0.529	1.012	0.051	0.000	0.525	0.000	0.084	0.044	0.000	0.077	0.052	0.052	0.697	0.721	17.738
2b	Effluent	0.37	1	1	0.434	0.019	0.057	0.000	0.519	0.000	0.067	0.035	0.000	0.081	-0.050	0.000	0.635	0.656	16.146
2c	Effluent	0.155	1	0.990	0.307	-1.299	0.228	0.051	0.325	0.017	0.041	0.013	0.000	0.091	-0.195	0.000	0.446	0.461	11.354
3	PH 1 in	0.385	0.930	0.710	0.749	3.302	0.039	0.066	0.309	0.020	0.000	0.000	0.000	0.110	0.296	0.296	0.736	0.761	18.720
	PH 2 out	0.76	0.996	0.915	0.749	3.302	0.046	0.037	0.462	0.017	0.030	0.014	0.001	0.123	0.299	0.299	0.915	0.945	23.258
	Effluent	0.495	1	1	0.749	3.302	0.044	0.000	0.532	0.000	0.090	0.048	0.000	0.075	0.275	0.275	0.930	0.961	23.651
4	Effluent	0.435	1	1	0.521	0.925	0.051	0.000	0.525	0.000	0.076	0.040	0.000	0.080	0.042	0.042	0.687	0.709	17.461
4b	Effluent	0.34	1	0.999	0.422	-0.105	0.059	0.000	0.517	0.000	0.064	0.033	0.000	0.081	-0.065	0.000	0.632	0.653	16.061
5	PH 1 in	0.36	0.931	0.741	0.772	3.546	0.044	0.081	0.318	0.026	0.000	0.000	0.000	0.109	0.317	0.317	0.770	0.795	19.575
	PH 2 out	0.42	0.974	0.853	0.772	3.546	0.045	0.170	0.369	0.063	0.023	0.009	0.000	0.108	0.303	0.303	0.852	0.880	21.657
	Effluent	0.42	1	1	0.772	3.546	0.050	0.000	0.526	0.000	0.098	0.051	0.000	0.068	0.292	0.292	0.937	0.968	23.830
6	Effluent	0.385	1	0.999	0.500	0.708	0.051	0.000	0.524	0.000	0.079	0.041	0.000	0.076	0.017	0.017	0.658	0.680	16.742
6b	Effluent	0.35	1	0.999	0.448	0.166	0.060	0.000	0.515	0.000	0.080	0.041	0.000	0.074	-0.038	0.000	0.631	0.652	16.040
6c	Effluent	0.26	1	0.997	0.354	-0.811	0.067	0.017	0.499	0.008	0.061	0.030	0.000	0.080	-0.139	0.000	0.617	0.638	15.693
7	Effluent	0.425	1	0.998	0.748	3.296	0.051	0.000	0.523	0.000	0.078	0.041	0.000	0.079	0.269	0.269	0.912	0.942	23.182

* Molar flows obtained from mass flows in mass balances, as: $\dot{n}_i = \frac{\dot{m}_i}{MW_i}$

Table H.5 2,4 DNP and ammonia experiments. Predicted gas percentages from molar flows (not considering air contamination)

Run	Location	CO ₂ [%]	CO [%]	N ₂ [%]	N ₂ O [%]	O ₂ [%]	H ₂ O vapour [%]
1	PH1	47.25	1.35	13.88	0.00	34.31	3.32
	PH2	52.00	1.44	10.42	2.47	30.46	3.32
	Effluent	54.91	0.00	8.99	3.76	29.12	3.32
2	Effluent	72.81	0.00	10.63	6.13	7.21	3.32
2b	Effluent	79.09	0.00	12.39	5.30	0.00	3.32
2c	Effluent	70.55	3.58	19.73	2.93	0.00	3.32
3	PH1	40.65	2.69	14.51	0.00	38.94	3.32
	PH2	48.87	1.82	12.99	1.48	31.62	3.32
	Effluent	55.34	0.00	7.83	5.00	28.63	3.32
4	Effluent	73.97	0.00	11.28	5.63	5.91	3.32
4b	Effluent	79.21	0.00	12.49	5.09	0.00	3.32
5	PH1	39.94	3.25	13.73	0.00	39.87	3.32
	PH2	41.93	7.12	12.26	0.98	34.49	3.32
	Effluent	54.30	0.00	6.98	5.31	30.19	3.32
6	Effluent	77.07	0.00	11.16	6.07	2.50	3.32
6b	Effluent	79.10	0.00	11.37	6.31	0.00	3.32
6c	Effluent	78.20	1.29	12.53	4.77	0.00	3.32
7	Effluent	55.58	0.00	8.35	4.33	28.53	3.32

Table H.6 2,4 DNP and ammonia experiments. Air contamination

Run	Location	x O ₂ , BCRI	x N ₂ , BCRI	x CO ₂ , BCRI	x O ₂ , vent	x N ₂ , vent	x CO ₂ , vent	Best fit x _a	Deviation from x O ₂ , BCRI [%]	Deviation from x N ₂ , BCRI [%]	Deviation from x CO ₂ , BCRI [%]	Average deviation of the errors [%]
1	PH1	0.526	0.302	0.143	0.343	0.139	0.472	0.280	24.1	-1.0	-22.6	15.90
	PH2	0.386	0.112	0.436	0.305	0.104	0.520	0.100	9.1	-6.0	-3.2	6.10
	Effluent	0.292	0.333	0.321	0.291	0.090	0.549	0.360	3.0	-0.9	-3.0	2.30
2	Effluent	0.235	0.299	0.401	0.072	0.106	0.728	0.420	10.5	-9.5	-2.1	7.37
2b	Effluent	0.163	0.471	0.313	0.000	0.124	0.791	0.540	5.0	-1.3	-5.1	3.80
2c	Effluent	0.140	0.581	0.227	0.000	0.197	0.706	0.660	0.1	-0.8	-1.3	0.73
3	PH1	0.571	0.186	0.200	0.389	0.145	0.407	0.120	20.3	-3.7	-15.8	13.27
	PH2	0.365	0.174	0.402	0.316	0.130	0.489	0.100	5.9	-2.1	-3.8	3.93
	Effluent	0.293	0.389	0.264	0.286	0.078	0.553	0.440	4.1	-0.3	-4.6	3.00
4	Effluent	0.213	0.507	0.231	0.059	0.113	0.740	0.600	6.4	-1.2	-6.4	4.67
4b	Effluent	0.181	0.623	0.154	0.000	0.125	0.792	0.760	2.1	-0.7	-3.6	2.13
5	PH1	0.555	0.194	0.204	0.399	0.137	0.399	0.100	17.5	-0.9	-15.6	11.33
	PH2	0.555	0.195	0.184	0.345	0.123	0.419	0.120	22.6	-0.7	-18.5	13.93
	Effluent	0.393	0.226	0.322	0.302	0.070	0.543	0.240	11.3	-1.7	-9.1	7.37
6	Effluent	0.236	0.284	0.416	0.025	0.112	0.771	0.440	13.0	-12.6	-1.6	9.07
6b	Effluent	0.179	0.310	0.444	0.000	0.114	0.791	0.300	11.6	-0.6	-11.0	7.73
6c	Effluent	0.065	0.295	0.564	0.000	0.125	0.782	0.260	1.0	-0.3	-1.4	0.90
7	Effluent	0.434	0.174	0.335	0.285	0.083	0.556	0.160	16.1	-2.3	-13.1	10.50

2,4 DNP and ammonia Run 1

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as 2,4 Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH3
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 1.450 kg/h 24.166667 g/min 74.70 % Excess
 Stoichiometric O2 flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.9660 gmol/min **See Note**

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2_in	RL6_in	Effluent (GLS)
Total Ammonia (µgN/g)	2000	868	723	1130	1000	1020	1010
Ratio NH3/TOC (mole/mole)	0.19367496	0.49954751	0.6444757	1.6649408		291.5562	433.0467
Total Organic Carbon (µgC/g)	8855.23043	1490	962	582	-	3	2
pH	9.2	8.22	8.08	8.14	8.44	8.37	7.95
Picric Acid (µg/g)	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,4-Dinitrophenol (µg/g)	22630	877.7	489.1	153.8	< 1	< 1	< 1
2,6-Dinitrophenol (µg/g)	111.8	< 1	< 1	< 1	< 1	< 1	< 1
2-Nitrophenol (µg/g)	< 1	358.6	< 1	< 1	< 1	< 1	< 1
4-Nitrophenol (µg/g)	< 1	115.3	< 1	< 1	< 1	< 1	< 1
Phenol (µg/g)	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Nitrate(as N) (µg/g)	< 0.1	1	1.2	7.3	0.2	0.8	0.6
Nitrite (as N) (µg/g)	< 0.1	7.3	1.6	12	< 0.1	0.2	< 0.1
carbonate (µg/g)	3953.33	40	0	40	520	360	60
bicarbonate (µg/g)	1893.33	2100	2160	3380	3300	3380	3480
Metals							
Calcium (µg/g)	N. M						0.2
Chromium (µg/g)	N. M						0.32
Copper (µg/g)	N. M						<0.1
Iron (µg/g)	N. M						<0.2
Potassium (µg/g)	N. M						1.64
Molybdenum (µg/g)	N. M						0.16
Sodium (µg/g)	N. M						0.82
Nickel (µg/g)	N. M						0.34

Gaseous Stream Analysis(not considering air contamination)

Sample Location	PH1	PH2	Effluent
Oxygen (%)	34.31	30.46	29.12
Nitrogen (%)	13.88	10.42	8.99
Nitrous Oxide (%)	0.00	2.47	3.76
Carbon Monoxide (%)	1.35	1.44	< 0.1
Carbon Dioxide (%)	47.25	52.00	54.91
Nitrous Dioxide (%)	< 0.1	< 0.1	< 0.1
Methane (%)	n.d	n.d	n.d
Ethane (%)	n.d	n.d	n.d
water vapor (%)	3.32	3.32	3.32
total	100.11	100.11	100.10

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2,4 DNP and ammonia Run 1

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	21.6%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00240	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			24.167			68.1%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	35.509			
Liquid Effluent							
Total Ammonia (as N)	17.031	0.788			18.5%		
TOC	12.011		0.002		0.0%	0.0%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00569		0.00160	0.1%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00936		0.00018	0.2%		0.0%
Carbonate (CO ₃)	60.00		0.00937	0.02811		0.1%	0.1%
Bicarbonate (HCO ₃)	61.00		0.53447	1.60341		6.8%	4.5%
Water (H ₂ O) (see note)	18.00			4.3955925			
Vent Gas							
Oxygen (O ₂)	32.00			9.0012			25.3%
Nitrogen (N ₂)	28.01	2.4328			57.1%		
Nitrous Oxide (N ₂ O)	44.01	1.0174		0.5811	23.9%		
Carbon Monoxide (CO)	28.01		0.0001	0.0002		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.3710	16.9731		81.1%	47.8%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.5131		0.0%	
Total Effluents		4.253	6.919	32.586			
Recovery (effluent/influent)x100	%	99.82	88.11	91.77			

Destruction Efficiencies	Effluent	Comments
Total Ammonia	99.996%	None detected in effluent
TOC	99.98%	None detected in effluent
CO yield	0.002	
CO ₂ yield	0.92	
N ₂ O	0.16	
N ₂ yield	0.390	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 2

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH3
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 1.016 kg/h 16.93817 g/min 22.44 % Excess
 Stoichiometric O2 flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.7210 gmol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2_in	RL6_in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1090
Ratio NH3/TOC (mole/mole)	0.19367496						467.3474
Total Organic Carbon (µgC/g)	8855.23043						2
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						0.4
Nitrite (µg/g)	< 0.1						0.2
carbonate (µg/g)	3953.33						40
bicarbonate (µg/g)	1893.33						3920
Metals							
Calcium (µg/g)							0.21
Chromium (µg/g)							0.17
Copper (µg/g)							0.42
Iron (µg/g)							<0.2
Potassium (µg/g)							1.31
Molybdenum (µg/g)							<0.1
Sodium (µg/g)							0.69
Nickel (µg/g)							0.17

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	7.21
Nitrogen (%)	10.63
Nitrous Oxide (%)	6.13
Carbon Monoxide (%)	< 0.1
Carbon Dioxide (%)	72.81
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
total	100.10

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream	Vent gas (GLS) effluent

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
Component	M.W.	14.0067 g/min	12.011 g/min	15.9994 g/min	% of infl.	% of infl.	% of infl.
Feed							
Total Ammonia (as NH3)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C6H3N3O7)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C6H4N2O5)	184.11	2.686	6.909	7.670	63.0%	88.0%	27.1%
2,6-Dinitrophenol (C6H4N2O5)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C6H6O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO3)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO2)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O2)	32.00			16.938			59.9%
Water (H2O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	28.280			
Liquid Effluent							
Total Ammonia (as NH3)	17.031	0.850			20.0%		
TOC	12.011		0.002		0.0%	0.0%	
Picric Acid (C6H3N3O7)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C6H4N2O5)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C6H4N2O5)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C6H5NO3)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C6H6O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO3)	61.99	0.00031		0.00000	0.0%	0.0%	0.0%
Nitrite (NO2)	45.99	0.00016		0.00018	0.0%		0.0%
Carbonate (CO3)	60.00		0.00625	0.01874		0.1%	0.1%
Bicarbonate (HCO3)	61.00		0.60205	1.80614		7.7%	6.4%
Water (H2O) (see note)	18.00			4.2885581			
Vent Gas							
Oxygen (O2)	32.00			1.6634			5.9%
Nitrogen (N2)	28.01	2.1470			50.4%		
Nitrous Oxide (N2O)	44.01	1.2380		0.7072	29.1%		
Carbon Monoxide (CO)	28.01		0.0001	0.0001		0.0%	0.0%
Carbon Dioxide (CO2)	44.01		6.3053	16.7981		80.3%	59.4%
Hydrogen (H2)	2.016						
Methane (CH4)	16.04		0.0000			0.0%	
Ethane (C2H6)	30.07		0.0000			0.0%	
water vapor	18.00			0.3830		0.0%	
Total Effluents		4.236	6.917	25.284			
Recovery (effluent/influent)x100	%	99.42	88.09	89.41			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	45.50%	
TOC	99.98%	None detected in effluent
CO yield	0.001	
CO2 yield	0.91	
N2O	0.20	
N2 yield	0.34	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 2b

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH3
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 0.833 kg/h 13.883333 g/min 0.36 % Excess
 Stoichiometric O2 flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.6560 gmol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2_in	RL6_in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1260
Ratio NH3/TOC (mole/mole)	0.19367496						540.2365
Total Organic Carbon (µgC/g)	8855.23043						2
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						0.2
Nitrite (µg/g)	< 0.1						0.1
carbonate (µg/g)	3953.33						500
bicarbonate (µg/g)	1893.33						3940
Metals							
Calcium (µg/g)							
Chromium (µg/g)							
Copper (µg/g)							
Iron (µg/g)							
Potassium (µg/g)							
Molybdenum (µg/g)							
Sodium (µg/g)							
Nickel (µg/g)							

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	0.00
Nitrogen (%)	12.39
Nitrous Oxide (%)	5.30
Carbon Monoxide (%)	< 0.1
Carbon Dioxide (%)	79.09
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
total	100.10

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream	Vent gas (GLS) effluent

2,4 DNP and ammonia Run 2b

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	30.4%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.2%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			13.883			55.0%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	25.225			
Liquid Effluent							
Total Ammonia (as NH ₃)	17.031	0.983			23.1%		
TOC	12.011		0.002		0.0%	0.0%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00016		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.07807	0.23421		1.0%	0.9%
Bicarbonate (HCO ₃)	61.00		0.60512	1.81535		7.7%	7.2%
Water (H ₂ O) (see note)	18.00			4.0611101			
Vent Gas							
Oxygen (O ₂)	32.00			0.0000			0.0%
Nitrogen (N ₂)	28.01	2.2769			53.4%		
Nitrous Oxide (N ₂ O)	44.01	0.9739		0.5563	22.9%		
Carbon Monoxide (CO)	28.01		0.0001	0.0001		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.2317	16.6020		79.4%	65.8%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.3485		0.0%	
Total Effluents		4.234	6.918	23.271			
Recovery (effluent/influent)x100	%	99.37	88.10	92.25			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	37.00%	
TOC	99.98%	None detected in effluent
CO yield	0.001	
CO ₂ yield	0.90	
N ₂ O	0.16	
N ₂ yield	0.36	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 2c

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH3
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 0.590 kg/h 9.8310757 g/min -28.93 % Excess
 Stoichiometric O2 flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.4610 g/mol/min **See Note**

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2_in	RL6_in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1690
Ratio NH3/TOC (mole/mole)	0.19367496						16.10229
Total Organic Carbon (µgC/g)	8855.23043						90
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						10.3
Nitrate (µg/g)	< 0.1						< 0.1
Nitrite (µg/g)	< 0.1						< 0.1
carbonate (µg/g)	3953.33						0
bicarbonate (µg/g)	1893.33						5940
Metals							
Calcium (µg/g)							
Chromium (µg/g)							
Copper (µg/g)							
Iron (µg/g)							
Potassium (µg/g)							
Molybdenum (µg/g)							
Sodium (µg/g)							
Nickel (µg/g)							

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	0.00
Nitrogen (%)	19.73
Nitrous Oxide (%)	2.93
Carbon Monoxide (%)	3.58
Carbon Dioxide (%)	70.55
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
	100.11

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2.4 DNP and ammonia Run 2c

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	36.2%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.2%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			9.831			46.4%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	21.173			
Liquid Effluent							
Total Ammonia (as NH ₃)	17.031	1.318			30.9%		
TOC	12.011		0.070		0.0%	0.9%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.006	0.001	0.0%	0.1%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00000	0.00000		0.0%	0.0%
Bicarbonate (HCO ₃)	61.00		0.91228	2.73685		11.6%	12.9%
Water (H ₂ O) (see note)	18.00			3.4858005			
Vent Gas							
Oxygen (O ₂)	32.00			0.0000			0.0%
Nitrogen (N ₂)	28.01	2.5480			59.8%		
Nitrous Oxide (N ₂ O)	44.01	0.3783		0.2161	8.9%		
Carbon Monoxide (CO)	28.01		0.1982	0.2641		2.5%	1.2%
Carbon Dioxide (CO ₂)	44.01		3.9064	10.4071		49.7%	49.2%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.2449		0.0%	
Total Effluents		4.245	5.095	17.113			
Recovery (effluent/influent)x100	%	99.63	64.88	80.82			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	15.50%	
TOC	98.98%	
CO yield	0.03	
CO ₂ yield	0.57	
N ₂ O	0.06	
N ₂ yield	0.41	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 3

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as 2,4 Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH3
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 1.438 kg/h 23.968452 g/min 73.27 % Excess
 Stoichiometric O2 flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.9610 g/mol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2in	PH2out	RL2_in	RL6_in	Effluent
Total Ammonia (as N) (µgN/g)	2000.00	1230.00	1280.00	479.00	380.00	989.00	1010.00
ratio NH3/TOC (mole/mole)	0.23						
Total Organic Carbon (µgC/g)	8858.04	2560.00	1110.00	752.00	45.00	5.00	2.0
pH	9.22	8.02	7.97	7.99	9.24	8.24	7.9
Picric acid (µg/g)	< 1	14.8	25.8	0	0	<0.1	<0.1
2,4-Dinitrophenol (µg/g)	22630	1581.5	421.4	91.5	0.3	<0.1	<0.1
2,6-Dinitrophenol (µg/g)	111.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2-Nitrophenol (µg/g)	< 1	231.1	< 1	< 1	1.9	< 1	< 1
4-Nitrophenol (µg/g)	< 1	166.1	< 1	< 1	0	< 1	< 1
Phenol (µg/g)	< 1	0	< 1	< 1	0	< 1	< 1
Nitrate (NO3) (as N) (µg/g)	< 0.1	1.4	0.7	3	0.5	<0.1	<0.1
Nitrite (NO2) (as N)(µg/g)	< 0.1	0.6	5.7	8.8	<0.1	<0.1	<0.1
Carbonate(CO3)	3953.33	0	0	0	520	320	0
Bicarbonate(HCO3)	1893.33	3080	1220	3560	760	3220	3470
Metals							
Calcium (µg/g)							0.27
Cobalt							<0.05
Chromium (µg/g)							0.24
Copper (µg/g)							0.13
Iron (µg/g)							<0.2
Potassium (µg/g)							0.69
Molybdenum (µg/g)							0.11
Sodium (µg/g)							1.03
Nickel (µg/g)							0.13

Gaseous Stream Analysis

Sample Location	PH1	PH2	Effluent
Oxygen (%)	38.94	31.62	28.63
Nitrogen (%)	14.51	12.99	7.83
Nitrous Oxide (%)	0.00	1.48	5.00
Carbon Monoxide (%)	2.69	1.82	< 0.1
Carbon Dioxide (%)	40.65	48.87	55.34
Nitrous Dioxide (%)	< 0.1	< 0.1	< 0.1
Methane (%)	n.d	n.d	n.d
Ethane (%)	n.d	n.d	n.d
water vapor [%]	3.32	3.32	3.32
total	100.11	100.10	100.12

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2,4 DNP and ammonia Run 3

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2,4dnp				
TOC	n/a		in 2,4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	21.7%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			23.968			67.9%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	35.310			
Liquid Effluent							
Total Ammonia (as NH ₃)	17.031	0.788			18.5%		
TOC	12.011		0.002		0.0%	0.0%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00027	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00000	0.00000		0.0%	0.0%
Bicarbonate (HCO ₃)	61.00		0.53293	1.59880		6.8%	4.5%
Water (H ₂ O) (see note)	18.00			4.3955925			
Vent Gas							
Oxygen (O ₂)	32.00			8.8040			24.9%
Nitrogen (N ₂)	28.01	2.1079			49.5%		
Nitrous Oxide (N ₂ O)	44.01	1.3459		0.7688	31.6%		
Carbon Monoxide (CO)	28.01		0.0001	0.0002		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.3877	17.0175		81.3%	48.2%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.5105		0.0%	
Total Effluents		4.242	6.925	32.587			
Recovery (effluent/influent)x100	%	99.56	88.18	92.29			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	49.50%	
TOC	99.98%	None detected in effluent
CO yield	0.002	
CO ₂ yield	0.92	
N ₂ O	0.22	
N ₂ yield	0.34	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2,4 DNP and ammonia Run 4

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH₃
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 1.00 kg/h 16.745879 g/min 21.05 % Excess
 Stoichiometric O₂ flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.7090 g/mol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2_in	RL6_in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1130
Ratio NH ₃ /TOC (mole/mole)	0.19367496						484.4978
Total Organic Carbon (µgC/g)	8855.23043						2
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						0.3
Nitrite (µg/g)	< 0.1						< 0.1
carbonate (µg/g)	3953.33						60
bicarbonate (µg/g)	1893.33						3940
Metals							
Calcium (µg/g)							0.670853
Chromium (µg/g)							0.14165
Copper (µg/g)							0.223907
Iron (µg/g)							<0.2
Potassium (µg/g)							1.212058
Molybdenum (µg/g)							<0.1
Sodium (µg/g)							1.722236
Nickel (µg/g)							0.126336

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	5.91
Nitrogen (%)	11.28
Nitrous Oxide (%)	5.63
Carbon Monoxide (%)	< 0.1
Carbon Dioxide (%)	73.97
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
total	100.11

Abbreviation

Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream	Vent gas (GLS) effluent

2.4 DNP and ammonia Run 4

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	27.3%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			16.746			59.6%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	28.088			
Liquid Effluent							
Total Ammonia (as NH ₃)	17.031	0.881			20.7%		
TOC	12.011		0.002		0.0%	0.0%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00937	0.02811		0.1%	0.1%
Bicarbonate (HCO ₃)	61.00		0.60512	1.81535		7.7%	6.5%
Water (H ₂ O) (see note)	18.00			4.235041			
Vent Gas							
Oxygen (O ₂)	32.00			1.3408			4.8%
Nitrogen (N ₂)	28.01	2.2404			52.6%		
Nitrous Oxide (N ₂ O)	44.01	1.1181		0.6387	26.2%		
Carbon Monoxide (CO)	28.01		0.0001	0.0001		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.2991	16.7817		80.2%	59.7%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.3766		0.0%	
Total Effluents		4.240	6.917	24.841			
Recovery (effluent/influent)x100	%	99.52	88.09	88.44			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	43.50%	
TOC	99.98%	
CO yield	0.001	
CO ₂ yield	0.91	
N ₂ O	0.18	
N ₂ yield	0.36	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2,4 DNP and ammonia Run 4b

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH₃
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 0.81 kg/h 13.5705 g/min -1.90 % Excess
 Stoichiometric O₂ flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.6530 gmol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2 in	RL6 in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1320
Ratio NH ₃ /TOC (mole/mole)	0.19367496						226.3848
Total Organic Carbon (µgC/g)	8855.23043						5
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						0.1
Nitrite (µg/g)	< 0.1						< 0.1
carbonate (µg/g)	3953.33						0
bicarbonate (µg/g)	1893.33						4580
Metals							
Calcium (µg/g)							0.23
Chromium (µg/g)							0.09
Copper (µg/g)							0.46
Iron (µg/g)							<0.2
Potassium (µg/g)							0.75
Molybdenum (µg/g)							<0.1
Sodium (µg/g)							0.82
Nickel (µg/g)							0.20

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	0.00
Nitrogen (%)	12.49
Nitrous Oxide (%)	5.09
Carbon Monoxide (%)	< 0.1
Carbon Dioxide (%)	79.21
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
total	100.11

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2,4 DNP and ammonia Run 4b

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
<i>Feed</i>							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	30.8%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.2%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			13.571			54.5%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	24.912			
<i>Liquid Effluent</i>							
Total Ammonia (as NH ₃)	17.031	1.030			24.2%		
TOC	12.011		0.004		0.0%	0.0%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00000	0.00000		0.0%	0.0%
Bicarbonate (HCO ₃)	61.00		0.70341	2.11023		9.0%	8.5%
Water (H ₂ O) (see note)	18.00			3.9808344			
<i>Vent Gas</i>							
Oxygen (O ₂)	32.00			0.0000			0.0%
Nitrogen (N ₂)	28.01	2.2848			53.6%		
Nitrous Oxide (N ₂ O)	44.01	0.9310		0.5318	21.8%		
Carbon Monoxide (CO)	28.01		0.0001	0.0001		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.2126	16.5511		79.1%	66.4%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.3469		0.0%	
Total Effluents		4.246	6.922	23.176			
Recovery (effluent/influent)x100	%	99.65	88.15	93.03			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	34.00%	
TOC	99.94%	
CO yield	0.001	
CO ₂ yield	0.90	
N ₂ O	0.15	
N ₂ yield	0.37	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 5

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as 2,4 Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH₃
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 1.483 kg/h 24.709772 g/min 78.62 % Excess
 Stoichiometric O₂ flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.9680 g/mol/min **See Note**

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2in	PH2out	RL2_in	RL6_in	Effluent
Total Ammonia (as N) (µgN/g)	2000.00	1280.00	1140.00	1160.00	812.00	1040.00	1160.00
ratio NH ₃ /TOC (mole/mole)	0.23						
Total Organic Carbon (µgC/g)	8858.04	2290.00	1870.00	1300.00	130.00	21.00	3.0
pH	9.22	7.97	7.97	8.07	8.88	8.38	7.9
Picric acid (µg/g)	< 1	14.6	48.2	<1	0.6	<1	<1
2,4-Dinitrophenol (µg/g)	22630	1556.9	1083.1	587.7	2.5	<1	<1
2,6-Dinitrophenol (µg/g)	111.8	<1	<1	<1	<1	<1	<1
2-Nitrophenol (µg/g)	< 1	534.5	<1	<1	4.6	1.1	<1
4-Nitrophenol (µg/g)	< 1	234.2	<1	<1	0.5	<1	<1
Phenol (µg/g)	< 1	< 1	<1	<1	<1	<1	<1
Nitrate (NO ₃) (as N) (µg/g)	< 0.1	< 0.1	1.5	1.1	0.4	0.2	0.1
Nitrite (NO ₂) (as N)(µg/g)	< 0.1	< 0.1	2.1	0.4	<0.1	<0.1	<0.1
Carbonate(CO ₃)	3953.33	0	0	120	0	360	200
Bicarbonate(HCO ₃)	1893.33	3420	4860	3380	2720	3760	3740
Metals							
Calcium (µg/g)							0.36
Cobalt							<0.05
Chromium (µg/g)							0.24
Copper (µg/g)							0.49
Iron (µg/g)							<0.2
Potassium (µg/g)							1.35
Molybdenum (µg/g)							0.12
Sodium (µg/g)							1.44
Nickel (µg/g)							0.14

Gaseous Stream Analysis

Sample Location	PH1	PH2	Effluent
Oxygen (%)	39.87	34.49	30.19
Nitrogen (%)	13.73	12.26	6.98
Nitrous Oxide (%)	0.00	0.98	5.31
Carbon Monoxide (%)	3.25	7.12	< 0.1
Carbon Dioxide (%)	39.94	41.93	54.30
Nitrous Dioxide (%)	< 0.1	< 0.1	< 0.1
Methane (%)	n.d	n.d	n.d
Ethane (%)	n.d	n.d	n.d
water vapor [%]	3.32	3.32	3.32
total	100.11	100.10	100.10

Abbreviation

Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 1 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2.4 DNP and ammonia Run 5

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	21.3%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			24.710			68.5%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	36.051			
Liquid Effluent							
Total Ammonia (as NH ₃)	17.031	0.905			21.2%		
TOC	12.011		0.002		0.0%	0.0%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00027	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.03123	0.09369		0.4%	0.3%
Bicarbonate (HCO ₃)	61.00		0.57440	1.72320		7.3%	4.8%
Water (H ₂ O) (see note)	18.00			4.1949031			
Vent Gas							
Oxygen (O ₂)	32.00			9.3513			25.9%
Nitrogen (N ₂)	28.01	1.8928			44.4%		
Nitrous Oxide (N ₂ O)	44.01	1.4397		0.0000	33.8%		
Carbon Monoxide (CO)	28.01		0.0001	0.0002		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.3133	16.8193		80.4%	46.7%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.5142		0.0%	
Total Effluents		4.238	6.924	32.185			
Recovery (effluent/influent)x100	%	99.46	88.17	89.27			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	42.00%	
TOC	99.97%	
CO yield	0.002	
CO ₂ yield	0.91	
N ₂ O	0.23	
N ₂ yield	0.30	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 6

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH3
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O2 flow rate: 0.96 kg/h 16.058348 g/min 16.08 % Excess
 Stoichiometric O2 flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.6800 gmol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2_in	RL6_in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1230
Ratio NH3/TOC (mole/mole)	0.19367496						105.4747
Total Organic Carbon (µgC/g)	8855.23043						10
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						0.1
Nitrite (µg/g)	< 0.1						< 0.1
carbonate (µg/g)	3953.33						40
bicarbonate (µg/g)	1893.33						3980
Metals							
Calcium (µg/g)							0.77
Chromium (µg/g)							0.13
Copper (µg/g)							0.37
Iron (µg/g)							<0.2
Potassium (µg/g)							1.64
Molybdenum (µg/g)							<0.1
Sodium (µg/g)							1.93
Nickel (µg/g)							0.13

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	2.50
Nitrogen (%)	11.16
Nitrous Oxide (%)	6.07
Carbon Monoxide (%)	< 0.1
Carbon Dioxide (%)	77.07
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor (%)	3.32
total	100.12

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2.4 DNP and ammonia Run 6

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	28.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			16.058			58.6%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	27.400			
Liquid Effluent							
Total Ammonia (as NH ₃)	17.031	0.959			22.5%		
TOC	12.011		0.008		0.0%	0.1%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00625	0.01874		0.1%	0.1%
Bicarbonate (HCO ₃)	61.00		0.61126	1.83378		7.8%	6.7%
Water (H ₂ O) (see note)	18.00			4.101248			
Vent Gas							
Oxygen (O ₂)	32.00			0.5440			2.0%
Nitrogen (N ₂)	28.01	2.1259			49.9%		
Nitrous Oxide (N ₂ O)	44.01	1.1561		0.6604	27.1%		
Carbon Monoxide (CO)	28.01		0.0001	0.0001		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.2947	16.7698		80.2%	61.2%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.3612		0.0%	
Total Effluents		4.242	6.922	23.930			
Recovery (effluent/influent)x100	%	99.56	88.15	87.33			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	38.50%	
TOC	99.89%	
CO yield	0.001	
CO ₂ yield	0.911	
N ₂ O	0.185	
N ₂ yield	0.341	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 6b

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH₃
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 0.86 kg/h 14.307429 g/min 3.43 % Excess
 Stoichiometric O₂ flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.6520 gmol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2_in	RL6_in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1300
Ratio NH ₃ /TOC (mole/mole)	0.19367496						222.9547
Total Organic Carbon (µgC/g)	8855.23043						5
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						< 0.1
Nitrite (µg/g)	< 0.1						< 0.1
carbonate (µg/g)	3953.33						0
bicarbonate (µg/g)	1893.33						4660
Metals							
Calcium (µg/g)							0.31
Chromium (µg/g)							0.11
Copper (µg/g)							0.44
Iron (µg/g)							<0.2
Potassium (µg/g)							0.63
Molybdenum (µg/g)							<0.1
Sodium (µg/g)							1.00
Nickel (µg/g)							0.15

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	0.00
Nitrogen (%)	11.37
Nitrous Oxide (%)	6.31
Carbon Monoxide (%)	< 0.1
Carbon Dioxide (%)	79.10
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
total	100.10

Abbreviation

Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2,4 DNP and ammonia Run 6b

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
Feed							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	29.9%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			14.307			55.8%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	25.649			
Liquid Effluent							
Total Ammonia (as NH ₃)	17.031	1.014			23.8%		
TOC	12.011		0.004		0.0%	0.0%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00000	0.00000		0.0%	0.0%
Bicarbonate (HCO ₃)	61.00		0.71570	2.14709		9.1%	8.4%
Water (H ₂ O) (see note)	18.00			4.007593			
Vent Gas							
Oxygen (O ₂)	32.00			0.0000			0.0%
Nitrogen (N ₂)	28.01	2.0767			48.7%		
Nitrous Oxide (N ₂ O)	44.01	1.1524		0.6583	27.0%		
Carbon Monoxide (CO)	28.01		0.0001	0.0001		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.1945	16.5028		78.9%	64.3%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.3463		0.0%	
Total Effluents		4.244	6.916	23.317			
Recovery (effluent/influent)x100	%	99.59	88.07	90.91			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	35.00%	
TOC	99.94%	
CO yield	0.001	
CO ₂ yield	0.896	
N ₂ O	0.185	
N ₂ yield	0.333	

Notes:

Vent gas flow calculated from molar balance, Table H.4

Water molar flows calculated according to Equation [31]

2,4 DNP and ammonia Run 6c

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH₃
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 0.68 kg/h 11.29 g/min -18.40 % Excess
 Stoichiometric O₂ flow rate: 0.83 kg/h 13.83 g/min
 Vent Gas Flow rate: 0.6380 gmol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 In	PH2 In	Ph2 out	RL2 In	RL6 In	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1480
Ratio NH ₃ /TOC (mole/mole)	0.19367496						40.93958
Total Organic Carbon (µgC/g)	8855.23043						31
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						< 1
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						< 0.1
Nitrite (µg/g)	< 0.1						< 0.1
carbonate (µg/g)	3953.33						0
bicarbonate (µg/g)	1893.33						5280
Metals							
Calcium (µg/g)							0.33
Chromium (µg/g)							<0.05
Copper (µg/g)							2.42
Iron (µg/g)							<0.2
Potassium (µg/g)							<0.5
Molybdenum (µg/g)							<0.1
Sodium (µg/g)							0.69
Nickel (µg/g)							0.12

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	0.00
Nitrogen (%)	12.53
Nitrous Oxide (%)	4.77
Carbon Monoxide (%)	1.29
Carbon Dioxide (%)	78.20
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
total	100.11

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream	Vent gas (GLS) effluent

2,4 DNP and ammonia Run 6c

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
<i>Feed</i>							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	33.9%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.2%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			11.289			49.9%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	22.630			
<i>Liquid Effluent</i>							
Total Ammonia (as NH ₃)	17.031	1.154			27.1%		
TOC	12.011		0.024		0.0%	0.3%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00000	0.00000		0.0%	0.0%
Bicarbonate (HCO ₃)	61.00		0.81092	2.43276		10.3%	10.8%
Water (H ₂ O) (see note)	18.00			3.7667657			
<i>Vent Gas</i>							
Oxygen (O ₂)	32.00			0.0000			0.0%
Nitrogen (N ₂)	28.01	2.2394			52.6%		
Nitrous Oxide (N ₂ O)	44.01	0.8524		0.4869	20.0%		
Carbon Monoxide (CO)	28.01		0.0989	0.1317		1.3%	0.6%
Carbon Dioxide (CO ₂)	44.01		5.9925	15.9647		76.3%	70.5%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.3389		0.0%	
Total Effluents		4.247	6.928	22.784			
Recovery (effluent/influent)x100	%	99.67	88.23	100.68			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	26.00%	
TOC	99.65%	
CO yield	0.014	
CO ₂ yield	0.867	
N ₂ O	0.137	
N ₂ yield	0.359	

Notes:

Vent gas flow calculated from molar balance, Table H.4
Water molar flows calculated according to Equation [31]

2.4 DNP and ammonia Run 7

Date of test: July 4th, 2002
 Data file: jul4.txt
 Feed: Ammonium 2,4 Dinitrophenolate
 Feed concentration: 2.264 wt% as 2,4 Dinitrophenol
 Feed total ammonia: 0.243 wt% as NH₃
 Feed TOC: 0.886 wt% as TOC
 Feed Flow rate: 0.780 litres/min
 O₂ flow rate: 1.437 kg/h 23.951905 g/min 73.15 % Excess
 Stoichiometric O₂ flow rate: 0.83 kg/h
 Vent Gas Flow rate: 0.9420 g/mol/min *See Note*

Aqueous Stream Analysis

Sample Location	Feed	PH1 in	PH2 in	Ph2 out	RL2 in	RL6 in	Effluent (GLS)
Total Ammonia (µgN/g)	2000						1150
Ratio NH ₃ /TOC (mole/mole)	0.19367496						65.74306
Total Organic Carbon (µgC/g)	8855.23043						15
pH	9.2						
Picric Acid (µg/g)	< 1						< 1
2,4-Dinitrophenol (µg/g)	22630						< 1
2,6-Dinitrophenol (µg/g)	111.8						< 1
2-Nitrophenol (µg/g)	< 1						0.5
4-Nitrophenol (µg/g)	< 1						< 1
Phenol (µg/g)	< 1						< 1
Nitrate (µg/g)	< 0.1						0.2
Nitrite (µg/g)	< 0.1						< 0.1
carbonate (µg/g)	3953.33						0
bicarbonate (µg/g)	1893.33						4020
Metals							
Calcium (µg/g)							0.26
Chromium (µg/g)							0.20
Copper (µg/g)							0.41
Iron (µg/g)							<0.2
Potassium (µg/g)							0.65
Molybdenum (µg/g)							0.12
Sodium (µg/g)							3.10
Nickel (µg/g)							0.12

Gaseous Stream Analysis

Sample Location	effluent
Oxygen (%)	28.53
Nitrogen (%)	8.35
Nitrous Oxide (%)	4.33
Carbon Monoxide (%)	< 0.1
Carbon Dioxide (%)	55.58
Hydrogen (%)	< 0.1
Methane (%)	n.d
Ethane (%)	n.d
water vapor [%]	3.32
total	100.11

Abbreviation

Abbreviation	Sample Location
Feed	Feed prior to test
Effluent	Final effluent
PH2_in	Preheater 2 Inlet
PH2_out	Preheater 2 Outlet
RL2_in	Reactor Section 2 Inlet
RL6_in	Reactor Section 6 Inlet
Gaseous stream PH1	Vent gas (GLS) PH1 in
Gaseous stream PH2	Vent gas (GLS) PH2
Gaseous stream effluent	Vent gas (GLS) effluent

2.4 DNP and ammonia Run 7

Mass Balance		Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen
		14.0067	12.011	15.9994	% of infl.	% of infl.	% of infl.
Component	M.W.	g/min	g/min	g/min			
<i>Feed</i>							
Total Ammonia (as NH ₃)	17.031	1.560			36.6%		
Total Carbon less TOC	n/a		in 2.4dnp				
TOC	n/a		in 2.4dnp				
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	2.686	6.909	7.670	63.0%	88.0%	21.7%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.013	0.034	0.038	0.3%	0.4%	0.1%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.000	0.000		0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00078		0.00267	0.0%		0.0%
Nitrite (NO ₂)	45.99	0.00078		0.00178	0.0%		0.0%
Carbonate	60.00		0.61728	2.46679			
Bicarbonate	61.00		0.29078	1.16203			
Oxygen (O ₂)	32.00			23.952			67.9%
Water (H ₂ O)	18.00			0.000			0.0%
Total Influent		4.261	7.853	35.294			
<i>Liquid Effluent</i>							
Total Ammonia (as NH ₃)	17.031	0.897			21.1%		
TOC	12.011		0.012		0.0%	0.1%	
Picric Acid (C ₆ H ₃ N ₃ O ₇)	229.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,4-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2,6-Dinitrophenol (C ₆ H ₄ N ₂ O ₅)	184.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
2-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
4-Nitrophenol (C ₆ H ₅ NO ₃)	139.11	0.000	0.000	0.000	0.0%	0.0%	0.0%
Phenol (C ₆ H ₆ O)	94.11		0.001	0.000	0.0%	0.0%	0.0%
Nitrate (NO ₃)	61.99	0.00008		0.00000	0.0%	0.0%	0.0%
Nitrite (NO ₂)	45.99	0.00008		0.00018	0.0%		0.0%
Carbonate (CO ₃)	60.00		0.00000	0.00000		0.0%	0.0%
Bicarbonate (HCO ₃)	61.00		0.61740	1.85221		7.9%	5.2%
Water (H ₂ O) (see note)	18.00			4.2082824			
<i>Vent Gas</i>							
Oxygen (O ₂)	32.00			8.5998			24.4%
Nitrogen (N ₂)	28.01	2.2035			51.7%		
Nitrous Oxide (N ₂ O)	44.01	1.1425		0.6526	26.8%		
Carbon Monoxide (CO)	28.01		0.0001	0.0002		0.0%	0.0%
Carbon Dioxide (CO ₂)	44.01		6.2885	16.7534		80.1%	47.5%
Hydrogen (H ₂)	2.016						
Methane (CH ₄)	16.04		0.0000			0.0%	
Ethane (C ₂ H ₆)	30.07		0.0000			0.0%	
water vapor	18.00			0.5004		0.0%	
Total Effluents		4.243	6.920	32.068			
Recovery (effluent/influent)x100	%	99.59	88.12	90.86			

Destruction Efficiencies	Effluent	Comments
Dinitrophenol	99.996%	None detected in effluent
Total Ammonia	42.50%	
TOC	99.83%	
CO yield	0.002	
CO ₂ yield	0.910	
N ₂ O	0.183	
N ₂ yield	0.353	

Notes:

Vent gas flow calculated from molar balance, Table H.4
 Water molar flows calculated according to Equation [31]

Deviations in oxygen excesses per runs

Note: The deviations corresponding to runs 2, 2b, 4, 4b, 6, 6b, 6c, and 7 are referred to in Appendix A, Table A.4

Table H.7 Uncertainties in oxygen flows. 2,4 DNP and ammonia experiment, runs 1, 3, and 5

Parameter	Run	1	3	5
O2 flow [V]	Average	2.11	2.11	2.12
	Max	2.14	2.13	2.16
	Min	2.10	2.10	2.11
O2 flow [kg/h]	Average	1.45	1.44	1.48
	Max	1.63	1.55	1.73
	Min	1.37	1.37	1.41
O2 excess [%]	Average	74.73	73.27	78.62
	Max	95.92	87.31	108.24
	Min	65.24	64.74	69.67
O2 excess (deviation from the mean) [%]	Max	21.19	14.04	29.62
	Min	-9.49	-8.53	-8.95

Appendix I Corrosion

Table I.1 Metals losses. 2,4 DNP, ammonia and ammonium sulphate experiments

	INC 625 composition (%wt)	Lost mg/L (from analyses)	Vol of waste treated [L]	total loss in g
Ni	62.69	81.1	58.00	4.7038
Cr	21.89	4.71	58.00	0.2732
Mo	9.01	231	58.00	13.3980
total				18.3750

Weight of 1 m ³ of INC 625= density [g/m ³]	8.44E+06
For 3/8" tubing without corrosion, the area is [m ²]	4.09E-05
internal diameter [mm]	6.22E+00
Thickness [mm]	1.65E+00
weight of the 3/8" tube per meter [g/m]	3.45E+02

Assuming uniform losses in a length of [m]	1 meter	0.8 meter	0.5 meter	0.1 meter
Weight of tube length without corrosion [g]	3.449E+02	2.760E+02	1.725E+02	3.449E+01
Weight of tube after losing material from corrosion [g]	3.266E+02	2.576E+02	1.541E+02	1.612E+01
new area after losing the material [m ²]	3.869E-05	3.815E-05	3.652E-05	1.910E-05
New internal diameter (corrosion in inner part of the tube) [mm]	6.431580167	6.485231216	6.643585282	8.143294235
New thickness [mm]	1.546709917	1.519884392	1.440707359	0.690852883
Thickness loss [mm]	0.106	0.133	0.212	0.962

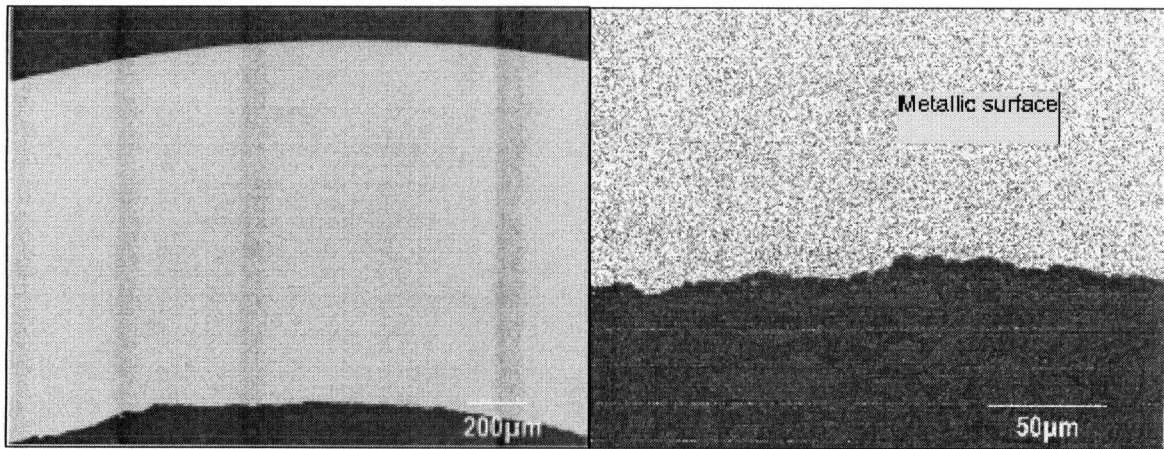


Figure I.1 Optical microscope image. Preheater 1, corroded section

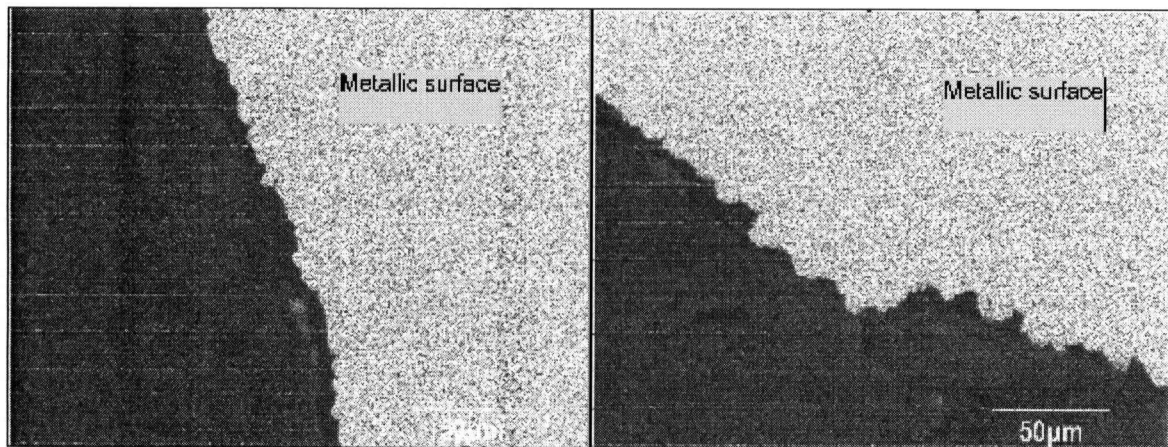


Figure I.2 Optical microscope image. Preheater 1, corroded section, pits

Appendix J Matlab programs and electronic files

Matlab files

Table J.1 Matlab files

File name (.m)	Text files (.txt)	Experiment	Functions
tables	k, cp, enth, prand, vis	-	Lookup table for thermodynamic data
oxygendata oxygenintrapolation	densoxygen, visoxygen	-	Lookup table and interpolation for oxygen densities
ratelawsanalysys	run1, run2, run3, run4, run5, run6, run7, run8, run9	Phenol	Residence time calculations, rate laws analyses, error analyses
convphenol	convphenol		Figure 3.7, Chapter 3
temprofiles2	run2percent		Temperature profiles runs 2.7 % wt.
temprofiles4	test		Temperature profiles runs 4 % wt.
dnpwaste1	waste1	2,4 DNP + ammonia + ammonium sulphate	Residence time calculations, concentration and conversion profiles, error analyses
pressurewaste1	pwaste1		Pressure and oxygen flow fluctuations
RHEX	-	Phenol and 2,4 DNP + ammonia + ammonium sulphate	Calculate PH1 in (RHX out, (cold side))
dnpwaste2	waste2	2,4 DNP + ammonia	Residence time calculations, concentration and conversion profiles, error analyses
pressurewaste2	pwaste2run1, pwaste2run2, pwaste2run22, pwaste2run23, pwaste2run3, pwaste2run4, pwaste2run42, pwaste2run5, pwaste2run6, pwaste2run62, pwaste2run63, pwaste2run7		Pressure and oxygen flow fluctuations

Excel files

Table J.2 Excel files

File name (.xls)	Experiment	Information
phenol	Phenol	Runs raw data, oxygen flows and pressure uncertainties, initial molar concentrations
sulphate red water	2,4 DNP + ammonia + ammonium sulphate	Run 0 raw data, oxygen flow and pressure uncertainties
red water no sulphate	2,4 DNP + ammonia	Runs raw data, oxygen flows and pressure uncertainties, nitrogen and carbon balances
mass balance all experiments	All	mass balances, gas flow calculations
PT calibration	-	Appendix A, first pressure transducer's calibration
secondPT calibration	-	Appendix A, second pressure transducer's calibration
gas flowmeter	-	Appendix B, gas flow meter correction table

Experiment data files (original files)

Table J.3 Experiments data files

File name (.txt)	Experiment	Information
jul11-1a	Phenol	Run 1
jul11-1b		Run 2
jul11-2b		Run 3, Run 4
jul19-1a		Run 5
jul19-1b		Run 6
jul25-2a		Run 7
jul25-2b		Run 8, Run 9
nov2601, nov26b01	2,4 DNP + ammonia + ammonium sulphate	Run 0
jul4	2,4 DNP + ammonia	All runs