STUDY OF THE PHASE BEHAVIOR OF MONO-NITRATED POLY-SUBSTITUTED AROMATIC NITROCOMPOUNDS

A Dissertation

by

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ABSTRACT

Mixed-acid nitration is a well-established process that has been conducted industrially for over 70 years. It involves highly exothermic reactions that must be managed to avoid thermal runaway events, a risk complicated by monomolecular decomposition reactions undertaken by the reaction products at elevated temperatures. Process disturbances that have the potential to cause thermal shocks or unexpected heating in the process are therefore a severe threat to the process and must be investigated. Recent work in literature shows that nitrobenzene is capable of forming microemulsions and undergoing transitions between different types of emulsified systems detailed by PA Winsor. This work was therefore undertaken to observe representative mixtures of sulfuric acid, water, and select simple aromatics to determine if microemulsions were forming in the system in composition and temperature ranges typical of industrial processes and to determine what, if any, impact the substitution of small functional groups onto the aromatic ring had on the microemulsion formation. Literature was reviewed to search for appropriate models that could be used to predict the formation of microemulsions in these and similar systems.

Microemulsions were determined to be forming in the mixed-acid nitration system and that additional functional groups on the aromatic ring could affect the microemulsion formation within the system, usually adversely. However, the formation of three phases

including a middle phase microemulsion – a key point of interest to this work with regard to operability of the process – did not occur in compositional ranges commonly seen and expected in industry. Additionally, the type-III and type-IV microemulsions which where the central focus of this work all collapsed at temperatures of around 30°C, well below the 60-100°C expected of continuous industrial nitration processes.

It was determined that existing models in literature for prediction microemulsions are ill suited to describe the behavior of this system. However, experimental results showing that this behavior poses no threat to the process show that developing a new model for systems such as this one is of little practical value.

DEDICATION

To my mother who never gave up on “the throw-away baby,” and never stopped believing in what I could accomplish.

To my step-father, who still has not gotten tired of me and my constant talking about my crazy ideas.

To Shandy, for helping me to once again see a path forward into a grander future.

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Thanks also go to the members of the MKOPSC Steering Committee who have assisted in my research and professional development. My gratitude is extended to the students and faculty at Texas A&M, as well as members of the B/CS community who have made my time at Texas A&M so full, rich, and rewarding.

NOMENCLATURE

DNB	Dinitrobenzene
DNT	Dinitrotoluene
EOS	Equation of State
MNB	Mononitrobenzene or nitrobenzene
MNT	Mononitrotoluene or nitrotoluene
MKOPSC	Mary Kay O’Connor Process Safety Center
mMNT	Metamononitrotoluene or 3-mononitrotoluene (3-MNT)
oMNT	Orthomononitrotoluene or 2-mononitrotoluene (2-MNT)
pMNT	Paramononitrotoluene or 4-mononitrotoluene (4-MNT)

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1. INTRODUCTION

This work investigated the effect of the addition and location of substituent groups onto aromatic benzene rings on the thermodynamic behavior of the mixed acid nitration system. Hopes are that the results would allow for improvements in the design and operability of such processes, leading to improved process safety and a reduction in incidents in this industrial sector.

Background

Aromatic nitro compounds are a class of highly energetic materials that have long been used in a variety of industrial applications. The most famous and widely used members of this class are those involving nitro groups (-NO_2) attached to six membered aromatic carbon rings, or benzene rings.[1,2] When only nitro groups are attached to the aromatic ring the compounds are known as nitrobenzenes. The addition of an alcohol (–OH) functional group results in nitrophenols, the addition of a methyl (-CH3) group results in nitrotoluenes, an amine (-NH3) group on the ring forms nitroanilenes, and alcohol and methyl groups together on the ring form nitrocresols.[3] This work emphasizes nitrotoluenes as representative chemicals from this class and attempts to compare their behavior to that of nitrobenzene in order to investigate the effects of additional substituent groups on the aromatic rings on the behavior of interest.

The nitration products of toluene, mononitrotoluene (MNT), and dinitrotoluene (DNT), are used most often as intermediates in the production of polyurethanes. For polyurethane production, toluene is nitrated twice to DNT, reduced to toluenediamine (TDA), and then converted to toluene diisocyanate (TDI) as outlined in figure 1. The TDI is then used to make the polyurethanes.[1,2] Because the positions at which the nitro groups attach to the aromatic rings determine the locations of the amine groups and other subsequent reactions, the location of the nitro groups on the aromatic ring are important when nitrotoluenes are produced. The 2,4- and 2,6- isomers of DNT are therefore valued over the 2,3-, 2,5-, 3,4- and 3,5- isomers.[4] The green box and arrows indicate the parts of this chain which involve the nitration reactions of interest to this work. Mononitrotoluenes are also used heavily in the production of aze, azo, and sulfur dyes, rubber chemicals, and agricultural chemicals.[5]

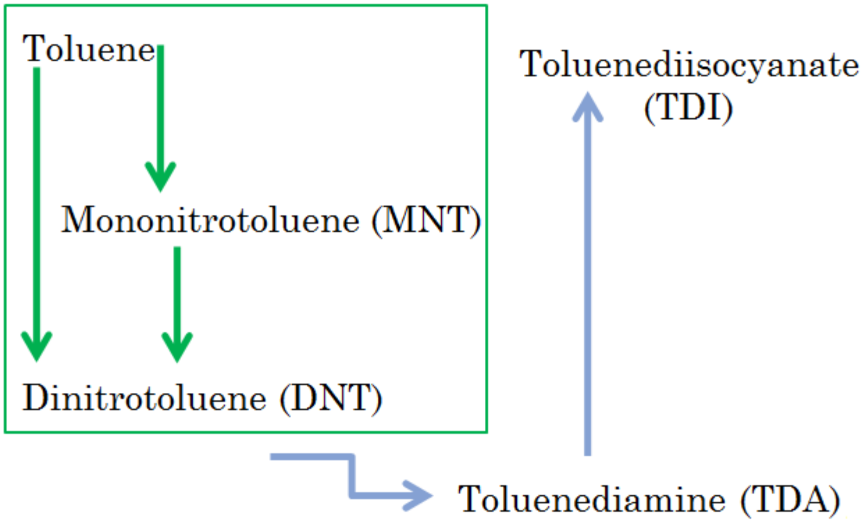

Figure 1: Typical usage and product sequence for toluene nitration.

These chemicals however participate in a variety of highly dangerous and potentially violent reactions, nitration and monomolecular decomposition included. These reactions lead to thermal runaway events, explosions, and fires which require measures to mitigate and prevent catastrophic incidents, some examples of which are provided in the next section. Nitration by mixed acid is a very old and, very well understood and mature process that has been conducted industrially for over 70 years now.[6] However it is also a very complex process which exhibits complex phase behavior,[7] material properties, and reactivity. The many associated hazards continue to cause accidents. Principle among these hazards is the inherent instability of the nitration products with their ability to undergo monomolecular decomposition reactions and the demonstrated incompatibilities with broad classes of other materials which make the nitration products even less stable when impure – as they are during processing. These incompatibilities and decomposition reactions have inspired continued interest and research.[8,9,10] Recent work in the field has attempted to find new, better, cleaner ways to carry out the nitration of toluene using solid state catalysts instead of sulfuric acid, in keeping with the traditional mixed acid process.[11,12] Yet, the mixed acid process is still predominant in industry and therefore it should remain a goal to make this process as safe and operable as possible.

The Chemical Safety Board (CSB) analyzed 167 "serious" reactive chemical related incidents within the United States from 1980 to mid-2001. Forty-eight of these incidents resulted in a total of 108 fatalities and 50 of these incidents affected the public. "Approximately 70 percent of the 167 incidents occurred in the chemical manufacturing industry. Thirty percent involved a variety of other industrial sectors that store, handle or use chemicals in bulk quantities."[13] It is essential to understand and be able to predict the behavior of highly reactive and exothermic systems in order to prevent such incidents and maintain safe operation. In systems that exhibit multi-phase equilibria, understanding this behavior is essential to implementing appropriate procedures, controls, and countermeasures to prevent incidents.

Aromatic Nitration, Sulfonation, and System Chemistry

Benzene and related compounds, like toluene, are referred to as "aromatic" compounds and are said to possess "aromaticity," which is defined as the unusual stability that results from a cyclic conjugated system of $4n+2$ π, "pi," electrons (as opposed to σ, "sigma" electrons). These conjugated systems of alternating single and double bonds give aromatic compounds a unique chemistry[3] which must be understood in order to safely control the system.

Electrophilic aromatic substitution is a common chemical reaction in which an electrophile, often a positively charged reactant that is attracted to an electron rich center,[14] reacts with an aromatic ring and displaces a weaker electrophile, usually hydrogen. Several common electrophilic substitution reactions require a catalyst to help them proceed at an appreciable rate.[3]

Nitration is an electrophilic substitution reaction in which a hydrogen atom attached to the ring is replaced by a nitro (-NO2) group, provided by a nitric acid molecule. This is catalyzed by sulfuric acid in a mechanism that can be seen in Figure 2.[3,15,16,17] Nitration is an extremely exothermic reaction that produces an enormous amount of heat.

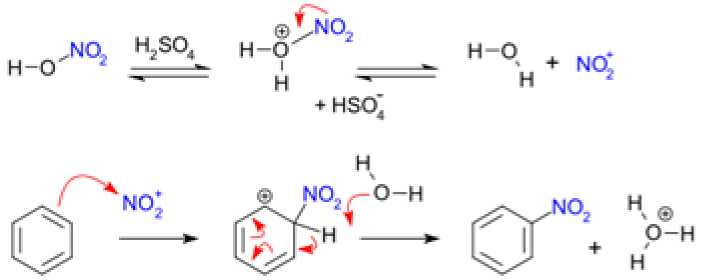

Figure 2: Mechanism for aromatic nitration catalyzed by sulfuric acid.

The sulfuric acid acts to liberate nitronium ions from the nitric acid, which are then free to attack the aromatic rings and replace hydrogen ions.[3,15] The reaction follows a roughly second-order Arrhenius rate model, depending on the concentration of nitric acid and the organic material in the aqueous phase. The reaction is generally assumed to proceed only in the aqueous phase as the nitronium ion cannot exist in appreciable concentrations in the organic phase.[18,19]

Sulfuric acid acts catalytically, affecting the size of the pre-exponential factor in the Arrhenius rate law expression. Increasing sulfuric acid concentrations from 50% to 80% has been shown to increase the rate of the nitration reaction by several orders of magnitude.[20] The concentration of the sulfuric acid in the aqueous phases is therefore critical to the design, safety, and operability of the process. It is perhaps worth noting that a patent issued by the United States in 1944 (2,362,743) presents a process for producing DNT without using any sulfuric acid, only 70% and 98% nitric acid, however, this process has been found to be the exception, not the rule, and not representative of current practice in the industry.[6]

In addition to the nitration reaction, a sulfonation reaction occurs in the reaction mixture. The mechanism for the production of the SO_3^+ ions is similar to the production of NO_2 ions for nitration and proceeds by the reversible reaction shown in Figure 3.[21]

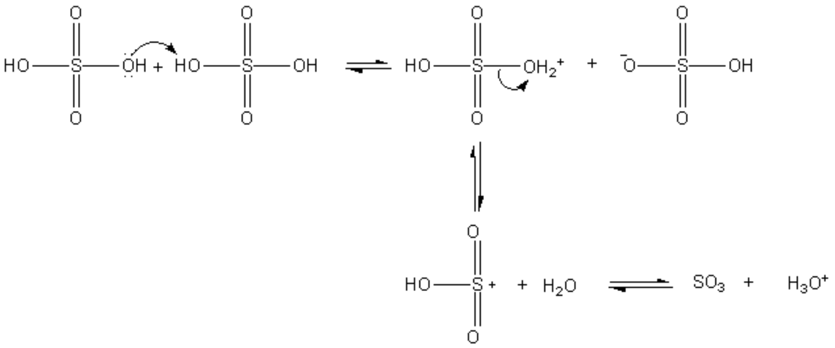

Figure 3: Mechanism for producing SO3+ ions from sulfuric acid.

The reaction for the SO_3 molecules with the aromatic ring is completely analogous to that of NO_2^+, except the sulfonation reaction is reversible where the nitration reaction is not.[3,14] The sulfonation reaction does not generally affect yields as the industry is aware of it and knows how to counter it. This reaction is also very slow compared to nitration and barely occurs at all with nitrobenzene in the temperature ranges of interest in this study. Therefore this reaction gets little attention in literature on nitration processes.

MNT is however substantially more reactive than nitrobenzene. The methyl group attached to the benzene ring in MNT is said to be "ring activating" and makes MNT roughly 25 times more reactive than nitrobenzene. Therefore the sulfonation reaction is much more noticeable with MNT than with nitrobenzene and should not be ignored.[3]

In addition to affecting the overall reactivity of the aromatic rings, substituted functional groups on the ring change the relative stability of transition states for the ring, making additional functional groups more likely to attach to the ring at specific locations.[3]

Once a functional group is attached to the ring, denoted by an R in Figure 4, the other positions at which functional groups can be substituted onto the ring are named based on their position relative to the attached group. They're referred to as ortho, meta, and para positions. As shown in the figure, there are two ortho- and meta- positions and one para-position on the six membered benzene ring. Different functional groups will tend to be either meta-directing, meaning that they make additional groups more likely to attach at the meta position because they stabilize that transition state, or they tend to be ortho- and para- directing, causing new functional groups to attach at one of those three positions.[3]

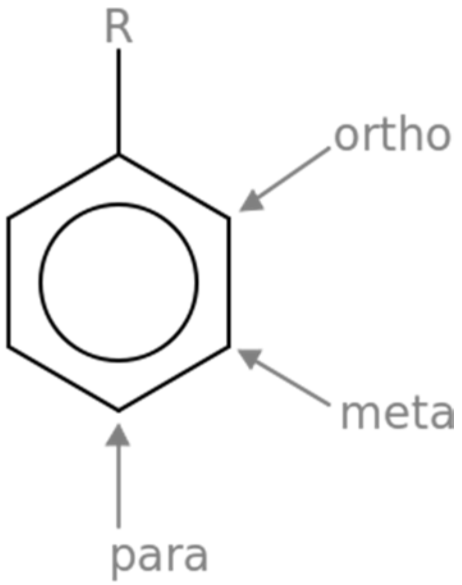

Figure 4: Graphic depiction of ortho-, meta-, and para- positions on a benzene ring.

There's a correlation between the ring activating/deactivating tendency of various functional groups and the site selectivity. Meta-directing functional groups are strongly deactivating. Ortho- and para- directing functional groups are roughly evenly split between ring activators and deactivators, however, the ortho- and para- directing deactivators are much weaker deactivators than the meta- directing functional groups.[3]

All of this has some important implications for the toluene nitration reaction system under consideration, as, in addition to being ring activating, the –CH3 methyl group attached to the ring in toluene is ortho- and para- directing such that the isomers formed by the reaction will usually be 63% ortho, 34% para, and 3% meta, forming mostly 2-nitrotoluene and 4-nitrotoluene. Once attached at an ortho- or para- position relative to the methyl group, the meta-directing nitro groups will tend to encourage the ring to form 2,4- or 2,6-dinitrotoluene. Given that the goal of most nitro toluene production is to produce the more valuable 2,4-dinitrotoluene, this is actually great for process selectivity.

Nitroaromatics are also capable of strong exothermic oxidation and dimerization reactions at temperatures above the normal process temperatures of the nitration reaction. If the operational temperature exceeds a certain safe limit, the additional heat generated can allow the process to produce even more heat, faster, accelerating the move to monomolecular thermal decomposition and detonation, which will be very dangerous.[21] While these reactions are not especially relevant to this work, they contribute to the larger set of thermal hazards associated with the system which are core to the motivation for this work.

Industrial Nitration

The nitration of toluene can be accomplished as a two phase batch, semi-batch, or continuous process and has been accomplished in all of those ways based on review of literature and patent records. When the goal is to produce a dinitrated product, the nitration can be conducted as a single stage process, in which toluene is made into DNT or, as a multi-stage process.[6,22,23,24] The process can also be conducted either isothermally, usually at around 60-100°C, or adiabatically with the process designed to keep the reaction mixture below 150°C to avoid undesired high temperature reactions.[9,11] In two stage processes the first and second nitrations are carried out to completion in single sequential stages.[6,22] Some processes use multiple stages and vessels in which the first and second nitration are broken up over two or more stages.[22,25]

The process produces nitrating acid, a mixture of nitric and sulfuric acid, by blending sulfuric acid – usually at 80-98 wt% - with nitric acid – usually at 70 wt% or 98 wt%.[6,22,23] Nitric acid exhibits an azeotrope with water at approximately 70 wt%. Breaking this azeotrope to produce 98 wt% acid is difficult and expensive, making 98 wt% far more expensive than 70% or lower acid. Therefore using the less concentrated acid is desirable whenever possible.

The acid fed to the reactor is usually 65-80 wt% sulfuric acid, 1-20 wt% nitric acid, and 5-30 wt% water depending on the demands of the process and which nitration is being conducted – first or second. The nitro group is ring deactivating and makes the aromatic ring less reactive so the sulfuric acid concentration is usually higher in the second nitration stage to drive the reaction to completion faster.[6,22] The reaction is often conducted with a slight excess of nitric acid relative to the toluene or MNT – usually approximately a 1.05:1 molar ratio.[24] This slight excess of nitric acid helps to prevent the formation of undesired sulfonic acid via the reversible sulfonation reaction discussed previously.[26]

After the reaction the aqueous phase consists of a depleted acid that's usually about 65-80% sulfuric acid, with the balance being mostly water. There will be some residual unreacted nitric acid and 2-9 wt% organics. For economic and waste management purposes this acid is heated to boil off excess water and re-concentrated so it can be recycled into the process with the addition of fresh nitric acid and sulfuric acid where necessary.[22,25] After leaving the reactor the different isomers of mono and DNT are separated, usually through a mixture of crystallization and distillation, but that process is not pertinent to this work.

Decomposition Reactions and Thermal Runaway Hazards

Extensive literature exists to support the ability of nitrocompounds to undergo monomolecular decomposition at elevated temperatures, releasing massive amounts of heat and evolving large amounts of gas which in turn generates high pressures within enclosed equipment.[8,27,28,29,30] The decomposition reaction has not been proven to be autocatalytic, but there is literature to suggest it might be.[28] Various nitrocompounds are capable of releasing over 1050 kJ/kg upon decomposition,[28] but the heats of decomposition for the isomers of nitrotoluene have been measured at 2070-2405 kJ/kg with DNT isomers releasing 3450-4000 kJ/kg.[8] There has been a great deal of work to determine the mechanisms and pathways of nitrocompound decomposition, but a definitive mechanism has been elusive, most likely because the decomposition reaction can follow multiple paths through multiple intermediates involving dozens of reactions. However, it is generally agreed that the decomposition will produce an assortment of smaller molecules including water, NOx compounds, methanes, ethanes, formaldehyde, and others.[31,32,33]

The intense amount of heat generated by the highly exothermic nitration, oxidation, and dimerization reactions that can occur within the process, has led some to provide a generic scenario leading to thermal runaway events and explosions in mixed acid processes. Under this generic case, insufficient cooling, a build-up of reactants, or an increase in sulfuric acid concentration can lead to a thermal runaway, followed by a thermal explosion, ending with a detonation of the reaction mixture.[29]

The temperature at which the decomposition reaction begins to proceed at an appreciable rate is open to some debate and can depend on the type of equipment used. The onset temperature is generally defined as the temperature at which the substance becomes appreciably self-heating, but the final reported value for the onset temperature usually depends on how the study in question defined "appreciably," and the sensitivity of the equipment used in the tests. Self-heating behavior also requires that the system be able to generate heat faster than it can dissipate it and therefore will also depend on factors such as surface area to volume ratios and system insulation. Therefore, a reported decomposition onset temperature should not be treated as a hard, or fixed value below which there is no risk of runaway. Rather, they are estimates and safety dictates that a substantial gap should be left between the process operating conditions and the reported onset temperature.[28,30]

The reported decomposition onset temperature for nitrotoluene is between 290 and 310°C, depending on the isomer, when found using a DSC. However, the nitroaromatics undergo exothermic reactions with a variety of common acids, bases, and other compounds which also seem to destabilize the nitroaromatics and are incompatible with them. When mixed with H_2SO_4 or HNO_3, as it would be in the mixed acid process, 2-nitrotoluene exhibits decomposition exotherms as low as 240°C or 160°C according to research with a DSC. So understanding these chemical incompatibilities is important to safe operation of the process and has been a point of continued interest in literature.[8,9]

Emulsion Science and System Phase Behavior

Emulsions in the broadest sense are colloids. Thomas Graham is credited with discovering colloids in the 1860s[34] though little interest was given to the materials at the time.[4] Colloids – often called the "forth state of matter" - are defined as substances composed of at least two phases wherein at least one of the phases exists as small particles, usually too small to see with the unaided eye.[34,35] In a colloid, two phases coexist in a system where-in one phase, the internal or dispersed phase, exists in microscopic layers, pockets, micelles, or corpuscles while the other phase, the external or continuous phase, occupies the space between these layers or pockets. This arrangement gives an extremely high surface area per unit volume between the dispersed and continuous phases and surface effects and surface properties are often dominant in the material.[34] The molecules in the emulsion can be organized in to thin sheets called laminae for a laminar or laminated colloid or the colloid may be organized into micelles or corpuscles for a micellular or corpuscular colloid.[18]

The formation and persistence of a colloid depends on a system’s ability to form dispersed particles which can in turn possess two properties. The particles must be able to resist settling through Brownian motion and the particles must be able to resist agglomeration, the formation of larger particles from smaller ones. Settling can be resisted if the particles are below a certain critical size. Agglomeration can be avoided if the particles have a means by which they can repel each other when they become close. For most colloids this is accomplished by using charged particles which will exhibit electrostatic repulsion.[35]

The name given to a class of colloids depends on the state of matter of the phases from which they’re composed, the size of the particles, and the way the phases are intermixed. Suspensions can be coarse or fine depending on the size of the particles involved and dilute or concentrated. Colloids include several subclasses of materials including foams, gels, some pastes, and others. Colloids composed of solid particles dispersed in a liquid phase are referred to as a ‘sol’ where those composed of solid or liquid particles dispersed in a gas are called aerosols. More specifically, solids dispersed in gases are sometimes called smokes and liquids dispersed in gases are sometimes called fogs. A colloid composed of two immiscible liquids is referred to as an emulsion.[35]

The formation and existence of emulsions likely depends on a low surface tension between the two immiscible phases, lowering the free energy requirements for forming the phase interface surface. An emulsifying agent or a surfactant is often required to form a stable emulsion. The surfactant can be a single substance or type of molecule or it can be a mixture of co-surfactants. The surfactant or co-surfactants are generally assumed to exist at the interface between the two phases, lowering the surface tension between the two phases. The relative surface tensions between the phases will determine which phase is dispersed in the other, not the relative amount of each phase present.[35,36]

Emulsions can be divided into three classes based on the size of their particles: traditional or macroemulsions, microemulsions, and nanoemulsions. Most traditional emulsions will eventually settle out into two phases unless periodic agitation and sheer forces are applied to the system to maintain the emulsion. Microemulsions have smaller particles that are below the critical size necessary to avoid settling. With a sufficiently low surface tension microemulsions can be energetically preferred and completely stable, never settling out and remaining emulsified permanently. Nanoemulsions have even smaller particles but are not stable. At extremely small particle sizes the interfacial surface area required becomes too great and the emulsion is no longer energetically favored. As such, nanoemulsions will eventually settle unless agitation is applied and will not form without initial mixing, however some nanoemulsions are capable of persisting for several months without settling.3[7]

Emulsions can exist in one of four different types of stable or metastable systems. P. A. Winsor presented a classification system for these different system types in 1947 in the first of a series of papers focusing on hydrotropy, solubilization, and, emulsification.[38,39] Winsor's work dealt heavily with solubilization using amphiphilic compounds also applies to emulsions formed via the use of surfactants. The classification system he proposed is now widely used in literature and is referred to as Winsor phase behavior. As such, his classification system will be used in this work. Winsor defined a type I system as a two phase system with a reasonably pure organic phase and an aqueous phase containing solubilized organic and surfactant. A type II system was defined as a two phase system with a pure aqueous phase and an organic phase with solubilized water and surfactant. A type III system is a three phase system with free aqueous and organic phases in addition to a third phase that he described as a solution of the surfactant, the organic, and water. Type IV systems have one phase wherein the water, organic and surfactant are emulsified or solubilized.[39] After the adoption of this classification system the type I, type II, type III, and type IV systems became known as Winsor-I, Winsor-II, Winsor-III, and Winsor-IV systems. In the same paper Winsor also outlined the ability of different types of systems to convert into other types in response to changes in system composition or temperature, type I systems becoming type II systems by passing through a type IV state in response to the addition of aqueous material for example. Alternatively, type III systems become type I and type II systems in response to increases in temperature. The stability of microemulsions was treated in more detail in later work by Kahlweit et al including the fact that 3-phase Winsor-III systems have a definable stable temperature range, above or below which they will collapse into Winsor-I or Winsor-II systems.[40]

This has significant implications for the safety and operability of the reactive system that is the focus of this research.

Because the system can exist with a single or multiple liquid phases the system is capable of operating under multiple distinct reaction regimes. These are summarized below.[41]

- Single phase homogeneous system wherein the system is controlled by the inherent reaction kinetics
- Two phase heterogeneous system where the system is sufficiently agitated, allowing for rapid mass transfer. The system is kinetically limited.
- Two phase heterogeneous system where the system lacks sufficient agitation. The system is limited by the mass transfer rate.
- Three phase heterogeneous system where the system is sufficiently agitated, allowing for rapid mass transfer. The system is kinetically limited.
- Three phase heterogeneous system where the system lacks sufficient agitation. The system is limited by the mass transfer rate.

Winsor's original work demonstrates that changes in system composition, such as can be caused by a proceeding reaction, or changes in the system temperature, as can be brought about by heat released from an exothermic reaction like nitration, can cause a transition from one type of system and from one of the reactive models listed above to another. In investigating the thermodynamics of microemulsions, Lam et al. showed that there were in fact three different types of phase inversions made possible by microemulsion forming systems, that all of these types of transitions are gradual, and do not occur in the same compositional ranges. Lam et al. ultimately state that microemulsions are "dynamic systems" wherein flexible interfaces are constantly "warped and twisted by thermal fluctuations."[42]

Using a model that does not accurately describe the system is inherently hazardous. Behavior that deviates significantly from the predictions of the model in use could lead operators to take inappropriate action. It can also lead to improperly designed controllers and designed responses from control systems that are either inadequate or inappropriate. However, this is not the only hazard potentially posed by this ability to transition between different types of systems. Evidence in the literature demonstrates that there is potential for the transition between system types itself to be hazardous to safe process operation.

Zaldivar, Westerterp and their collegues[18,19,43,44] conducted extensive studies of the nitration of benzene to nitrobenzene in a two phase equilibrium, including phase inversions occurring within semi-batch mixed acid nitration process.

In a semi-batch process that exhibits liquid-liquid equilibria, the process is initially loaded with one component, which makes up the principle component of one phase. The other component, which makes up most of the second phase, is added to the reactor gradually. If a catalyst is involved in the reaction it may be added in bulk to the process at the beginning of the batch operation with the first component or it may be added gradually with the second component. The first phase is referred to as the continuous phase, similar to the terminology used in emulsion science, as discussed previously. The second phase, which is dispersed in the first by continuous agitation, is termed the dispersed phase – again echoing the terminology of emulsion. As the volume of the dispersed phase gradually increases the continuous phase, which is not increasing in volume, can no longer prevent the dispersed phase from coalescing into a continuum fluid. This forces the system to undergo a "phase inversion" wherein the continuous phase becomes the dispersed phase and vice versa.[18]

In studying the phase inversion within this system Zaldivar and Westerterp[18] found that, when the inversion occurred, the heat transfer coefficient of the system dropped abruptly and the interfacial area between the phases increased. This showed that a phase inversion within a semi-batch nitration system could be hazardous if the system had built-up unreacted nitric acid in the aqueous phase which would be available for reaction. The event could lead to a thermal shock to the system, causing a spike in heat generation and the temperature of the system which could in turn cause a runaway reaction.[18]

If similar behavior were to be observed in a continuous system, where we expect the system to constantly contain an inventory of both reactants, during a transition between types of emulsified systems it would present a hazard to the process and should be investigated.

Motivation

Reactive chemical hazards have been shown on many occasions to be capable of causing catastrophic incidents in the chemical process industries. These hazards require continued effort on the part of researchers to mitigate them across many processes and industrial sectors. Findings in literature regarding the reactivity, stability, and incompatibility issues experienced with aromatic nitrocompounds, in addition to the demonstrated hazardous nature of the system, the mixed acid process was chosen for investigation in hopes of finding a means for eliminating or better controlling process hazards. Study of the mixed-acid process uncovered thermodynamic properties of the system that allowed for the formation of emulsified systems with properties distinct from the traditional two phase treatment of the process. It was believed that this behavior, coupled with other hazardous properties of the system and materials involved, could cause or contribute to thermal runaway events and other hazardous scenarios that could cause losses in the process industries. This research was therefore undertaken to determine if the identified thermodynamic traits of the system could or would pose hazards to the process under typical industrial conditions, and, if so, try to determine ways to control, mitigate, or eliminate those hazards.

2. REVIEW OF MODELING TECHNIQUES AND MICROEMULSION SCIENCE

Early interest in modeling microemulsions largely centered around their possible uses in enhanced oil recovery, or using them as organized fluids for chemical applications. However, some studied them to understand the materials and behavior from a purely scientific perspective.[45] There was some disagreement between researchers early on as to whether microemulsions were largely disorganized or, as suggested by some, they existed as interpenetrating regions of bicontinuous immiscible fluids, which was the approach taken by Talmon and Prager, supported by Clausse et al. and adopted by most later modelers.[45] Some modelers did however favor the disorganized phase view, including Biais et al, who proposed a pseudophase model based on vapor pressure measurements, treating the system as an equilibrium of up to 4 liquid phases and a gaseous phase using equilibrium constants and chemical potentials.[46] This solutions-based approach does not appear to have gained much favor and acceptance however.

As a result of the early interest in enhanced oil recovery, much of the early research emphasizes the use of compounds like salts, and short chain alcohols as surfactants and cosurfactants, where acids –like sulfuric acid and processes like the mixed-acid system - were largely ignored.

The Talmon-Prager Model

Talmon and Prager proposed the first statistical thermodynamic model for microemulsion formation in 1978 based on an idea put forth in a 1976 paper in Nature by Scriven.[47] The model they proposed was far from perfect and was in many ways a simple first attempt at modeling microemulsion formation behavior based on first principles. However, it provided a starting point and something for other researchers to modify and build on, which they did. The 1980s saw a proliferation of many different models and approaches to modeling microemulsions, some of which gained more widespread acceptance.

The model proposed by Talmon and Prager assumed a three component system of water, a single organic species and a single surfactant species. The model divides the system into random polyhedra called Voronoi polyhedra and Voronoi tesselations. The Voronoi polyhedral are used to specify nearest neighbor relationships and characterize the structure of non-crystalline solids and liquid phases, often when seeking to study the dynamics of ordered liquids.[36]

The model was in principle able to deal with organic mixtures or co-surfactants, but could only do so by assuming the composition of the organic or the surfactant was constant and the relative amount of each species was constant. The water and the organic species are assumed to be completely immiscible by the model.[36]

The model also makes a few other assumptions including that the surfactant monolayer was of zero thickness. It considers only the entropy change of mixing, does not correctly account for the curvature energy of the surfactant film and ignores energetic interactions between layers and film boundaries. It assumes that the energy of a curved surface is the same, regardless of direction of curvature (i.e. it doesn't matter if oil or water is on the outside of the droplet). Like most of the models that followed, it assumes the volume fraction of the surfactant is negligible (<3% of total system).[36]

Also similar with many of the models that followed, the Talmon-Prager model makes assumptions that favor an equal volume fraction of water and oil and therefore the model can become less accurate as the organic to aqueous volume ratio becomes more skewed in favor of one phase or the other. While this assumption or weakness persists throughout many early models, this could be a natural outgrowth of an observation made by Tabony in 1986.[48] He points out that stable dispersions can be made over wide ranges of oil and water volume fractions and, parroting the findings of Winsor 40 years prior, one can make a microemulsion go from being one of water droplets in oil to oil droplets in water simply by gradually changing the volume fractions. He then observed that this raises questions about and sparks special interest in the middle region in which the volume fractions of oil and water are about even. If this transition band were considered more critical or more interesting at the time of early modeling efforts, accuracy in this compositional region might have been seen as especially critical.[36,48]

This assumes that interfacial area per surfactant molecule was fixed and therefore the amount of surfactant controlled the size of the interfacial area. [36] This leads logically to a certain treatment of Winsor type microemulsions. Under this view, a Winsor-IV system is one in which there is only one apparent phase composed of bicontinuous regions of oil and water that are stabilized by a sufficient quality of surfactant. However, as the quantity of water or oil becomes too great for a given amount of surfactant, “excess” water and/or oil can be rejected to separate, traditional continuous phases, leading to Winsor-I, Winsor-II and Winsor-III type systems.[49]

Their model attempts to predict the entropy of the system and then uses G = -TS to predict the free energy change of the system. This, relationship, along with their entropy equation which made entropy a function of the system volume fractions and three other parameters, built into the model critical compositional and temperature dependencies, reflecting the behavior observed in experiments with microemulsions. [36]

The Talmon-Prager model received significant criticism in the years following its publication because of its many assumptions and limitations, some of which tended to lead to and favor the prediction of three phase formation. The paper itself acknowledges that their predictions have only a qualitative similarity to what is observed with experiments and that correlations would have to be developed so that their three parameters could be deduced based/predicted from the surfactant structure, rather than selected to fit experimental results.[36]

Refining Microemulsion Modeling

Jouffroy, Levinson and de Gennes became some of the first to offer a competing model for microemulsions that was based heavily on the Talmon-Prager model, leading to the two being referenced and commented on together in much of the literature that followed. The new model attempted to address some of the weaknesses of the earlier model. The "uncertain size" of the voronoi polyhedra is replaced with cubes with the lengths of the sides set to the persistence length, ε_k. Rather than looking for minimums in the free energy surface, the new model assumed that the equilibrium should occur close to "a situation of zero interfacial tension" and accounted for the fact that one curvature is preferred with a bancroft parameter.

The De Gennes model, as it later came to be called, ultimately proved to be a step backwards from the Talmon-Prager model in that it failed to predict any three phase formation behavior, which had already been widely observed with microemulsions experimentally.[50] In commenting on the Talmon-Prager and De Gennes models, Taupin noted that they'd "been very successful and illuminating in many monophasic microemulsions, but [seem] more questionable for the three phase microemulsion system" which was of greatest interest to this work.[47]

The model by Widom that followed in 1984 contradicted de Gennes by depending only weakly on bending properties of the surfactant film. While Widom also used a Bancroft parameter for curvature energy and still assumed a zero-thickness for the surfactant film, the new model still did not attempt to explain phase sensitivity on properties of the surfactant film, like the chemical structure of the surfactant, and salinity.[51] Widom used generalized field approximations to account for membrane curvature energies and interaction energies between particles of water, oil, and the surfactant. Approximations that Hofsass and Kleinert, among others, later tried to relax.[52]

Taupin, Dvolaitzky, and Ober chose to emphasize the need for a model that factors in the energy and entropy effects related to flexible membranes, membrane interactions, and long range interactions between particles.[53]

Cates, Andelman, Safran, and Roux published a series of papers in 1986, 1987, and 1988 in which they proposed a new model (1986) and then a slightly modified and improved variation in (1988). Both papers made largely similar assumptions including the use of a cubic division of space, and Bancroft parameter. On larger scales they used a random mixing approximation but accounted for bending and undulating of interfacial films on smaller scales.[54,55]

As is explained later in more detail, the Cates model calculates the free energy change of the system to determine when microemulsion formation is favorable and will occur like the Talmon-Prager model and most of the other contemporary models. Also in kind with Talmon-Prager the Cates model calculates the entropy of the microemulsion as a function of the volume fractions of oil and water in the system. However, the cates model adds a second, separate term to the free energy equation that's not present in the Talmon Prager model to account for surface bending energy of interfaces in the microemulsion.[55]

The key difference between the 1986 and 1988 models was that the 1988 model used a different method for calculating the free energy of the system, which can account for more types of microemulsion structure. [54,55]

The following equations detail the model from the 1988 paper.

$$F_{\mu} = F_{Bend}(K_0, C_0, \Phi, \Phi_S) - \mathrm{TS}(\Phi, \Phi_S)$$

where:

F_{μ}= Free energy of the system

F_{Bend}=Bending energy of the surfactant film separating the bicontinuous regions

T=System temperature

S=System entropy

The bending energy of the surfactant film is given by:

$$F_{Bend}(K_0, C_0, \Phi, \Phi_S) = \frac{8\pi}{\xi^3} K(\xi)\Phi(1-\Phi)[1-2C_0\xi(1-2\Phi)]$$

where:

Φ = probability of a space being filled with water

Φ_S= volume fraction of surfactant

ξ = structural grain length scale

$K(\xi)$ = effective bending constant

$$\xi = \frac{6a\ \Phi(1-\Phi)}{\Phi_S}$$

$$\xi_K = ae^{\left(\frac{1}{\tau}\right)} = ae^{\frac{4\pi K_0}{\alpha k_B T}}$$

where:

a = thickness of the surfactant monolayer, assumed constant.

ξ_K = characteristic persistence length

Since this is assumed to be a monolayer, the appropriate choice for “a” could be the length or average thickness of a surfactant molecule.

α is assumed to be equal to 1 in the literature but it’s actually a parameter on the order of 1 that the calculations are very sensitive to.

$$K(\xi) = K_0\left[1 - \frac{\alpha k_B T}{4\pi K_0}\ln\left(\frac{\xi}{a}\right)\right]$$

K_0 and C_0 are elasticity parameters and “are expected to depend strongly on the particular surfactant selected, on the type and concentration of cosurfactant, on salt concentration, and also on temperature.

The entropy of the system is given by:

$$S = -\left(\frac{1}{\xi^3}\right) k_B[\Phi ln\Phi + (1-\Phi)\ln(1-\Phi)]$$

where:

k_B = $1.380648813(10^{-23})\frac{J}{K}$ (Boltzmann’s constant)

Combine the preceding equations to get:

$$F_\mu = \frac{8\pi}{\xi^3}K(\xi)\Phi(1-\Phi)[1-2C_0\xi(1-2\Phi)] + \mathrm{T}\left(\frac{1}{\xi^3}\right) k_B[\Phi ln\Phi + (1-\Phi)\ln(1-\Phi)]$$

This makes the free energy of the microemulsion dependent on system temperature, the constituent volume fractions, a, α, K_o, and C_o, making it a function of three state variables and four parameters that can be tuned to make the model fit an experimental system.

These are a selection of proposed models that came out of this period which stand out among multiple others. Researchers showed continued interest in improving the modeling of microemulsion systems in the 1990s with the number of new models being proposed slowing significantly in the last decade. A more sophisticated thermodynamic model was proposed by Nagarajan and Ruckenstein in 2000 with correlations for droplet size distributions and activity coefficients.[56] Then in 2008 Wennerstrom and Olsson proposed a model based on combining the work of de Gennes and Taupin with earlier work by Helfirch on curvature energy with the refinements by Widom, Andelman, Cates, Roux, and Safran to propose a new related model that also accounted for the interactions between charged ionic molecules.[57] These updated models offer refinements but still have many of the same underlying assumptions and overall structure of the preceding models just discussed.

3. METHODOLOGY

Relevant Material Hazards

Sulfuric acid will be stored at roughly 98% purity in industrial processes,[23] but in the process it will be present between 65-90%. For the research to be conducted stock sulfuric acid specified by the manufacturer to be 95-98% pure will be used and diluted as necessary. Sulfuric acid is harmful to the mucous membranes of the body, including the lungs. It is not flammable or combustible, but upon combustion or reaction with incompatible materials, it will form toxic sulfur oxide (SOx) compounds. Incompatible materials include bases, halides, cyanides, chlorates, fulminates, carbides, etc.[58]

The exothermic mixing of water with concentrated acid should always be remembered. When water is mixed with concentrated acid a massive release of energy from the heat of dilution can cause the water to vaporize, causing an explosive vapor expansion which can also result in acid splashing.[59]

Nitric acid is stored at either 70% or 98% in industrial processes, possibly both.[6]Nitric acid is one of the most powerful oxidizers and can be extremely hazardous if mixed with organic materials. It will release toxic nitrogen oxide (NOx) compounds upon combustion and reaction with incompatible materials.[60] However, in the interest of safety, to prevent uncontrolled exothermic reactions from occurring during the experiments, nitric acid was not used or introduced to the experimental system during this work.

Toluene is a colorless combustible liquid that boils at approximately 110°C. It has an auto-ignition temperature of 535°C, which is highly unlikely to be reached under normal process conditions or under the experimental conditions of this study. It has a closed cup flash point of only 4°C, well below even typical ambient laboratory conditions. With a density of 0.865 g/mL at 25°C it will float on water. It has an LEL of 1.2% and an UEL of 7%.[61] Given all of this, toluene is a significant fire hazard in the process and presents a fire hazard during the experiments conducted for this work. However, the material is also toxic, a suspected carcinogen, a reproductive toxin, and teratogen. It is capable of causing "DNA damage" to anyone exposed including fetuses.[61] Direct exposure to this material should be avoided and minimized.

All three isomers of MNT have fairly similar fire and health hazards associated with them. All three are toxic chemicals with acute and long term (chronic) health effects. All three will cause skin damage and are capable of being absorbed into the body through the skin where they exhibit target organ toxicity. All three isomers have closed cup flash points of 95-106 °C, and all three are capable of a highly exothermic monomolecular decomposition. 4-Nitrotoluene – or paramononitrotoluene (pMNT) is a crystalline solid at STP, but melts around 55°C and will be a liquid under typical process conditions. The 2-MNT and 3-MNT – also known as orthomononitrotoluen (oMNT) and metamononitrotoluene (mMNT) - are liquids at STP with densities of roughly 1.15 to 1.3 g/cm^3.[62,63,64] The aqueous phase of the process is mostly sulfuric acid and nitric acid, and will have a density between 1.4 and 1.8 g/cm^3. This means that these isomers are heavier than reasonably pure water, but they are lighter than and will float on top of the aqueous phase of the process. These compounds will form toxic NOx compounds upon combustion or decomposition.[59]

Validating Use of Sulfuric Acid in Place of Mixed Acid

In order to avoid the hazards associated with the nitration reaction, including the heat released and the possibility of the mixture heating itself to its decomposition temperature, it was decided to use pure sulfuric acid rather than nitric acid in the experiments conducted.

It was assumed that this substitution would make the experiments considerably safer while not substantially affecting the overall behavior of the system, so that the results obtained would mirror what would be seen in the actual mixed acid system. In testing the validity of this assumption, two questions can be considered. First, is the sulfuric acid structurally similar to the nitric acid so that we can assume the two molecules would behave similarly in solution? Second, is an aqueous phase composed of nitric and sulfuric acid energetically similar to one composed of just sulfuric acid, since, based on prior modeling work in this area, we expect emulsion formation to depend on the Gibb's free energy change of the system versus the energy required for interface formation.[3]

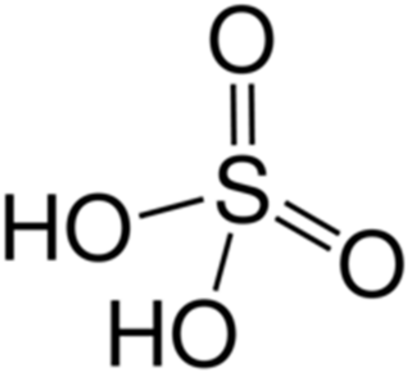

Figure 5: Sulfuric acid chemical structure

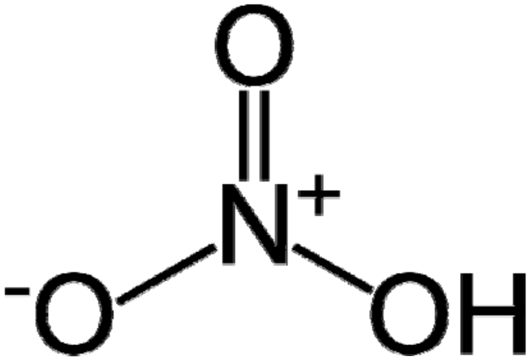

Figure 6: Nitric acid chemical structure.

A review of the chemical structures for the acids – shown in figures 5 and 6 - shows that they're structurally similar with doubly and singly bonded oxygen atoms bonded to a central non-oxygen atom with an electronegativity weaker than that of oxygen.[36] Both molecules are expected to shed 1-2 hydrogen atoms in aqueous solutions and should behave in a reasonably similar way in the mixed aqueous and organic system.

With regard to the second question, in 1992 Zaldivar et al[43] conducted research on the heat of dilution of the sulfuric-nitric mixed acid system used in nitration reactions and developed the following model for the heat of dilution:[43]

$$\Delta H_d = \sum_{k=1}^{n} \Delta(n_k L_k)$$

$$dH_d = \sum_{k=1}^{3} n_k dL_k + L_k dn_k$$

$$L_k = \prod_{i=1}^{i} \left(\sum_{j=1}^{i} a_{k_{ij}} x_i^{j-1} \right)$$

Their experiments and models place the energy minimum for both pure nitric acid and sulfuric acid mixed with water at approximately 55 wt% and 65 wt% acid respectively. However, the pure nitric acid releases no more than 210 kJ/kg where pure sulfuric acid can release up to 315 kJ/kg upon dilution.[43] Mixtures of nitric and sulfuric acid fall between the extremes of the two pure acids. Therefore, while the shape of the energy curves are similar for mixed acid versus sulfuric acid aqueous phases, the sulfuric acid will be at a lower relative energy state.

Overall, therefore, it is believed that the pure sulfuric acid used in these experiments will behave in a manner reasonably similar to the mixed acid that would be expected in industry, but is not a perfect replacement for it.

Experimental Description and Procedure Initial Tests

This phase of experimentation was to be conducted without nitric acid and, therefore, no nitration reaction can occur. The sample material for these experiments was held in a 22 mm diameter, ~300 mm glass tube that was custom manufactured in the Chemistry Department's glass shop. The total volume of the sample contained in the tube – both organic and aqueous phases – was approximately 50 mL.

A picture of the apparatus is shown in Figure 7 and a schematic of the apparatus is shown in Figure 8. The sample was heated in these trials by an apparatus composed of a cylindrical heater with a fiberglass interior, connected to a temperature controller and a variac. The temperature controller read the temperature of the water bath near the sample via a thermocouple and adjusted power to the heater through the variac to control the temperature of the experimental sample. Because the fiberglass interior of the heater was not waterproof and a water bath was required as a heat transfer medium, an open-topped steel cylinder was fabricated and inserted into the heater to contain the water bath. A rubber sealing element was introduced to limit heat loss between the heater and the cylinder/bath. The apparatus was assembled by the Chemical Engineering machine shop and operated in a fume hood in lab 429 of the Brown building. The fume hood was used to control the threat of toxic vapors from the organic compounds and aqueous acids used in the experiment.

Figure 7: Picture of apparatus used for initial phase observation tests

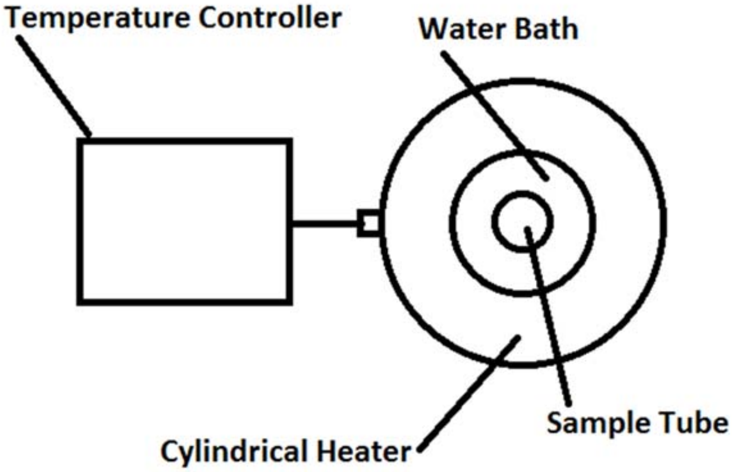

Figure 8: Diagram of the basic layout of the apparatus for the initial tests.

The sample tube was held in the water bath by a steel wire cradle with a hanger, shown in Figure 9. The handle allowed the sample tube to be conveniently removed from the water bath and limited the risk of researchers being injured by placing hands or other extremities too close to the sample while it was being heated.

Figure 9: Image of the 22 mm x 300 mm glass tube in the steel cradle.

The acid used for the aqueous phase in these experiments was prepared by diluting 95% stock sulfuric acid purchased from Sigma Aldrich. The experimental mixture was prepared by mixing water, the stock acid, and the organic material in the glass tube at ambient temperature (~20 °C) and allowed to settle for one hour before visually checking for middle-phase microemulsion formation.

The temperature of the system was then raised from room temperature to roughly 50°C. Once the temperature of the system has stabilized the tube will be removed to check for the formation of an emulsion. Test tubes were removed from the heater using test tube holders or clamps. Each tube was then returned to the housing and the process was repeated with the temperature being raised in 10°C increments. If an emulsion phase was not observed at 50°C, the system was heated until 90°C was reached and checked at 10°C increments to determine if an emulsion formed in the range of interest. The experiments were discontinued at 90°C to avoid boiling off the water bath.

Procedure for Initial Experiments:

1. Insure that the sample tube is clean and ready for use.
2. Add the amount of water to the sample tube necessary for diluting the stock 95% acid to the desired concentration (70 wt%, 80 wt%, or 90 wt%).
3. Slowly add the stock acid to the water, allowing the mixture in the tube to cool as more acid is added.
4. Add the desired quantity of the organic material (Nitrobenzene, 2-Nitrotoluene, or 3-Nitrotoluene) to the cooled diluted acid.
5. Allow the mixture to settle at ambient temperature.
6. Check the mixture for middle-phase emulsion formation and image the sample.
7. Turn on the heater and set it to the first temperature set-point (50°C)
8. Allow the mixture to settle at the new temperature set-point for 1 hour.
9. Check the mixture for middle-phase emulsion formation and image the sample.
10. Increase the temperature by 10°C to the next set-point.
11. Allow the mixture to settle at the new temperature set-point for one hour.
12. Check the mixture for middle-phase emulsion formation and image the sample.

13. Repeat steps 10-12 until 90°C is reached.

Experimental Description and Procedure for 2nd Round Trials

In continuing the experiments in the hopes of covering a wider range of acid concentrations and system compositions, the decision was made to move away from the cylindrical heater and the water bath in favor of a digital dry block heater. The dry block heater eliminated the problems experienced in the first round of experiments with the water in the bath evaporating. This allowed the tests to run for a longer period of time. Also, while the old apparatus was able to maintain temperatures to within 3°C of the set-point, the dry block heater was capable of staying within 0.5°C of the set-point. The block heater also allowed for several samples to be run at once, rather than just one, allowing more tests to be conducted more quickly. The dry-block heater also used tubes with a smaller diameter, allowing tests to be run using less material, representing a smaller hazard, and producing less waste.

This phase of experimentation was conducted without nitric acid and, therefore, no nitration reaction can occur. The experiments were conducted with the experimental mixture in a tube containing around 8-9 mL total volume. The test tubes were made of pyrex and heated in a digital dry block heating system shown in Figure 10. This heater has an open top. The tops of the test tubes were lightly capped in order to limit evaporation from the tubes and limit the potential for other materials to enter the tube though condensation or other means. A loose seal helped maintain atmospheric pressure while limiting vaporization mass transfer. The heater was kept in a fume hood to protect against toxic vapors.

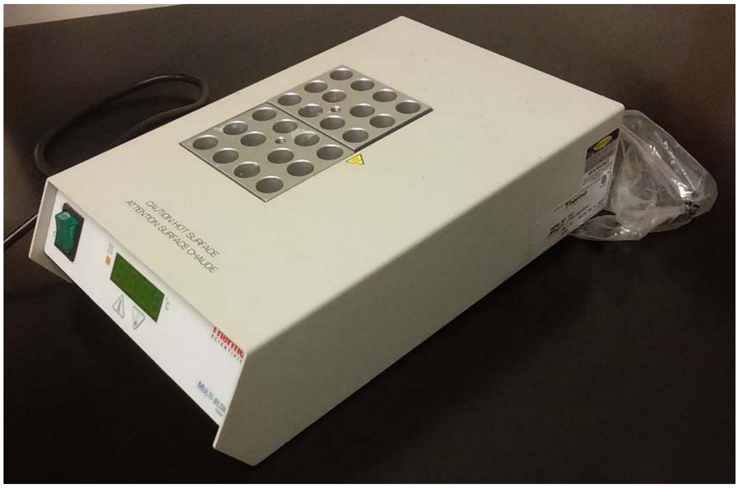

Figure 10: Modular dry block heater.

The sulfuric acid of the desired concentration was added to the chosen organic material and stirred on a magnetic stir plate, while heated to approximately 75-80°C in a glass vial in order to accelerate the reversible sulfonation reaction. This allowed the sample to reach equilibrium with respect to this reaction more quickly. Heated mixing continued for 1-2 hours. After the heated mixing and stirring the material was transferred to one of the pyrex tubes, capped with parafilm, labeled, and loaded into the apparatus. Five sample tubes were be loaded into the apparatus for each run, each representing a different composition/ratio of organic to aqueous phase volume. The samples were allowed to settle overnight after mixing. The temperature of the system was raised from room temperature

(~20 °C) to roughly 50°C. Once the temperature of the system has stabilized the tube is removed to check for the formation of an emulsion. Test tubes were removed from the heater using test tube holders or clamps. Each tube was then returned to the housing and the process was repeated with the temperature being raised in 10°C increments. If an emulsion phase was not observed at 50°C, the system was heated until 100°C is reached and checked at 10°C increments to determine if an emulsion had formed in the range of interest. If an emulsion phase was observed at 50°C the system was incrementally heated until the emulsion collapsed or until 100°C was reached. The experiment was stopped at 100°C even if the emulsion had not collapsed to avoid boiling of the aqueous phase. The samples were allowed to stay at each temperature set-point for roughly 24 hours – usually between 21 to 27 hours.

This process was conducted over a range of concentrations of sulfuric acid. Experiments were conducted starting with lower concentrations of sulfuric acid, around 70% initially, and the acid concentrations were incrementally increased in successive trials.

Procedure for Phase Observation Experiments:

1. Obtain 5 new clean 16 mm diameter tubes and place them in the block heater.
2. Add the desired amount of acid (2-6 mL) to a 50 mL glass tube for sample preparation (acid of the desired concentration should have been prepared previously and stored in a properly labeled 250 mL bottle).

3. Slowly add the organic material (MNT, toluene, benzene, nitrobenzene) to the glass vial and the acid.
4. Return the acid and aromatic storage bottles to the storage areas in the hallway.
5. Place the glass vial on the magnetic stir plate and insert a small magnetic stir bar. Turn on the magnetic stir plate, setting it to approximately 700 rpm and turn on the heating element with a setting of approximately 75°C.
6. Discontinue heating, remove the stir bar, transfer the sample to a pyrex tube using funnels as appropriate, cap the pyrex tube with parafilm, label it, and place it in the apparatus.
7. Clean and prepare the glass vial for another mixing procedure.
8. Repeat steps 2 to 7 for the other 4 test samples required for the desired run.
9. Return the acid and aromatic storage bottles to the storage areas in the hallway.
10. Allow the system to settle overnight.
11. Image the system through use of a digital camera. Take measurements regarding the relative volume of each phase. Collect samples of phases as appropriate.
12. Turn on dry block heater and set the temperature to 50°C.
13. Leave the system overnight to allow it to settle at the new temperature.
14. Image the system through use of a digital camera. Take measurements regarding the relative volume of each phase.
15. Increase the temperature set-point by 10°C.
16. Repeat steps 13-15 until 100°C is reached.
17. Deactivate the heater and allow the system to return to ambient temperature.

18. Image the system for comparison to the original state.
19. Dispose of the chemicals by emptying the samples into appropriate waste bottles.
20. Rinse the tubes to remove excessive amounts of residual chemicals and dispose of the tubes as glass/sharp waste.

Temperature Calibration Runs

Before running the second round of tests in the dry block heater a series of runs were performed using tubes full of mineral oil instead of the ternary mixture of interest in order to verify that the machine is working properly to determine calibration curves. Also, since the slots in the block heater are relatively shallow and the heater cannot effectively heat portions of the sample tubes that are above the top of the heating blocks, tests were conducted with tubes filled well above the top of the heating blocks to determine the effect this would have on the temperature of the sample.

Three runs were performed in total with 8-9 oil filled tubes in different positions in the heater. The dual heater has a total of 24 slots between the two blocks. The temperature of the oil inside each tube was measured using a mercury thermometer at temperatures in 10°C increments starting at 50°C and continuing to 90°C or 110°C as deemed appropriate. The block heater is capable of achieving roughly 130°C but that temperature was beyond the temperature range of interest for this research. The positions of the oil filled tubes for each trial are shown in Figures 11, 12, and 13. The positions in the heater that were occupied by a tube in each case are labeled with a number in the figures. The corresponding data for each trial are in Tables 1, 2, and 3, with the position numbers in the tables corresponding to the labeled positions in the appropriate figure. For the first trial run, tubes 7 and 8 were filled to a much higher level to determine how great of an effect fill level differences have on the steady state temperature of the samples at various temperature set points.

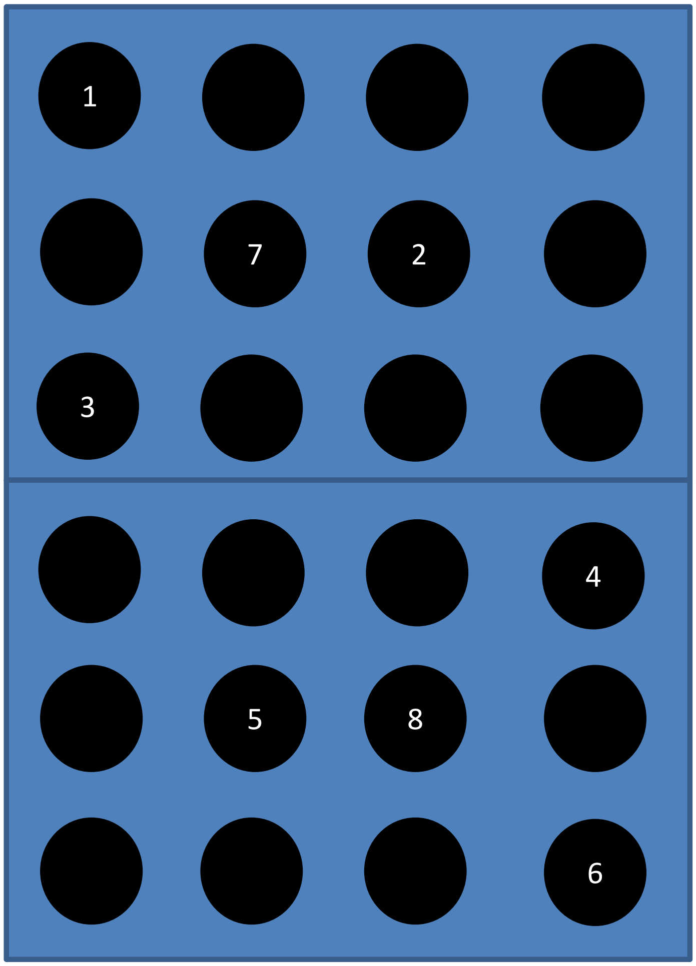

Figure 11: Diagram of occupied heater positions for the first calibration test.

Table 1: Temperature Data for Calibration Test 1

	Set-Point				
Position	50	60	70	80	90
1	48.5	57.5	65.5	75.0	83.0
2	49.0	59.0	67.0	75.0	83.0
3	48.5	57.5	65.5	75.0	83.0
4	48.5	56.0	65.0	72.5	80.0
5	48.0	56.0	64.0	71.0	80.0
6	46.0	53.0	61.0	68.0	75.0
7	42.5	50.0	57.0	66.0	72.0
8	40.5	47.0	54.0	61.0	67.5

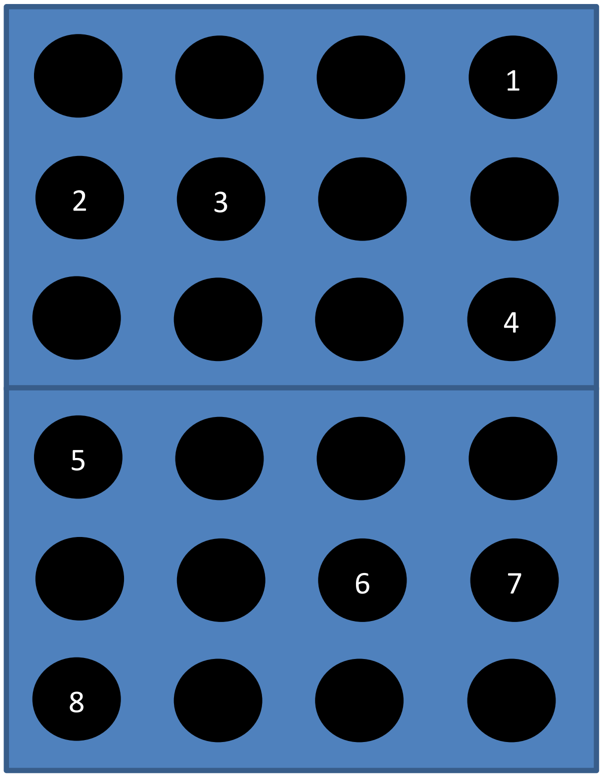

Figure 12: Diagram of occupied heater positions for the second calibration test.

Table 2: Temperature Data for Calibration Test 2

	Set-Point				
Position	50	60	70	80	90
1	49.5	59.0	66.5	75.5	81.5
2	51.0	60.0	68.0	75.5	81.5
3	51.5	61.0	67.5	76.5	82.0
4	49.0	59.0	66.5	75.0	81.5
5	47.0	56.0	64.0	73.5	79.0
6	48.0	56.5	65.0	73.5	80.0
7	47.5	56.0	64.5	74.0	79.5
8	47.0	55.5	63.0	71.0	78.0

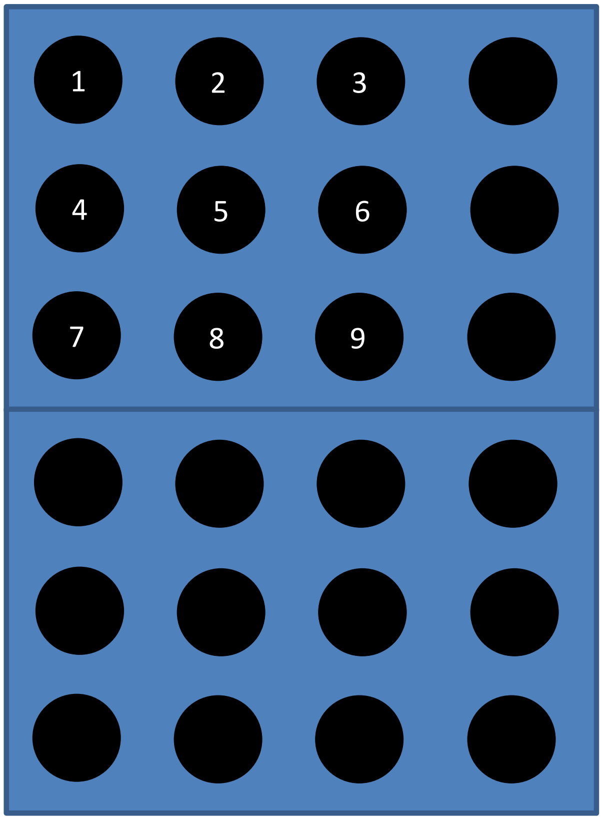

Figure 13: Diagram of occupied heater positions for the third calibration test.

Table 3: Temperature Data for Calibration Test 3

	Set-Point						
Position	50	60	70	80	90	100	110
1	48.0	58.5	68.0	76.0	83.0	93.0	102.0
2	48.5	58.5	68.0	76.0	82.5	93.0	102.5
3	48.0	58.0	68.0	76.0	83.0	93.5	103.0
4	49.0	59.5	69.0	76.5	82.5	93.5	102.0
5	49.0	60.0	69.0	76.5	84.0	93.5	102.0
6	49.0	59.5	69.0	76.5	83.5	93.0	102.0
7	48.5	59.0	68.5	75.5	82.5	93.5	102.0
8	48.5	59.0	68.5	75.5	82.5	93.0	102.0
9	48.5	58.5	68.0	75.0	82.5	93.0	102.0

The results showed an advantage to having all of the neighboring positions filled with a tube. Based on the results of the third trial as compared to the others, this improved the consistency of the temperatures across all the sample tubes and helped them stay closer to the desired set point in some cases.

The results of these tests led to the use of oil-filled “dummy” tubes in slots adjacent to the samples, organized as per Figure 14 with the positions occupied by a sample indicated by a number and the positions filled with a dummy tube marked with a “D.”

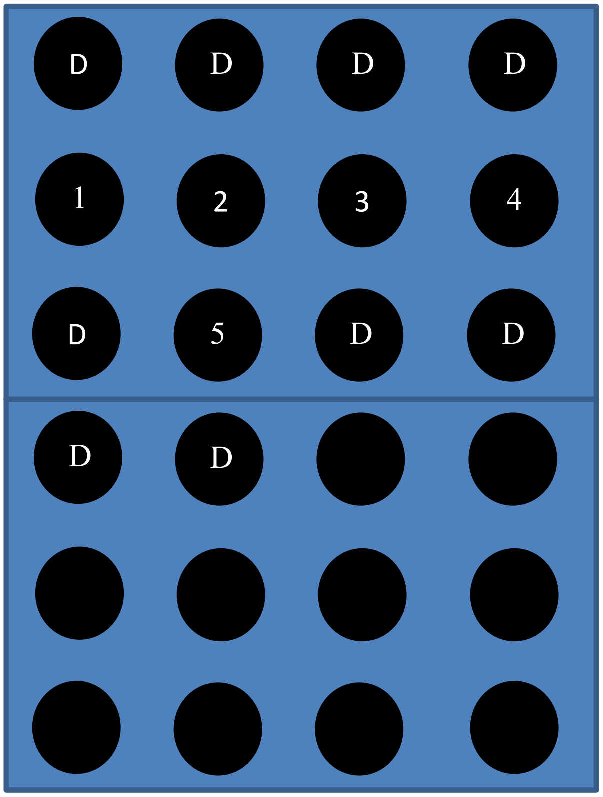

Figure 14: Diagram of occupied heater positions for the phase observation experiments.

The results also led to the decision to increase the temperature set-point at higher temperatures to overcome the temperature deficit observed in the calibration run temperature measurements. Based on the observations in the calibration runs the temperature set-points used during the experiments were: 50°C, 60°C, 70°C, 82°C, 93°C, and 104°C.

Acid Mixing Procedure

The acid used in the experiments conducted for this research was prepared from a 95+ wt% sulfuric acid procured from Sigma Aldrich. The 70, 80, and 90 wt% acids were prepared by diluting the stock concentrated acid based per the calculations shown in Table 4 below.

Table 4: Acid Dilution Calculations

Amount of Starting Acid (mL)	Mass of H_2SO_4	Mass of initial solution
90	157.248	163.8
Desired weight % of final acid	Final Mass of solution	Mass of water to be added (g)
90%	168	4
80%	189	25
70%	216	52
60%	252	88
50%	302	138
Weight % of the starting Acid*		96%
Density of Starting Fluid**:		1.82
*Specified at 95-98 wt% (assumed 96% for calculation)		g/cm^3
**Specified at 1.80-1.84 g/cm^3		
Water assumed at 1 g/cm^3		

90 mL of the 95-98 wt% stock acid (assumed to be 96% for these calculations) was diluted with 4 mL, 25 mL, and 52 mL of water to produce the 90, 80, and 70 wt% acid respectively as per the table below. Tests for 60% and 50% were not necessary since no emulsion forming behavior was shown by the system at 70%.

Parafilm Effectiveness

After early experiments were conducted using a cylindrical heater and a water bath concerns were raised as to evaporation from the sample tube or water entering the sample through condensation or other means. This was a particular concern when the water bath was in use because water condensation was often visible inside and outside the sample tube. The switch to using a dry block heater removed some of these concerns but not all of them, especially given the longer duration of the experiments planned for the second round of trials. To help insure that water and other chemicals were not entering and leaving the sample tubes the samples were capped with parafilm – a wax saranwrap-like material – to lightly seal the tubes. The sample tubes were weighed at the beginning and end of several of the trial runs - runs 4 through 11 - with the weight of the label, sample, parafilm, and tube included, in order to determine if the parafilm was effectively preventing the sample from losing mass to the environment or gaining mass by absorbing water from the surroundings. Weighing did not occur on runs 12 and 13 because the digital balance malfunctioned.

The results of the weighing are presented in the following tables.

Table 5: Run 4 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	21.80 g	21.80 g	0.00 g
2	23.29 g	23.27 g	-0.02 g
3	22.48 g	22.48 g	0.00 g
4	24.47 g	24.47 g	0.00 g
5	23.30 g	23.29 g	-0.01 g

Table 6: Run 5 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	21.19 g	21.21 g	0.02 g
2	22.33 g	22.33 g	0.00 g
3	23.35 g	23.37 g	0.02 g
4	24.21 g	24.22 g	0.01 g
5	22.91 g	22.94 g	0.03 g

Table 7: Run 6 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	20.75 g	20.75 g	0.00 g
2	22.57 g	22.57 g	0.00 g
3	21.46 g	21.47 g	0.01 g
4	23.20 g	23.22 g	0.02 g
5	23.37 g	23.38 g	0.01 g

Table 8: Run 7 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	22.53 g	22.54 g	0.01 g
2	23.46 g	23.46 g	0.00 g
3	22.33 g	22.33 g	0.00 g
4	22.39 g	22.39 g	0.00 g
5	22.39 g	22.41 g	0.02 g

Table 9: Run 8 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	22.83 g	22.85 g	0.02 g
2	23.52 g	23.56 g	0.04 g
3	21.75 g	21.85 g	0.10 g
4	22.28 g	22.29 g	0.01 g
5	21.02 g	21.05 g	0.03 g

Table 10: Run 9 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	22.01 g	22.03 g	0.02 g
2	24.34 g	24.44 g	0.10 g
3	23.03 g	23.03 g	0.00 g
4	20.43 g	20.42 g	-0.01 g
5	21.98 g	21.97 g	-0.01 g

Table 11: Run 10 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	22.58 g	22.58 g	0.00 g
2	23.31 g	23.32 g	0.01 g
3	21.67 g	21.67 g	0.00 g
4	22.20 g	22.21 g	0.01 g
5	20.63 g	20.64 g	0.01 g

Table 12: Run 11 initial and final mass

Tube	Initial Weight	Final Weight	Change
1	22.73 g	22.73 g	0.00 g
2	23.64 g	23.64 g	0.00 g
3	21.50 g	21.51 g	0.01 g
4	22.38 g	22.38 g	0.00 g
5	20.85 g	20.85 g	0.00 g

The results showed that in most cases the parafilm caps kept the change in the mass of the sample tubes at 0.02 g or less in almost all cases. In a few cases where changes in mass of 0.1 g are observed it is believed that a poor seal was obtained with the parafilm, allowing increased mass transfer between the tube and the surroundings. The average absolute mass change across all samples is 0.014 grams with a standard deviation of 0.022 g. If the two instances of 0.1 g mass increases are neglected as outliers representing poor seals, the average absolute mass change is 0.0095 g with a standard deviation of only 0.010 g.

4. RESULTS

Results of Initial Tests

The initial round of tests was conducted in early 2012 as a proof of concept for the research. The main goal of these experiments were to determine if any microemulsion formation was being observed at all with MNT and MNB to see if the concept was worth pursuing further. And also to find and correct any unexpected problems before moving on to a more thorough experimental design and examination of the problem. In the interest of safety the decision was made to begin using lower concentrations of acid and work towards progressively higher acid concentrations.

The first experiment conducted as part of this stage of the research mixed 21ml 3-nitrotoluene, 21ml 95-98% sulfuric acid, and 8ml water, giving an approximately 69 wt% sulfuric acid for the aqueous phase. It had been hoped that this experiment would merely confirm that no middle third phase behavior was being observed at this lower acid concentration but the test immediately raised concerns. The normally yellow MNT began to discolor and become a darker brown or black color with a very distinct black band at the interface between the aqueous and organic phases which can be seen in Figure 15. The pure yellow color of the MNT stayed the longest at the top of the organic phase as the darker color moved up the organic phase and began to seep into the aqueous phase.

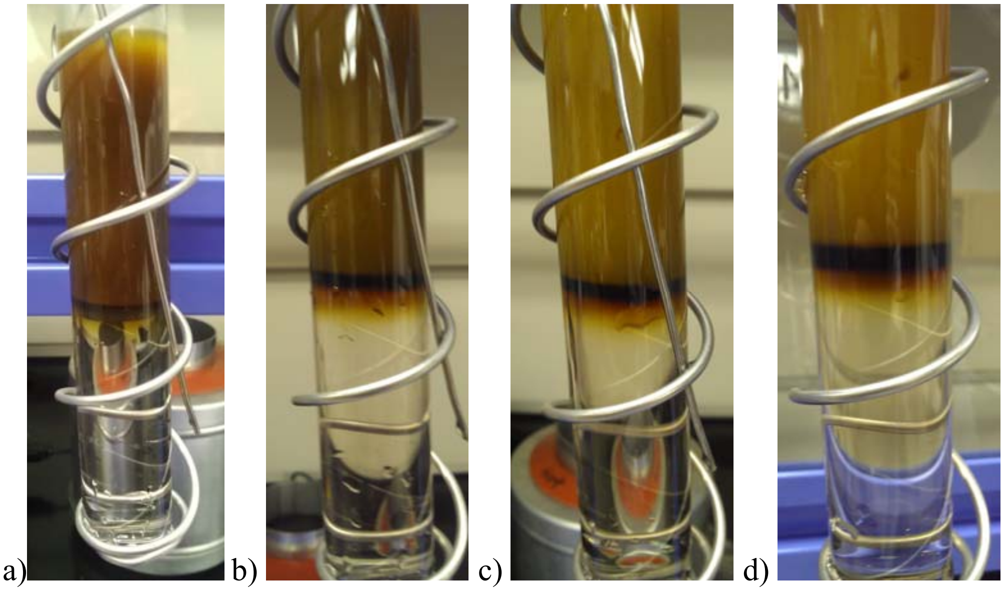

Figure 15: Photographic results of the first experiment with 3-MNT and 69 wt% sulfuric acid with the mixture at a) 60°C, b) 70°C, c) 80°C, and d) 90°C taken chronologically in order of ascending temperature.

Up to this point it had been believed that, without nitric acid in the mixture, the experiments would be completely non-reactive. The formation of the black band near the phase interface was strongly suggestive of a reaction occurring.

A second experiment, consisting of three tests or runs where-in 22 mL 95% H2SO4 and 22 mL 3-Nitrotoluene where mixed and left at different temperature set-points for varying lengths of time, confirmed that the formation of the black band and material was dependent on the temperature of the system and the concentration of the sulfuric acid, was therefore most likely following a rate-law, and was therefore most likely indicative of a reaction occurring in the system.

A third experiment using 21mL of MNB and approximately 30mL of 70 wt% acid. This test was intended to determine if the black material formed with the MNB as it had with the MNT and if it would occur at the same rate. The lower concentration of acid was selected for safety and because microemulsion formation was not expected with this surfactant concentration based on prior research[7] which would allow for the formation of the black material to be studied in a traditional two phase system without being influenced by the emulsion formation. The test showed that, while the black material would form with MNB, it was much slower, linking the problem to the increased reactivity of the MNT due to the methyl group on the ring, effectively proving a reaction, but not what was being formed.

It had erroneously been believed up to this point in the work that the sulfonation reaction would not proceed at temperatures this low and this was largely true with MNB, however the more reactive MNT immediately began showing signs of the sulfonation reaction. In the absence of tests to confirm the formation of nitrotoluene-sulfonic acid, the system composition lead naturally to the suspicion that this was the compound forming in the system and consultation with industry experts familiar with the process confirmed this - in industry they call the sulfonic acid “black acid” but it’s actually a dark “tea” color.[26]

In the absence of agitation in the system the sulfonation reaction occurred slowly at or near the interface between the aqueous and organic phases, then the sulfonated products diffused into the rest of the system.

After the determination that the sulfonation reactor was occurring with the MNT, the decision was made to run a test with 95 wt% acid and the MNB to see if microemulsion formation could be observed. A mixture of 29 mL H_2SO_4 mixed and 21 mL MNB that was mixed for 5 minutes resulted in a single phase mixture that did not separate. This we now know is a Winsor-IV system.

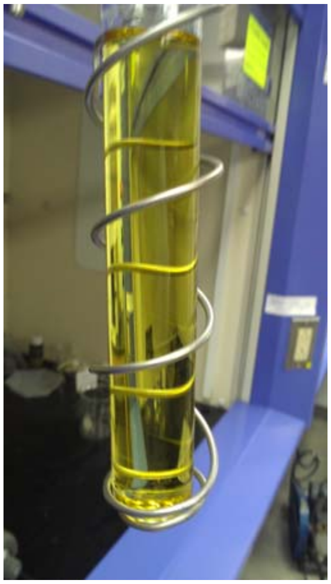

Figure 16: 29 mL H_2SO_4 mixed with 21 mL Nitrobenzene. System formed into a single phase.

The volume fractions of the mixture were adjusted to 16 mL H_2SO_4 and 33 mL Nitrobenzene in order to force a phase separation, which it did.

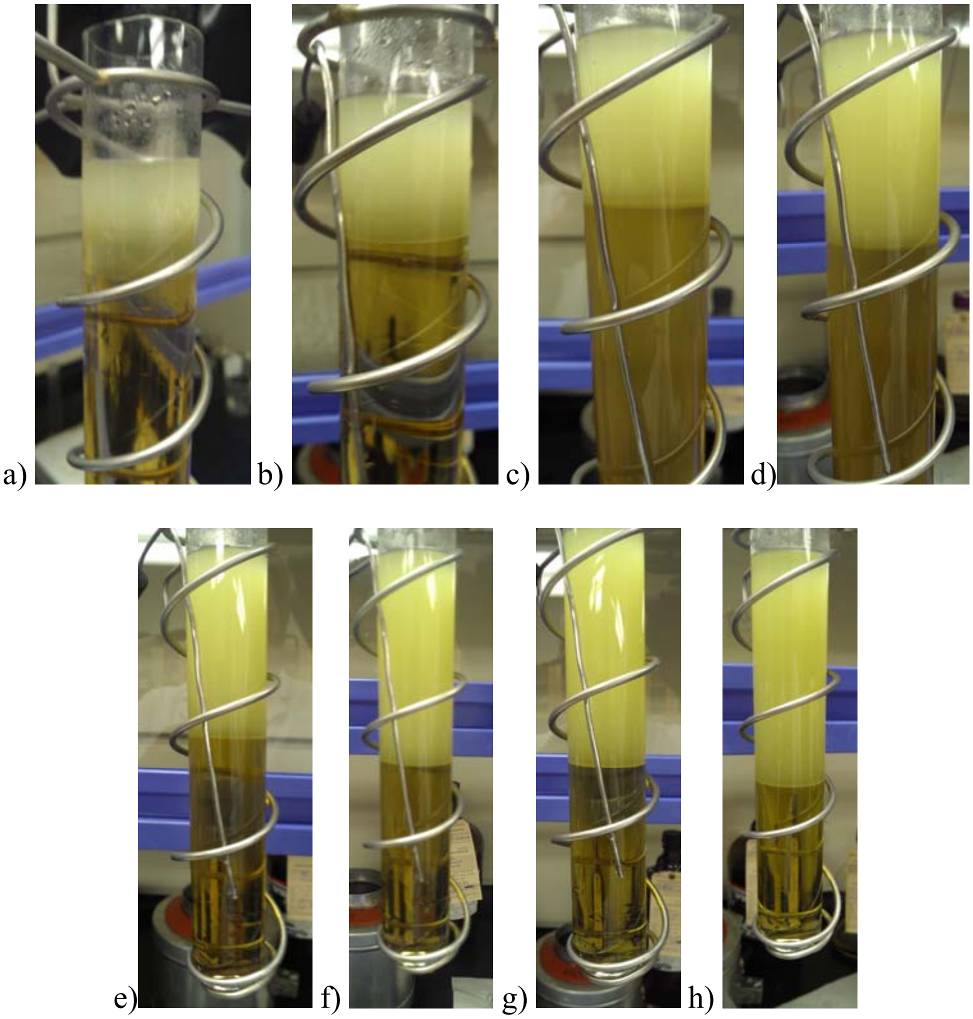

Figure 17: 16 mL H_2SO_4 and 33 mL Nitrobenzene at various times and temperatures

Figure 17a shows the mixture at ambient temperatures at around 12:30PM. Figure 17b shows the mixture at a 60°C set point at 1:00PM, immediately after achieving the set point. Figure 17c shows the mixture at 60°C at 1:45PM, after having approximately 45 minutes to settle. Figure 17d shows the mixture at 2:30PM at a 70°C set point. Figure 17e shows the mixture at 3:35, still at a 70°C set point. Figure 17f is of the mixture at 5:00PM at 76°C. Figure 17g shows the mixture at 6:00PM at 80°C. Figure 17h shows the mixture at

90°C at 6:50PM. The amount of time the sample was allowed to settle at each set point was shortened at higher temperature settings because the water bath was evaporating from the heater too rapidly.

This result confirmed the formation of microemulsions in the mixed acid system. The three phase separation or, alternatively, the formation of a single phase, occurred spontaneously without the need for continuous or periodic agitation. The three phase behavior also collapsed into a two phase system with sufficient heating. This showed and provided early proof that the system was forming a microemulsion and not a nanoemulsion which, as discussed previously cannot form spontaneously and will eventually collapse.

The middle phase microemulsion seemed to have nearly completely if not completely disappeared by the time the system had been allowed to settle for an hour at the 60 °C set point. With subsequent increasing of the temperature set point the upper organic phase appeared to grow or enlarge while the lower aqueous phase, which had turned a pale yellow, appeared to shrink, suggesting that the temperature increase caused a change in the ability of the organic to mix into the aqueous acid phase.

Having obtained a result that confirmed microemulsion formation with MNB, it was desired to confirm the behavior in MNT, without the result being influenced by the gradual progress of the sulfonation reaction. To achieve this, the mixture was agitated to accelerate the sulfonation reaction to allow it to achieve equilibrium more quickly, and then allowed to settle. The results are shown in Figure 18. The color shift in the 3-nitrotoluene mixture brought on by the sulfonation reaction had the added benefit of making the banding of the three phase system much clearer and easier to see.

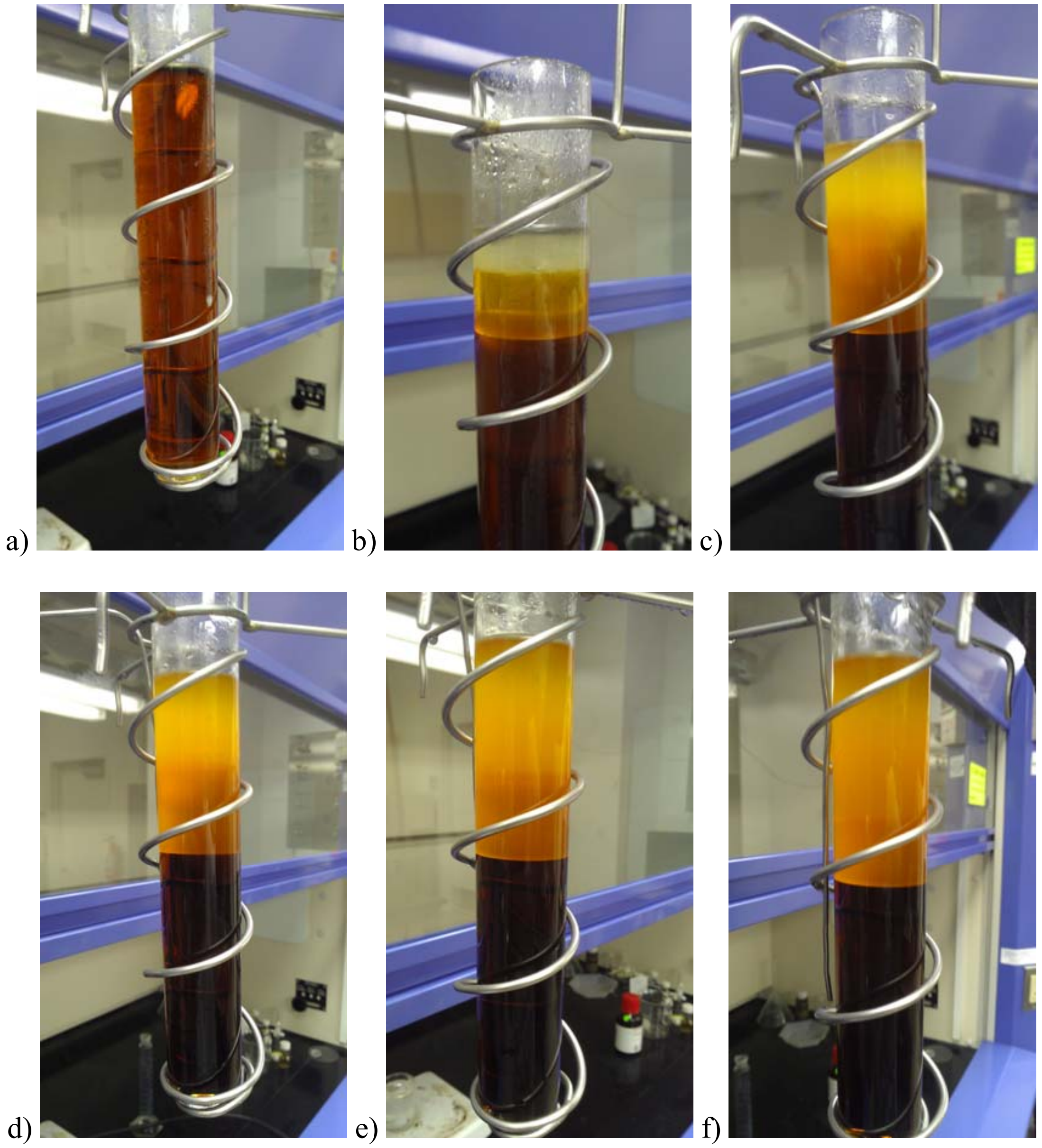

Figure 18: Results from trail with 16 mL H_2SO_4 mixed with 33 mL 3-nitrotoluene.

Figure 18a shows the trial mixture immediately after agitation was stopped and the mixture was transferred from the mixing vessel to the sample tube for the heater. Figure 18b shows the mixture after being allowed to settle for two days without agitation. Figure 18c shows the mixture heated to 60°C where 18d, 18e, and 18f show the mixture at 70°C, 80°C, and 90°C respectively.

In a fashion similar to the test with MNB, the clear three phase separation seen in 18b began to collapse immediately upon heating to 60°C and it was again observed that the upper organic phase again began to grow rapidly at the expense of the lower acidic phase as the temperature increased.

However, while these tests provided initial confirmation of microemulsion formation, they did not:

- test a wide enough range of acid concentrations to adequately describe the effect of acid/surfactant concentration of the emulsion formation behavior
- test a wide enough variety of system compositions to adequately investigate the effect of the organic to aqueous volume ratio on the emulsion formation

Questions were also raised shortly after conducting the 4th and 5th experiments, noted above, that allowing the system only one hour to settle at a new temperature set point was not sufficient. It was noted that at the time the sample was imaged and the set point increased in the 4th and 5th tests that the system still appeared to be settling and that it may not have truly achieved a new equilibrium state at the time the set point was again increased.

It was based on these results therefore that the second round of experiments were planned and initiated with a wider range of acid concentrations, mixture ratios, and temperatures with longer wait times before set point changes.

Results of Phase Observation Tests

The second stage phase observation experiments were conducted in mid to late 2014 after acquisition of the digital dry block heater and conducting the calibration tests discussed in section 3. The acids of the required concentrations were prepared and trials were conducted as per the methodologies detailed in section 3. A total of 13 tests were conducted with 5 samples per test as outlined in Table 13 below.

Table 13: Completed Runs

	NB	2-NT	3-NT
70%	Trial 1	Trial 11	Trial 10
80%	Trial 2	Trial 12	Trial 9
90%	Trial 3	Trial 6	Trial 13
95%	Trial 4	Trials 5&7	Trial 8

As explained previously, each sample in a trial had a different ratio of the organic to the aqueous phase, but the same organic material and concentration of acid. Each trial paired a different combination of one of the three organics and one of the four concentrations of acid being used, except for tests 5 and 7 which used the same acid concentration and organic species. In the case of 5 and 7, one test used samples that had been agitated and allowed to reach equilibrium before the test began and the other used unagitated samples in which the sulfonation reaction was not allowed to reach equilibrium before beginning the test.

Tables 14-16 present the number of phases that were observed with each sample after settling at ambient conditions before sample heating began.

Table 14: Number of phases observed with MNB

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	2	2	2	2	2
80%	2	2	2	2	2
90%	2	2	2	3	3
95%	1	1	1	3	3

Table 15: Number of phases observed with 2-MNT

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	2	2	2	2	2
80%	2	2	2	2	2
90%	2	2	2	2 or 3	2 or 3
95%	1	1	1	2 or 3	3

Table 16: Number of phases observed with 3-MNT

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	2	2	2	2	2
80%	3	3	2	2	2
90%	1	1	1	2	2
95%	1	1	1	3	3

Again, the spontaneous formation of one phase and three phase equilibria was observed in the mixed acid system, but only at acid concentrations at or above 80 wt%, as expected based on prior work.[7]

Summaries of each of the 13 trials conducted with the dry block heaters are presented in Appendix A.

This level of analysis does not allow one to conclusively differentiate between a Winsor-I, Winsor-II, and a non-emulsion-forming system as all three form two phases. However, we can visually identify the formation of a Winsor-IV and Winsor-III system. Tables 17, 18, and 19 therefore indicate the samples where type IV and type III systems could be observed forming at ambient conditions.

Table 17: Emulsion formation observed with MNB

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%					
80%					
90%				III	III
95%	IV	IV	IV	III	III

Table 18: Emulsion formation observed with 2-MNT

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%					
80%					
90%				III	III
95%	IV	IV	IV	III	III

Table 19: Emulsion formation observed with 3-MNT

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%					
80%	III	III			
90%	IV	IV	IV		
95%	IV	IV	IV	III	III

As expected, the microemulsion formation, and the type of system formed varied not only with the mixture ratio, and the acid concentration, but also with the organic used. More specifically, given that the organics studied were MNB and two MNT isomers, the microemulsion behavior was influenced by the presence and location of the methyl group attached to the aromatic ring in the case of the MNT isomers.

Additionally, the results of trials 5 and 7 as well as 6 and 13 show that the system sometimes exhibits microemulsion formation before the sulfonation reaction has proceeded fully but does not after that reversible reaction has reached equilibrium. This demonstrates that the sulfonation reaction has a negative or adverse effect on the system's ability or tendency to form microemulsions.

If we further consider the findings of previous work – that the addition of dinitrobenzene and dinitrated products had an adverse effect on microemulsion formation[7] – and consider the structures of the molecules in Figure 19, a trend becomes apparent.

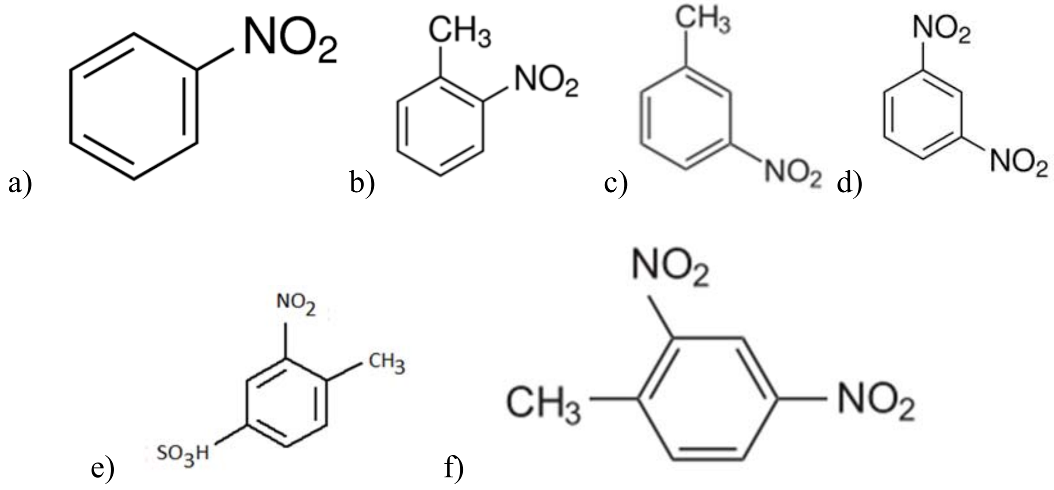

Figure 19: Molecular structures of a) MNB b) 2-MNT c) 3-MNT d) DNB e) 2-nitrotoluene-5-sulfonic acid f) DNT

The additional functional groups on the aromatic ring tend to make the formation of microemulsions in the mixed-acid system less favorable, likely due to steric effects or due to changes in the polarity and dielectric moment of the organic molecules. This further suggests that higher substituted aromatics and those with larger groups substituted onto the ring would be expected to show less of a tendency to form middle phase microemulsions than those studied in this work.

In all cases where it was observed, the middle phase microemulsion collapsed when the temperature of the system was elevated to temperatures typical of industrial processes and the type IV systems collapsed into 2-phase systems upon heating which is consistent with microemulsion behavior. However, the type III and IV systems not only collapsed below temperatures typical for the process, but at temperatures barely above ambient lab conditions, around 25°C. The heat of mixing generated during the preparation of the mixed acid – as discussed in section 3 - would be enough to raise the aqueous phase and the system as a whole above that temperature, even without additional heating.

This finding further limits the potential threat that this emulsion formation behavior might pose to industrial nitration processes. Slightly pre-heating reactants before introducing them to the process can effectively prevent microemulsion formation in the reactor.

The fact that the sulfonation occurred principally at the phase interface in the early experiments with low concentration acid suggests that at low concentrations the materials are not forming a microemulstion in the form of a Winsor-I or Winsor-II system. They're merely separating out into aqueous and organic phases. This supports the belief that the system is not forming emulsions with low surfactant volume fractions, an assumption critical to the microemulsion models currently available.

The fact that the organic phase tended to grow while the aqueous phase shrank as temperature increased in the early tests, as well as the later ones, tell us that with higher acid concentrations and a large amount of organic relative to the aqueous, the system was forming a Winsor-I system with excess organic material forming a separate phase apart from the aqueous phase which contained solubilized organic.

In the second round of trials, the dark color observed in both the upper and lower phases observed when the one phase Winsor-IV systems collapse into two phases suggests that there is a significant amount of nitrotoluene-sulfonic acid in both the upper and lower phases. Based on this there is likely a substantial amount of the aqueous acid in the organic phase with excess water and acid forming a second phase and we are most likely observing the transition from a Winsor-IV to a Winsor-II system.

In light of these findings, it can be concluded that microemulsions will not form in the mixed acid system during reasonably normal operating conditions for continuous processes and there will be no transitions between types of microemulsified systems in such processes. Therefore the microemulsion formation will have no impact on the modeling of mixed acid nitration reactors and transitions between emulsified states are not expected to be the cause of thermal shocks in the process.

Failure of Equations of State to Predict Microemulsion Formation

Microemulsions are modeled using statistical thermodynamic models as outlined in section 3. Equations of state (EOS) are not designed to predict microemulsion formation and traditionally aren't used for that purpose. However, in the interest of investigating other avenues for predictive modeling of the system Aspen Plus was used to generate ternary diagrams for mixtures of sulfuric acid, nitrotoluene, and water to determine if any of the common EOS could predict the formation of three simultaneous phases. None did.

Implications for and Difficulties with Predictive Modeling of Microemulsion Formation in the Mixed Acid Nitration System

The results of the experiments seriously call into question the applicability of available models to the system under consideration. The Winsor-IV and Winsor-III systems were only observed in cases with sulfuric acid concentrations of 80 wt% and above. Available models for microemulsions tend to assume that the volume fraction of the surfactant is negligible, or at least very small. At 80 wt% there is one mole of H_2SO_4 for every 0.3-2.5 moles of water in the system as can be seen in Table 20 and between 0.25 and 1.5 moles of the organic species for each mole of H_2SO_4 depending on the mixture ratio used as detailed in Tables 21, 22, and 23. Thus the mole and volume fractions of the system that are occupied by the surfactant are clearly not negligible in the region or interest for these experiments. This in turn challenges other key assumptions of most available models in that:

1) It is known that water and the organic are not completely immiscible in each other
2) It is not reasonable to expect the formation of a surfactant monolayer at the oil/water boundary.
3) It is not reasonable to assume that the surfactant(s) will exist only at the oil-water phase interface.
4) It is not reasonable to use the amount of surfactant available as a way of determining the maximum area of the oil-water interface in the microemulsion phase and therefore a way of fixing the maximum amount of the middle phase microemulsion that can form.

Table 20: Molar ratios of water to sulfuric acid based on acid concentration.

Density of H2SO4	@22 deg C		mols H2O/mL		mols H2SO4/mL		mol H_2O/mol acid
70%	1.61	g/mL	0.027	mols/mL	0.011	mols/mL	2.33
80%	1.73	g/mL	0.019	mols/mL	0.014	mols/mL	1.36
90%	1.81	g/mL	0.010	mols/mL	0.017	mols/mL	0.60
95%	1.83	g/mL	0.005	mols/mL	0.018	mols/mL	0.29

Additionally, no available models are able to account for the possibility of reversible or irreversible reactions occurring between the organic species and the surfactants or co-surfactants, nor are the models able to account for dimerization or trimerization of the surfactant molecule. This can occur with concentrated sulfuric acid, sometimes forming materials like the S_3O_9 structure shown in Figure 20.

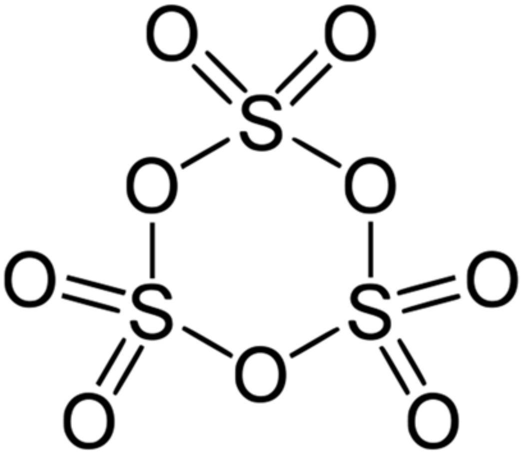

Figure 20: SO_3 trimer structure

The available models also tend to perform best or assume that the volume fraction of each component is approximately equal. In Table 21 we see that, in mixtures that would be typical of the industrial processes described previously from literature, we expect the molar and volume ratios of the system to favor water heavily over the organic.

Table 21: Representative process mixtures and molar ratios

Representative Mixture:		Representative Mixture:		Representative Mixture:	
20	wt% nitric acid	15	wt% nitric acid	10	wt% nitric acid
10	wt% Water	10	wt% Water	30	wt% Water
70	wt% Sulfuric acid	75	wt% sulfuric acid	60	wt% sulfuric acid
Corresponding mol%		Corresponding mol%		Corresponding mol%	
20	mol% nitric acid	15	mol% nitric acid	7	mol% nitric acid
35	mol% water	36	mol% water	68	mol% water
45	mol% sulfuric acid	49	mol% sulfuric acid	25	mol% sulfuric acid
Important molar ratios:		Important molar ratios:		Important molar ratios:	
1.86	mol acid/mol H_2O	1.81	mol acid/mol H_2O	0.46	mol acid/mol H_2O
3.25	mol acid/mol organic	4.21	mol acid/mol organic	4.85	mol acid/mol organic
0.57	mol organic/mol H_2O	0.43	mol organic/mol H_2O	0.10	mol organic/mol H_2O

While only molar ratios are computed in the table it should be noted that the organic material is normally 15-20% more dense than water, so the volumetric ratios would be even more skewed in favor of water over the organic.

The molar ratios that existed in the experiments conducted are presented in Tables 22 through 27, with Tables 22-24 showing the molar ratio of the organic to the acid surfactant and Tables 25-27 giving the molar ratio of the organic to water.

Table 22: Moles MNB/Mole H2SO4 in total system

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	0.282	0.423	0.847	1.693	2.540
80%	0.230	0.345	0.691	1.381	2.072
90%	0.195	0.292	0.584	1.169	1.753
95%	0.183	0.274	0.548	1.096	1.643

Table 23: Moles 2-MNT/Mole H2SO4 in total system

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	0.246	0.369	0.739	1.477	2.216
80%	0.201	0.301	0.603	1.205	1.808
90%	0.170	0.255	0.510	1.020	1.530
95%	0.159	0.239	0.478	0.956	1.434

Table 24: Moles 3-MNT/Mole H2SO4 in total system

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	0.245	0.367	0.735	1.470	2.204
80%	0.200	0.300	0.600	1.199	1.799
90%	0.169	0.254	0.507	1.015	1.522
95%	0.159	0.238	0.476	0.951	1.427

Table 25: Moles MNB/Mole Water in total system

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	0.121	0.181	0.363	0.726	1.088
80%	0.169	0.254	0.507	1.015	1.522
90%	0.322	0.483	0.966	1.932	2.898
95%	0.637	0.956	1.912	3.824	5.735

Table 26: Moles 2-MNT/Mole Water in total system

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	0.106	0.158	0.317	0.633	0.950
80%	0.148	0.221	0.443	0.886	1.328
90%	0.281	0.422	0.843	1.686	2.529
95%	0.556	0.834	1.668	3.336	5.005

Table 27: Moles 3-MNT/Mole Water in total system

Acid Concentration	Aqueous:Organic Volumetric Ratio				
	3:1	2:1	1:1	1:2	1:3
70%	0.105	0.157	0.315	0.630	0.945
80%	0.147	0.220	0.441	0.881	1.322
90%	0.280	0.419	0.839	1.677	2.516
95%	0.553	0.830	1.660	3.319	4.979

Based on a comparison of the expected process mixture ratios to the experiments conducted, we see that most processes will be expected to operate in a compositional range consistent with the upper to middle left hand side of Tables 21 through 26, where were see acid concentrations around 70 to 90 wt% and aqueous to organic ratios of 3:1 or 2:1. However, we're observing emulsion formation and three phase co-existence mostly in the 90-95% acid concentration ranges and mostly with aqueous to organic ratios of 1:2 or 1:3. Therefore, based on these results, even if an existing microemulsion model could be expected to yield reasonably accurate predictions for this system, the results would likely have little bearing on reactor and process operations as we expect the reactor to experience mostly only the traditional two phase behavior. Since the model would therefore have limited actual utility, the development of a model that could account for these issues and accurately model this system would have little value.

5. SUMMARY

Mixed-acid nitration is a well-established process that has been conducted industrially for over 70 years. It involves highly exothermic reactions that must be managed to avoid thermal runaway events, a risk complicated by monomolecular decomposition reactions undertaken by the reaction products at elevated temperatures. Process disturbances that have the potential to cause thermal shocks or unexpected heating in the process are therefore a severe threat to the process and must be investigated. Recent work in literature shows that nitrobenzene is capable of forming microemulsions and undergoing transitions between different types of emulsified systems detailed by PA Winsor.

This work was therefore undertaken to observe representative mixtures of sulfuric acid, water, and select simple aromatics to determine if microemulsions were forming in the system in composition and temperature ranges typical of industrial processes and to determine what, if any, impact the substitution of small functional groups onto the aromatic ring had on the microemulsion formation. This was accomplished by examining samples containing three different organics: nitrobenzene and two nitrotoluene isomers, and four different concentrations of sulfuric acid: 70 wt%, 80 wt%, 90 wt%, and 95 wt%. Pure Sulfuric acid was used instead of the mixture of nitric and sulfuric acid that would normally be used in industrial processes to prevent nitration from occurring in the sample mixtures out of concerns for safety. A review of available literature has shown that this practice is common in academic research into the mixed acid system and it appears valid in the case of this work. The samples were heated to and allowed to settle at a selection of temperature set points ranging from 50 to 110°C. The samples were agitated prior to beginning the experiments to allow for reversible sulfonation reactions to reach equilibrium where necessary and the sample tubes were capped with parafilm afterwards to limit mass exchange with the atmosphere during the duration of the experiment.

Microemulsions were determined to be forming in the mixed-acid nitration system and that additional functional groups on the aromatic ring did affect the microemulsion formation within the system, usually adversely. However, the formation of three phases including a middle phase microemulsion – a key point of interest to this work with regard to operability of the process – did not occur in compositional ranges commonly seen and expected in industry. Additionally, the type-III and type-IV microemulsions which where the central focus of this work all collapsed at temperatures of around 30°C, well below the 60-100°C expected of continuous industrial nitration processes. Based on these observations, it was concluded that microemulsions will not form in the mixed acid system during reasonably normal operating conditions for continuous processes and there will be no transitions between types of microemulsified systems in such processes. Therefore the microemulsion formation will have no impact on the modeling of mixed acid nitration reactors and transitions between emulsified states are not expected to be the cause of thermal shocks in the process.

Literature was reviewed to search for appropriate models that could be used to predict the formation of microemulsions in these and similar systems. Multiple papers and models were identified and examined with regards to their strengths and the applicability of their underlying assumptions to the system of interest. It was determined that existing models in literature for prediction microemulsions are ill suited to describe the behavior of this system. The existing models work best in situations where the volume fractions of the organic and aqueous phases are about equal, assume that the surfactant molecules form a mono layer at the aqueous-organic phase interface and are present only at the interface, and assume that the volume fraction of the surfactant in the system is small or negligible. None of these critical assumptions are valid in this system.

However, experimental results show that this behavior poses no threat to the process, which means that developing a new model for systems such as this one is of little practical value.

6. RECOMMENDATIONS

Based on the results obtained through this research, it is not recommended that work regarding this system be continued by others in MKOPSC. The results of this work have shown that the emulsion formation is not occurring under typical process conditions. The three phase emulsions that were the primary focus of this work are forming in concentration ranges consistent with process conditions that are far too low for industrial nitration processes. The single phase emulsions are forming in concentration ranges that are too acid-rich. These systems have likewise demonstrated that they will begin to devolve into more traditional two phase systems at temperatures well below typical process operating temperatures. Based on this, the phase phenomena studied is not likely to pose a significant threat to the operability of the process and does not warrant further investigation. Additionally, the question may become entirely moot in time if solid state catalyst nitration processes are successful in replacing the older mixed-acid process considered in this work.

However, the thermodynamics of reactive systems, phase equilibria, emulsion formation, phase inversions, thermodynamic state transitions, and the modeling thereof should be of continued interest to MKOPSC and researchers where they are found to have the potential to impact the safe operation of the process. Specifically with regard to microemulsions, there may be value in attempting to generate new predictive models which do not favor mixtures with a 1:1 aqueous to organic volumetric ratio or which do not require a low surfactant volume faction. Either of these developments would create predictive models more applicable any systems found to be similar to this one.

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APPENDIX A

EXPERIMENTAL RESULTS

Experiment 1

Nitrobenzene with 70% Sulfuric Acid.

Acid prepared by mixing 90 mL of 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 52 mL of water.

Tube 1: 6 mL 70% H_2SO_4 w/ 2 mL nitrobenzene.

Tube 2: 6 mL 70% H_2SO_4 w/ 3 mL nitrobenzene.

Tube 3: 4 mL 70% H_2SO_4 w/ 4 mL nitrobenzene.

Tube 4: 3 mL 70% H_2SO_4 w/ 6 mL nitrobenzene.

Tube 5: 2 mL 70% H_2SO_4 w/ 6 mL nitrobenzene.

-No three phase behavior was observed in any of the tubes in this trial.

-No Sulfonic Acid formation was observed in this trial

Temperatures observed (set-points):

50 °C

60 °C

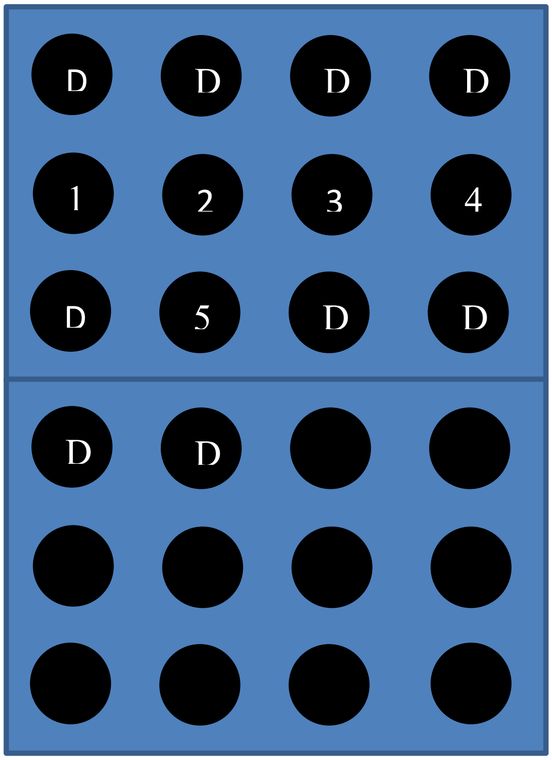
70 °C

82 °C

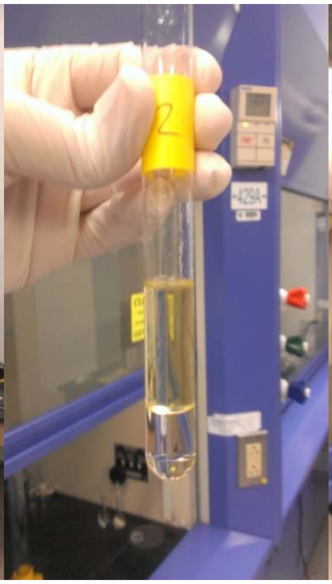
93 °C

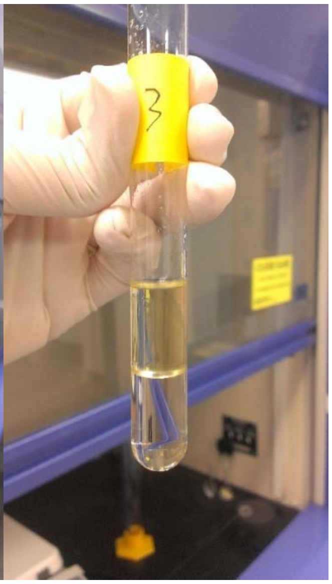
104 °C

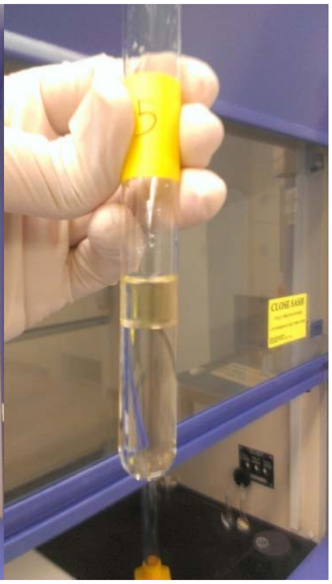
115 °C



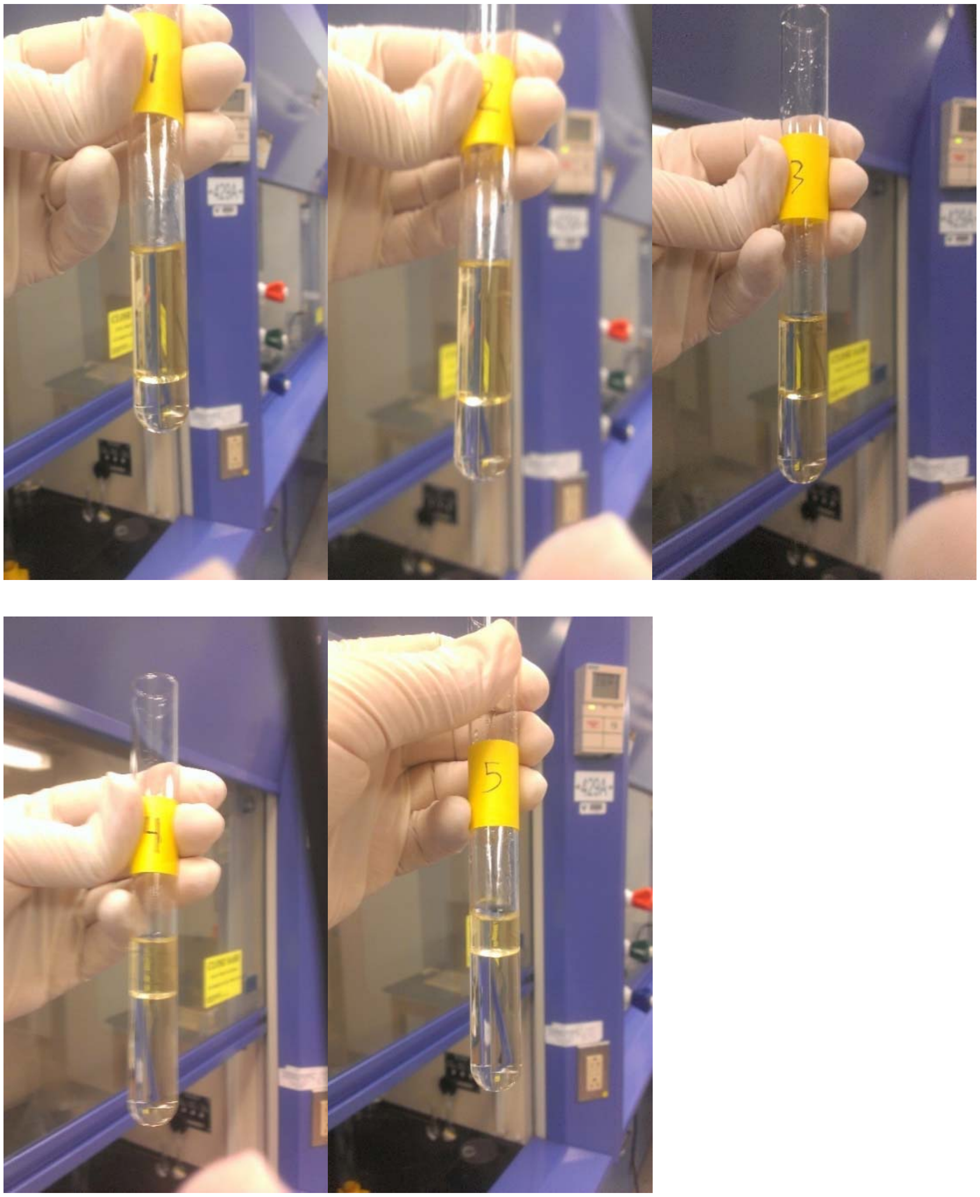
50 °C



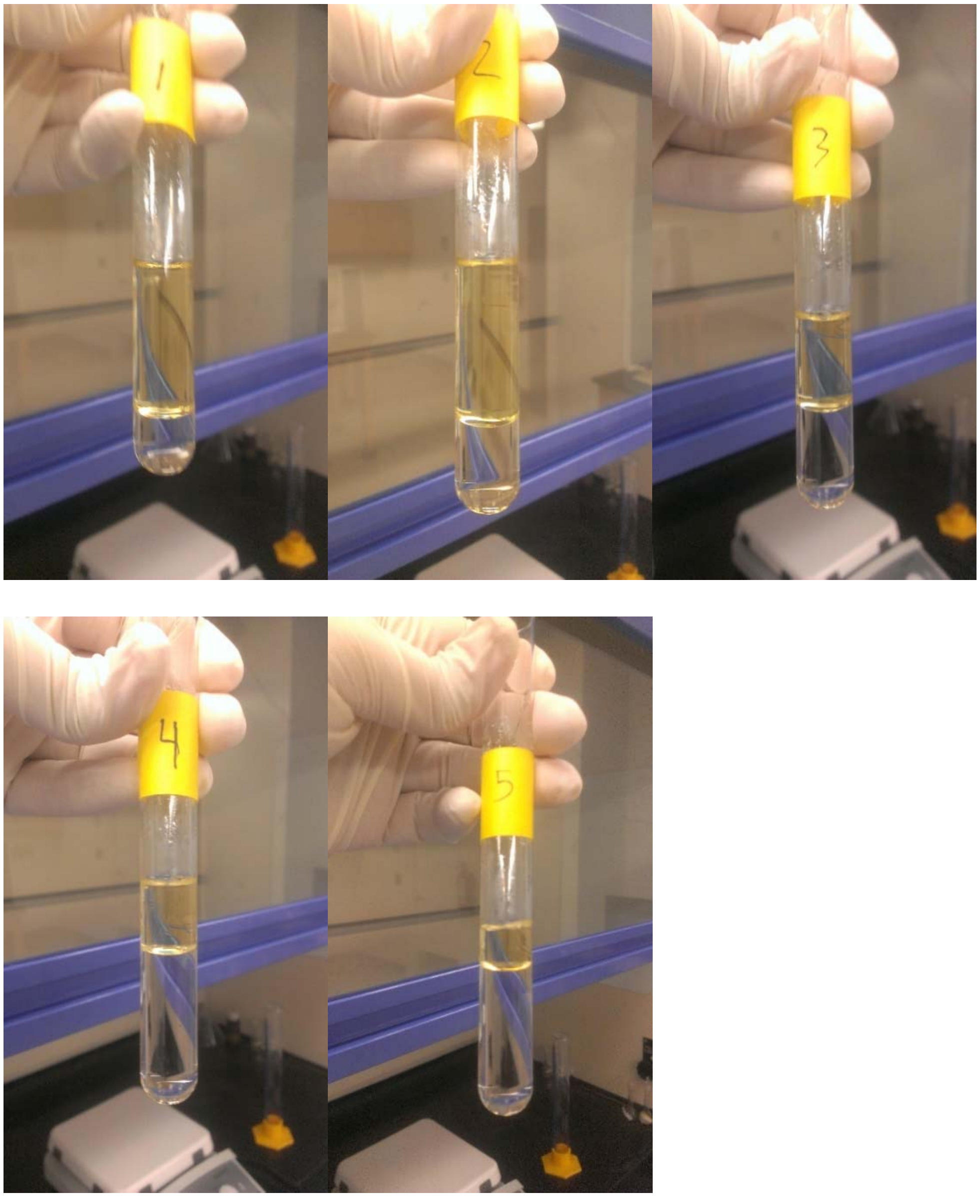




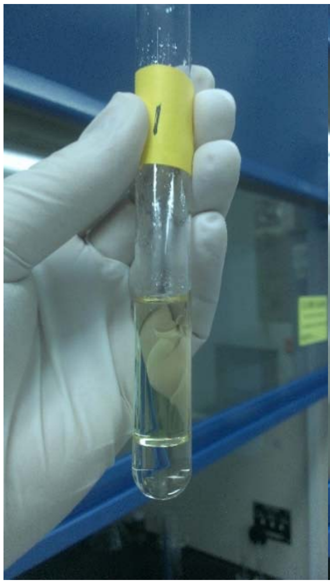
60 °C

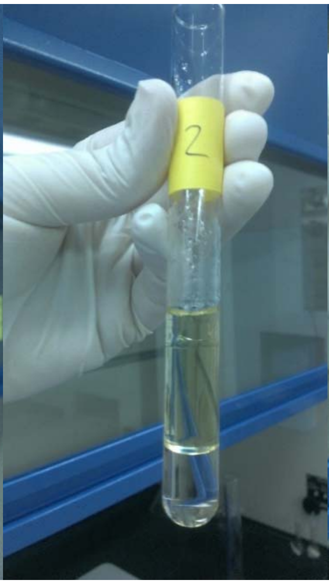


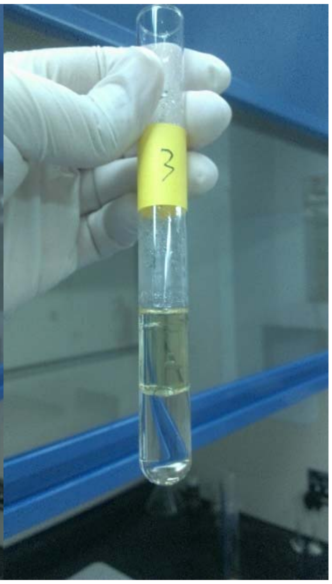
70 °C

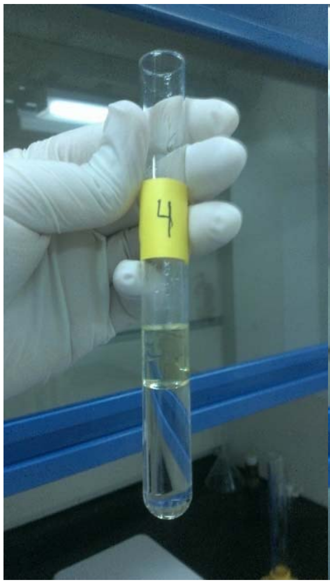


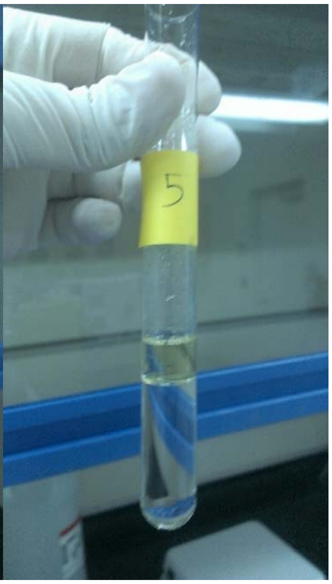
82 °C



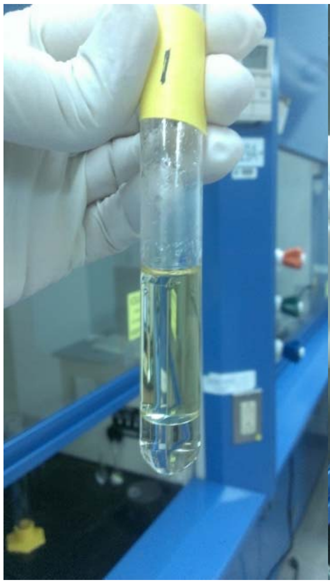


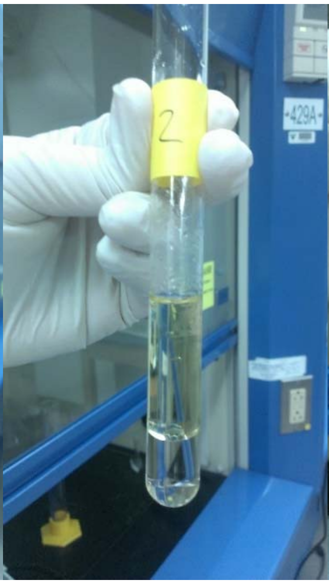


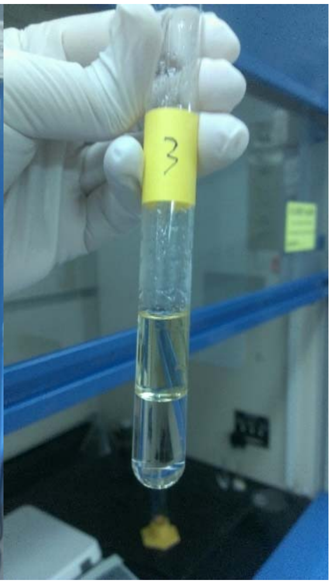


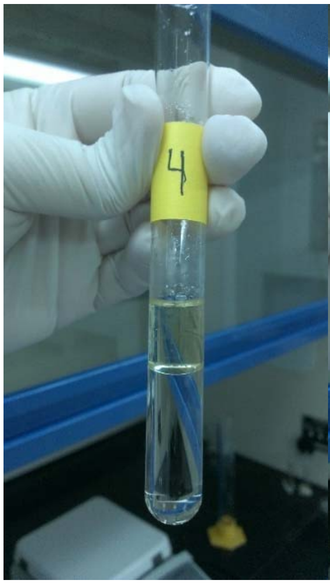


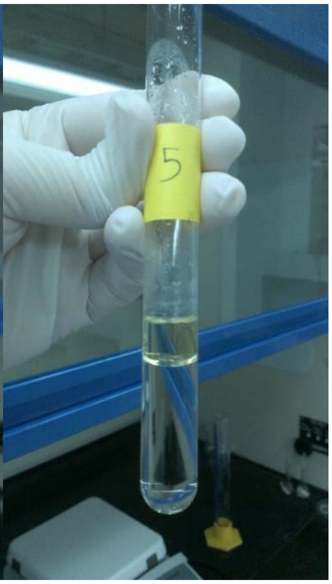
93 °C



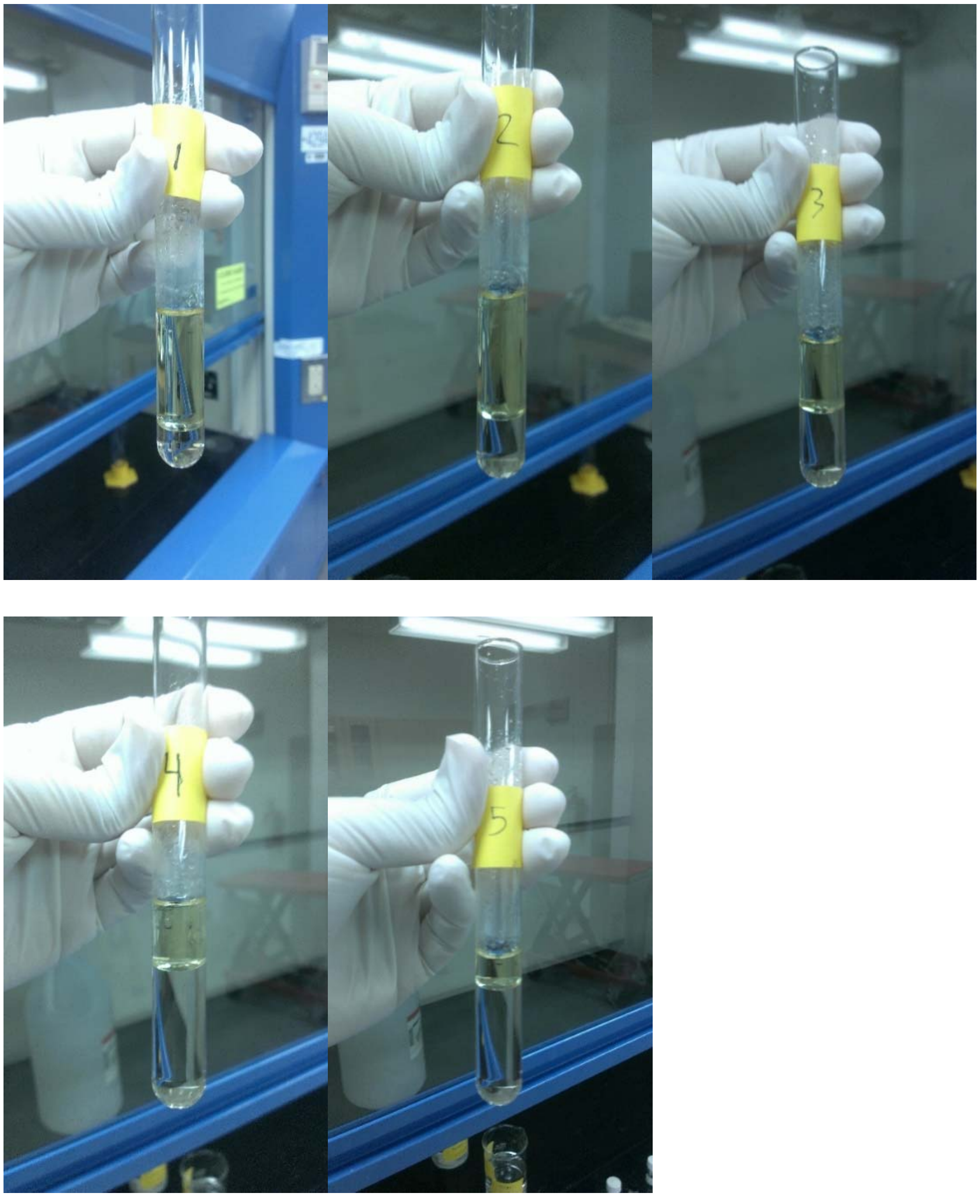




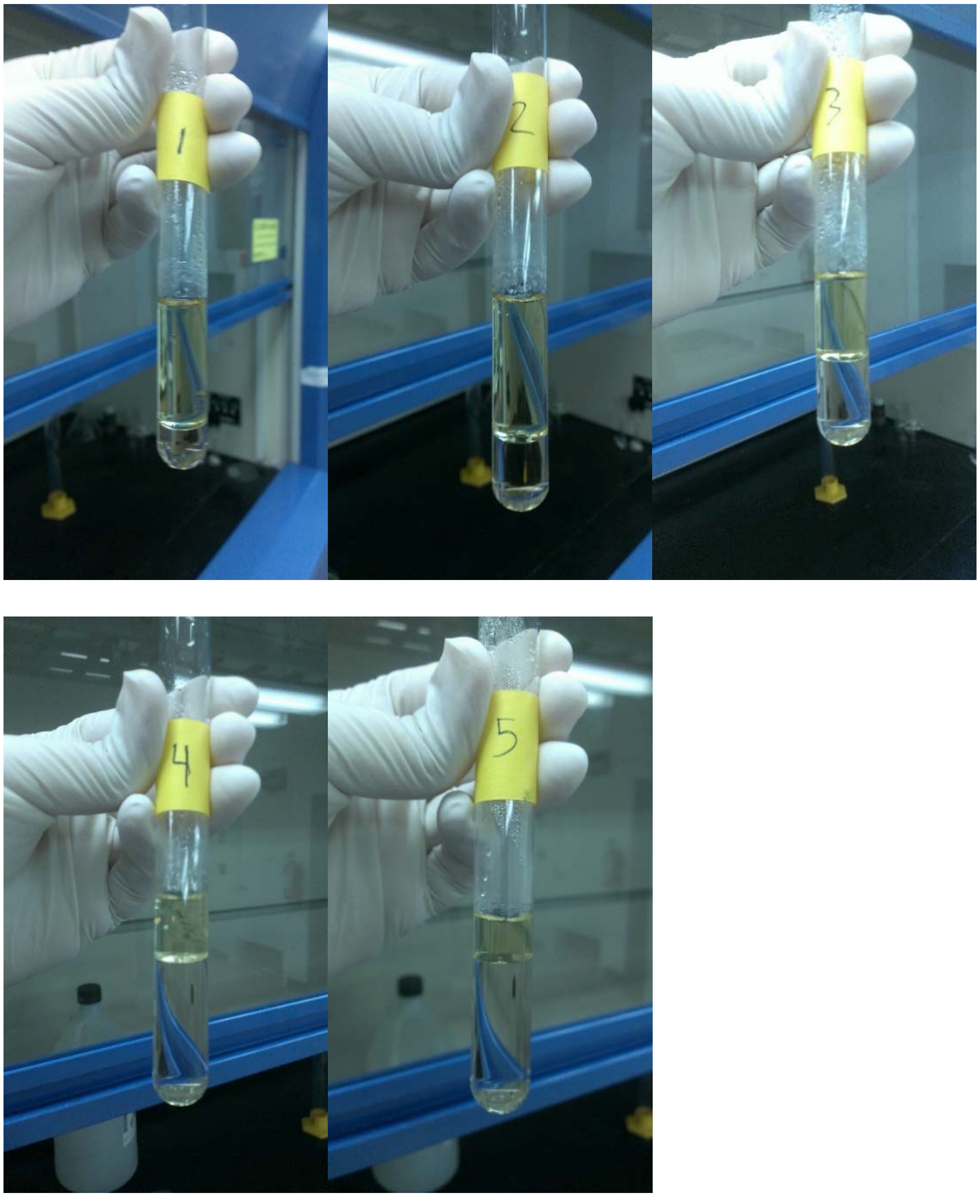




104 °C (02-26-2014)



115 °C (02-27-2014)



Experiment 2

Nitrobenzene with 80% Sulfuric Acid.

Acid prepared by mixing 90 mL of 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 25 mL of water.

Tube 1: 6 mL 80% H_2SO_4 w/ 2 mL nitrobenzene.

Tube 2: 6 mL 80% H_2SO_4 w/ 3 mL nitrobenzene.

Tube 3: 4 mL 80% H_2SO_4 w/ 4 mL nitrobenzene.

Tube 4: 3 mL 80% H_2SO_4 w/ 6 mL nitrobenzene.

Tube 5: 2 mL 80% H_2SO_4 w/ 6 mL nitrobenzene.

-Same tube layout used as for experiment 1

-No three phase behavior was observed in any of the tubes in this trial.

-Limited Sulfonic Acid formation was observed in this trial

Temperatures observed (set-points):

50 °C

60 °C

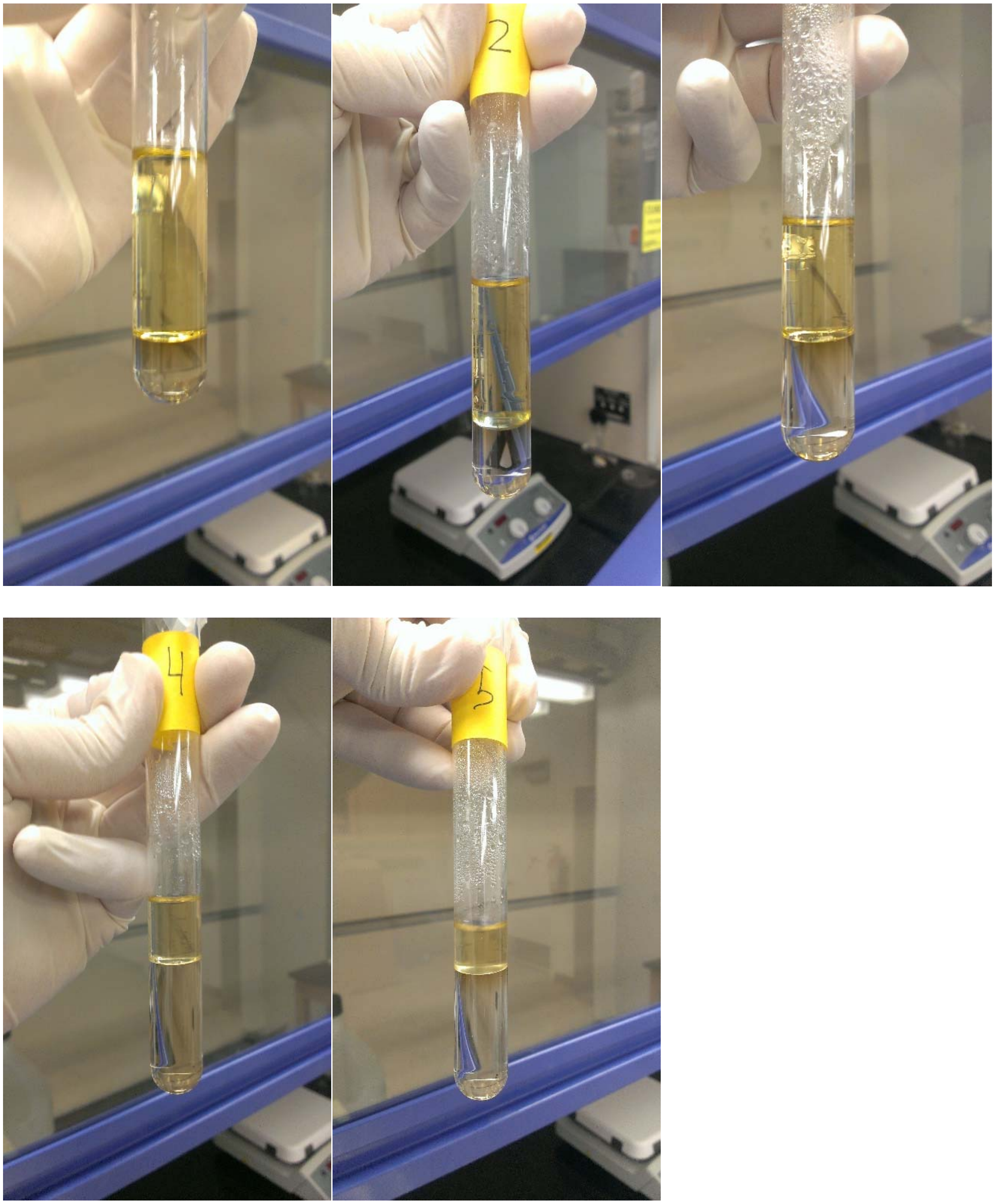
70 °C

82 °C

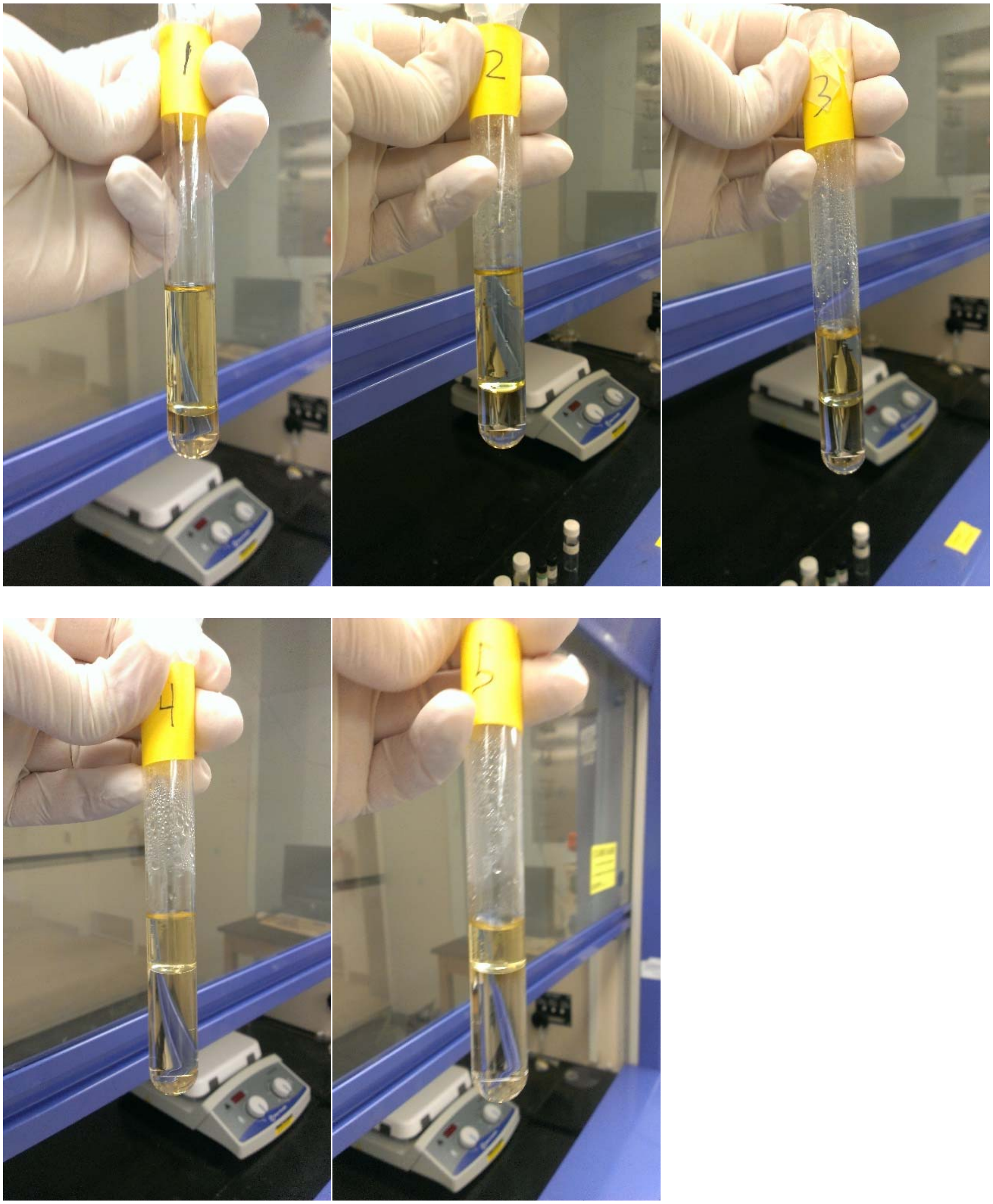
93 °C

104 °C

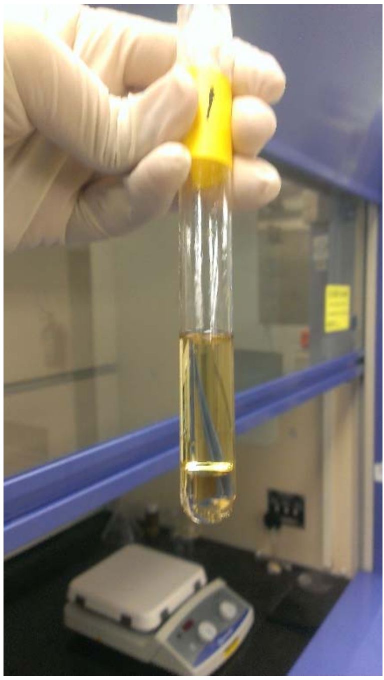
50 °C

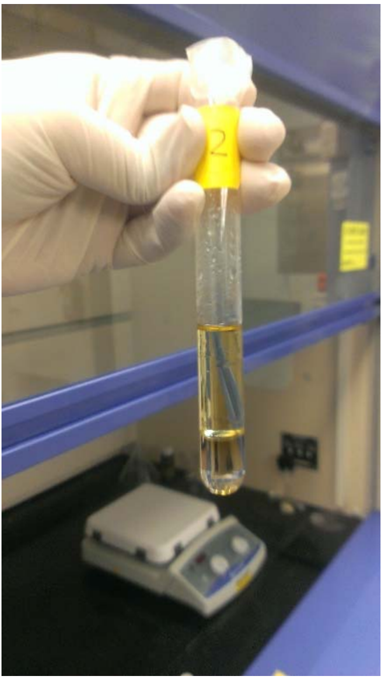


60 °C



70 °C



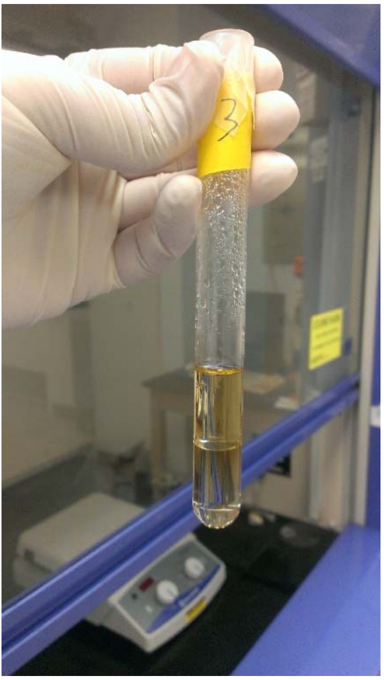


82 °C

93 °C


1

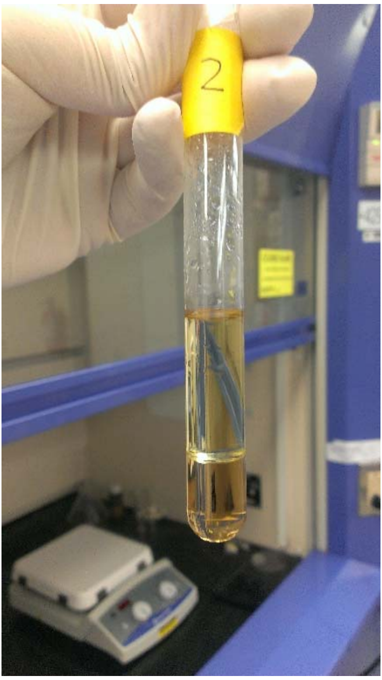

2

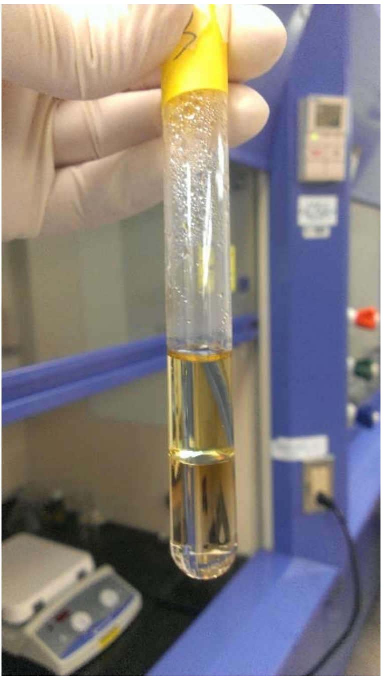

3

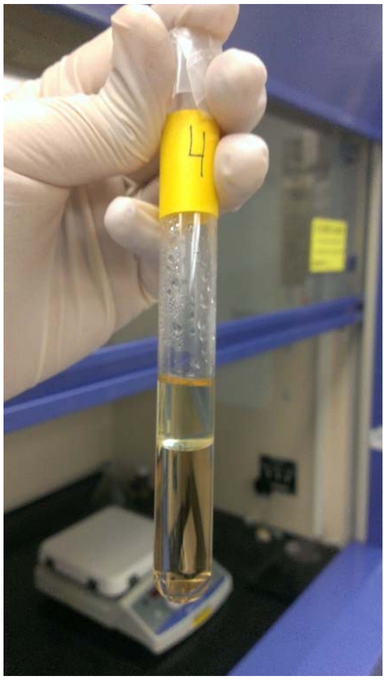

4

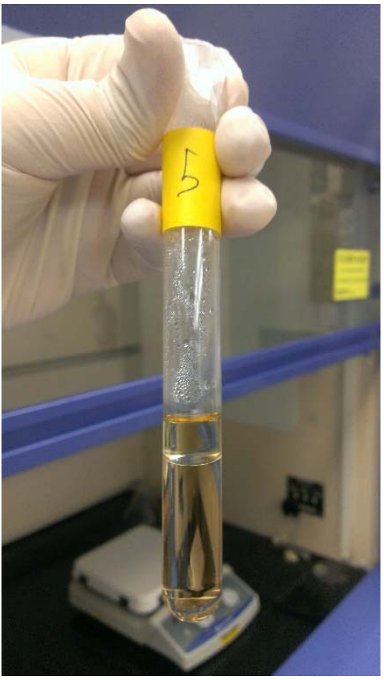

5
429A

104 °C









Experiment 3

Nitrobenzene with 90% Sulfuric Acid.

Acid is 90 mL 95-98 wt% Sulfuric Acid (assumed 96 wt%) mixed with 4 mL water

Tube 5: 6 mL 90% H_2SO_4 w/ 2 mL nitrobenzene.

Tube 3: 6 mL 90% H_2SO_4 w/ 3 mL nitrobenzene.

Tube 3: 4 mL 90% H_2SO_4 w/ 4 mL nitrobenzene.

Tube 2: 3 mL 90% H_2SO_4 w/ 6 mL nitrobenzene.

Tube 1: 2 mL 90% H_2SO_4 w/ 6 mL nitrobenzene.

-Same tube layout used as for experiment 1

-Tubes 1 and 2 showed signs of emulsion formation at ambient temperatures but not at elevated temperatures, at which they showed 2 phases. Tubes 3, 4, and 5 initially showed 2 phase separation but eventually formed one aqueous phase, likely due to the excess of acid, and the progression of the sulfonation reaction, which seems to increase the solubility of the organic material in the aqueous phase.

Temperatures observed (set-points):

50 °C

60 °C

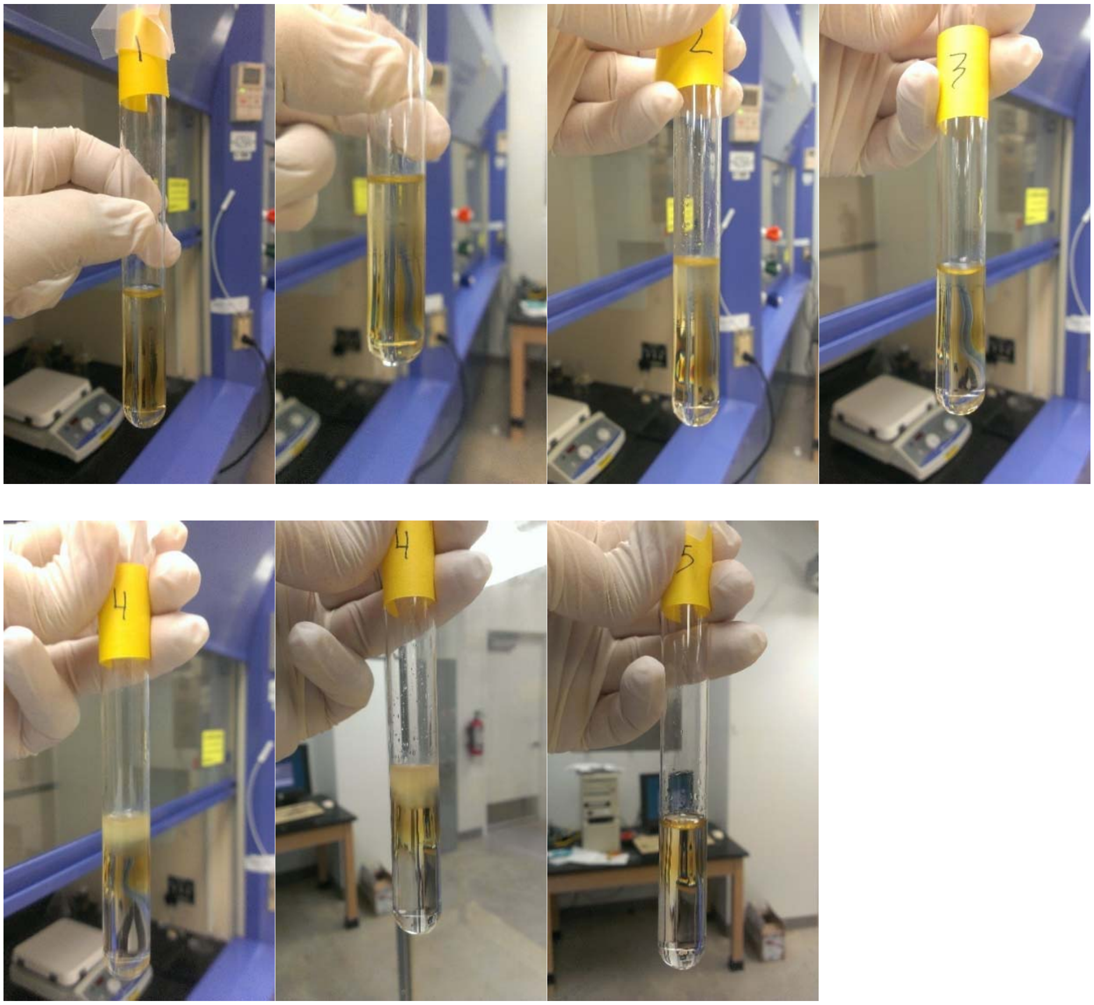
70 °C

82 °C

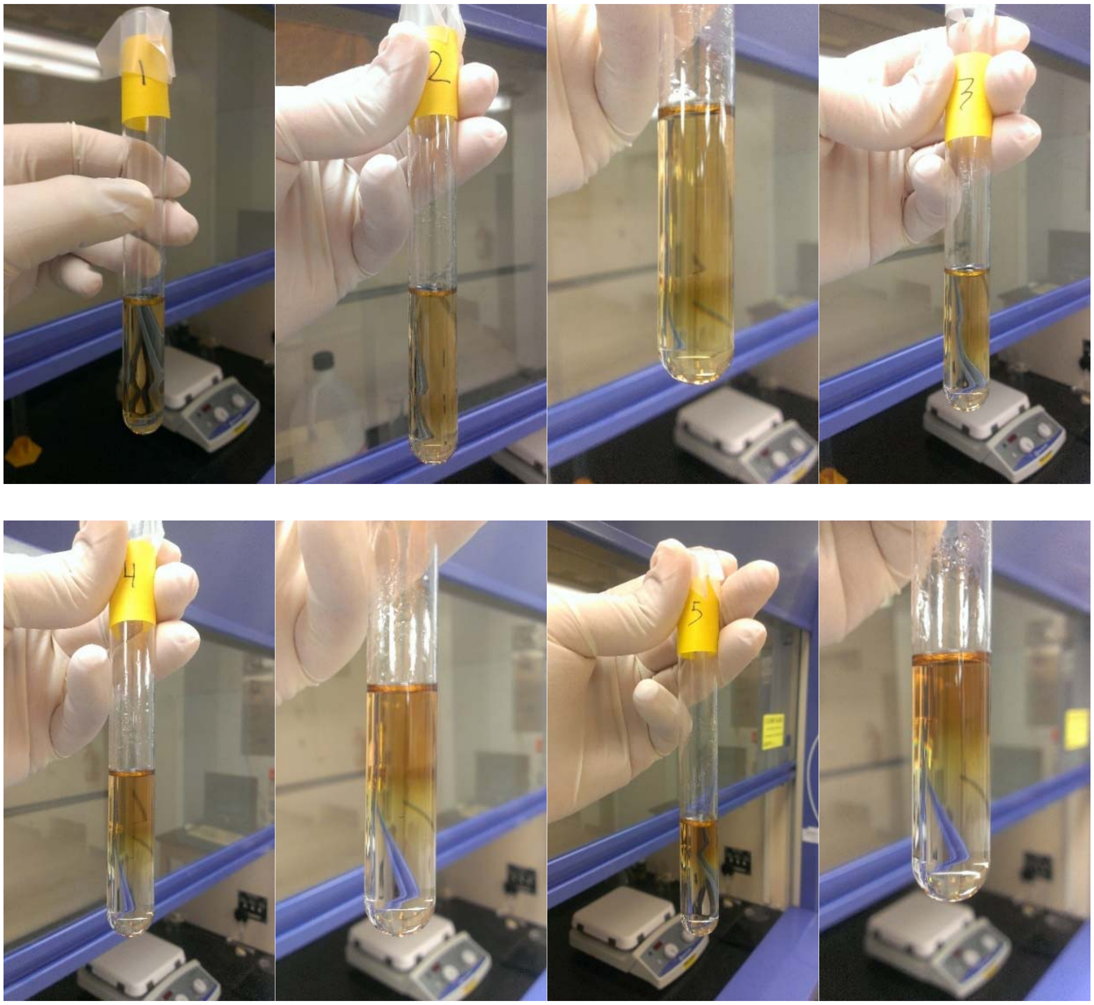
93 °C

Ambient

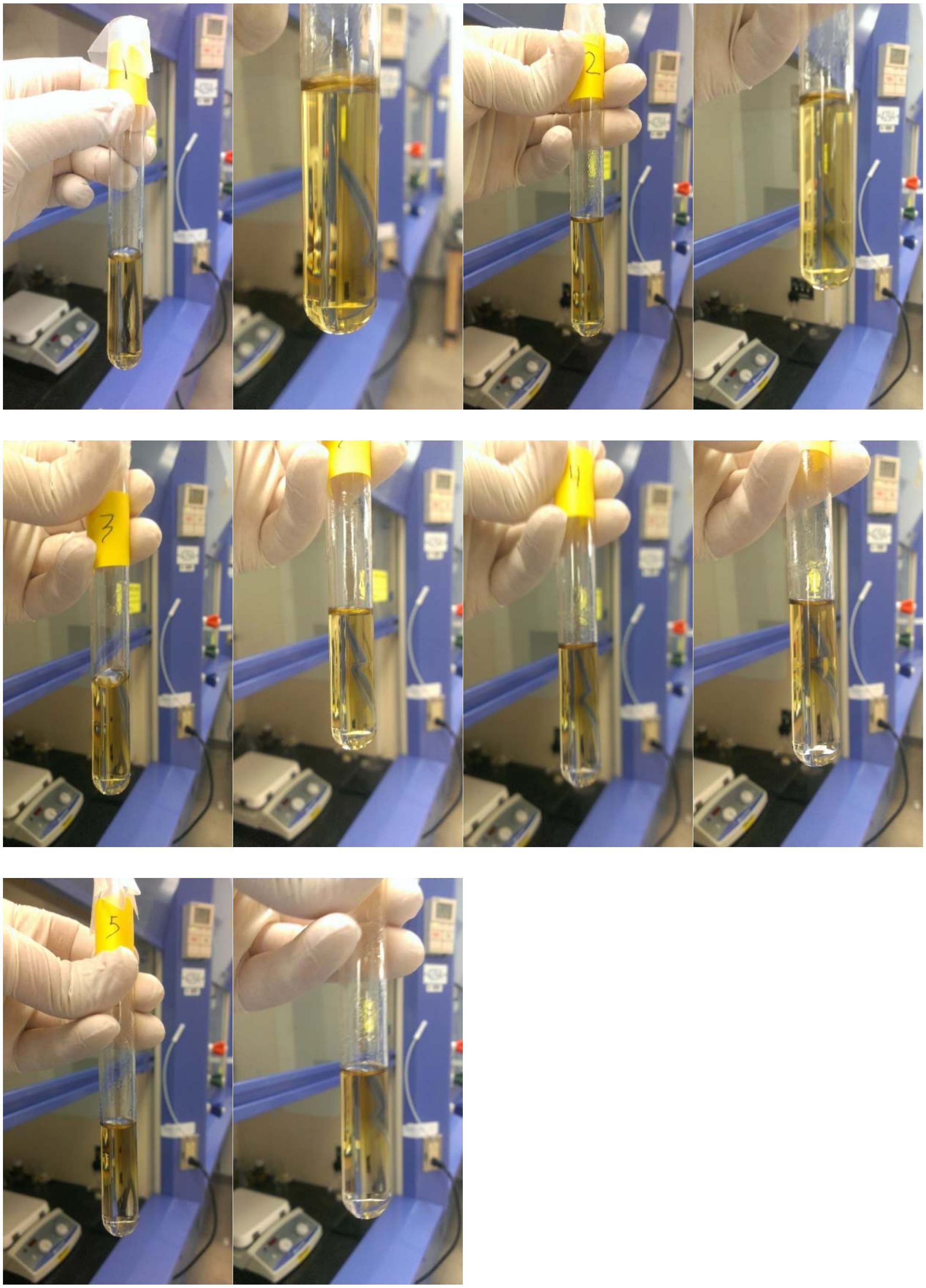
Ambient – Pre-run



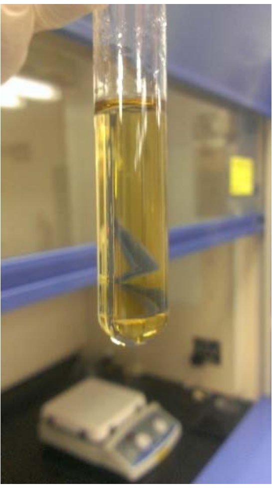
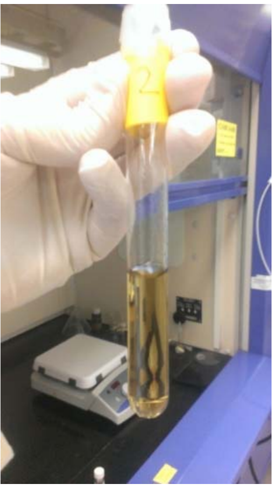
50 °C

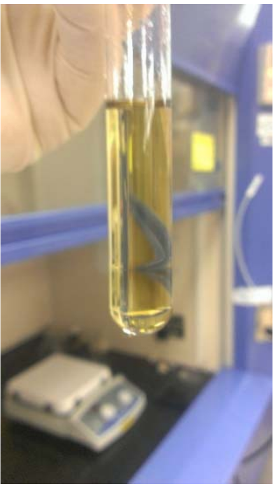
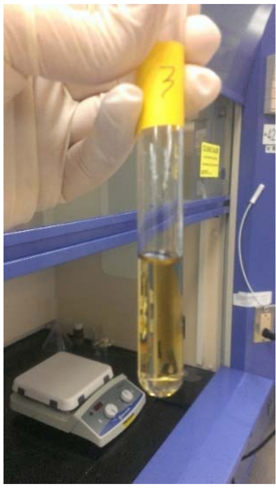


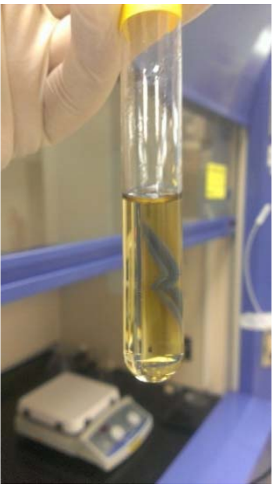
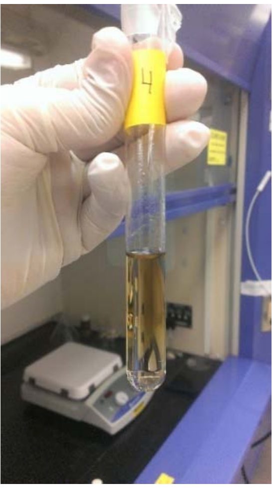
60 °C

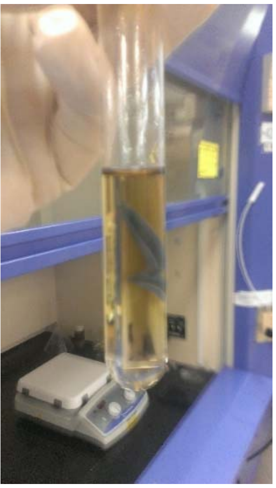


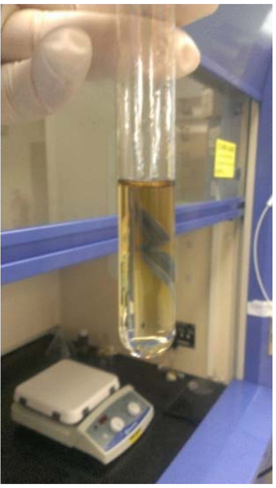
70 °C

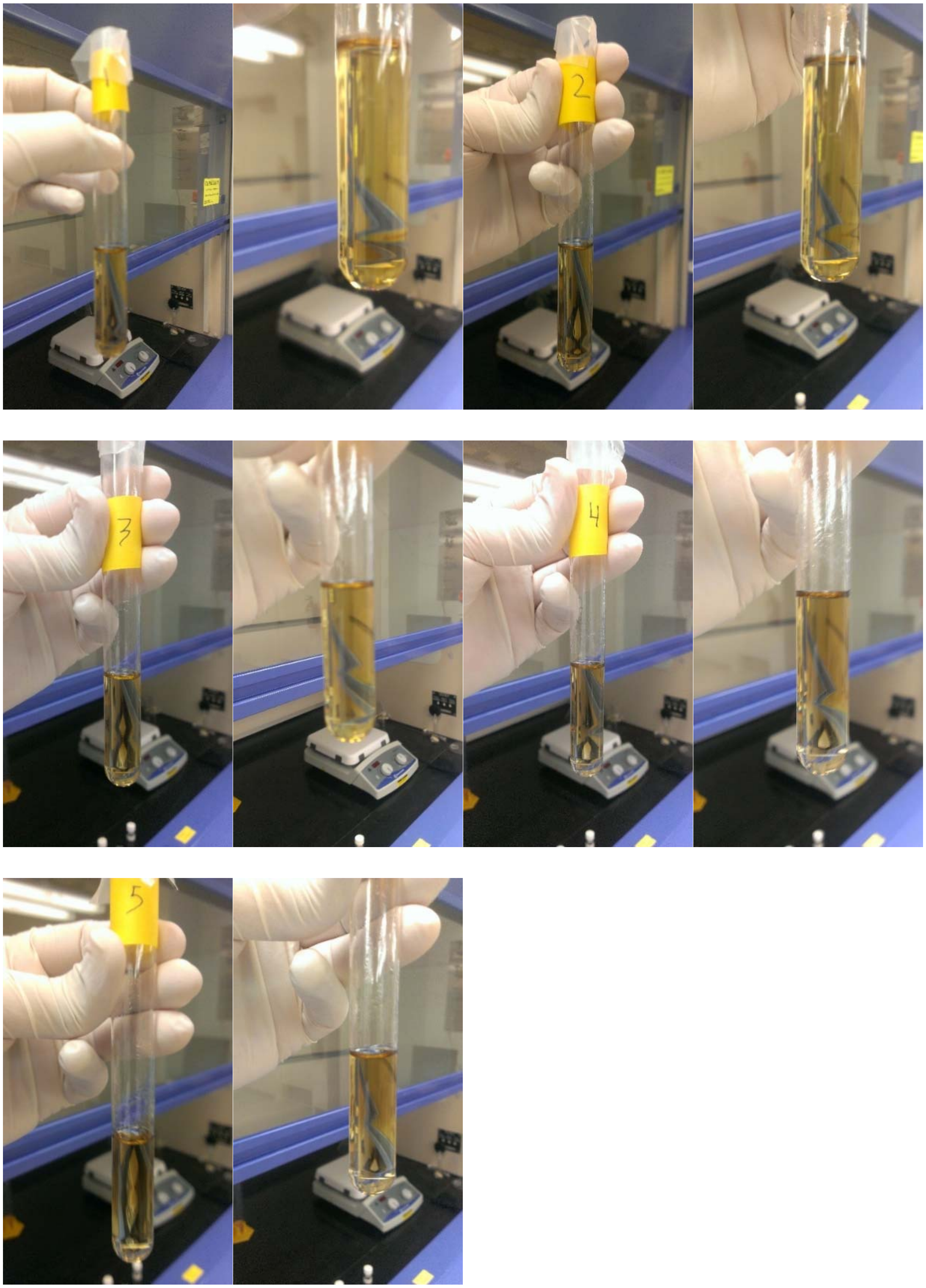



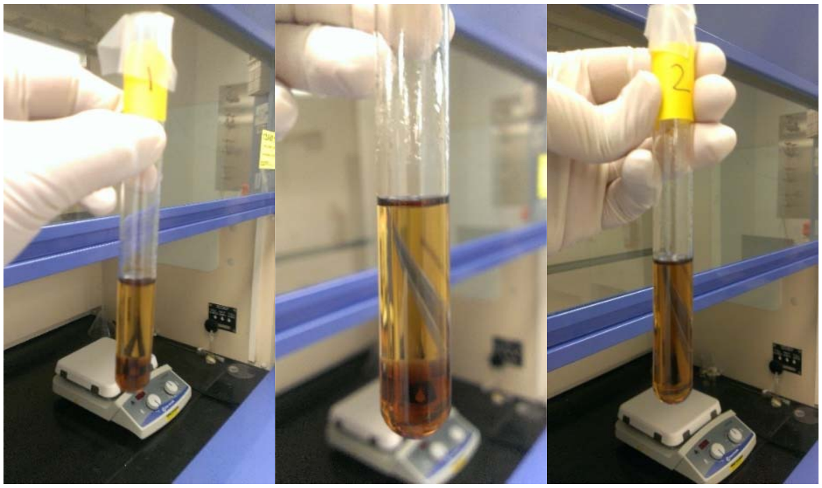


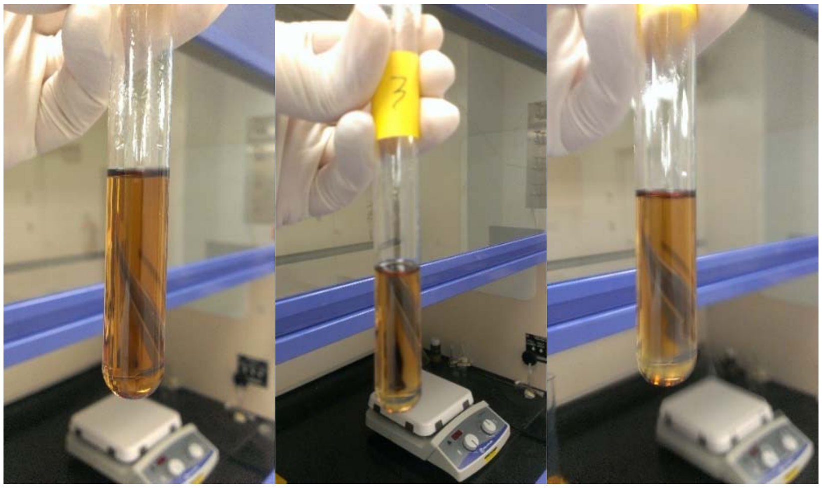



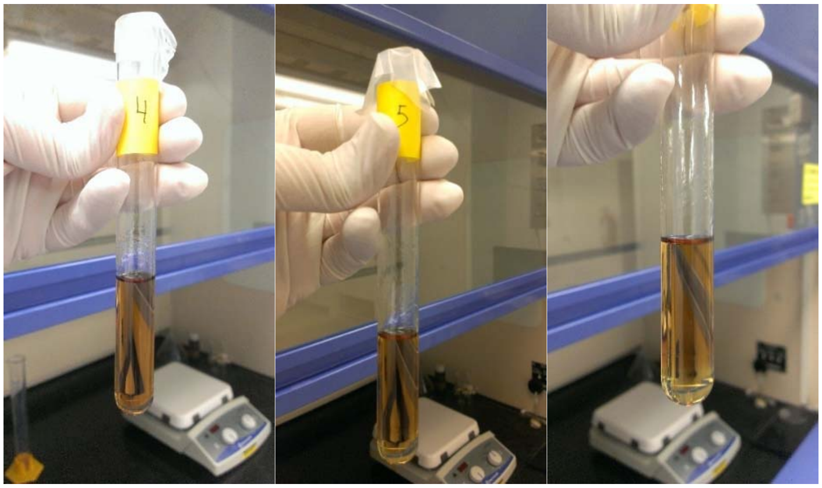
82 °C



93 °C







Ambient Ending

Experiment 4

Nitrobenzene with 95% Sulfuric Acid.

Acid is 95-98 wt% Sulfuric Acid (assumed 96 wt%)

Tube 5: 6 mL 95% H_2SO_4 w/ 2 mL nitrobenzene.

Tube 4: 6 mL 95% H_2SO_4 w/ 3 mL nitrobenzene.

Tube 3: 4 mL 95% H_2SO_4 w/ 4 mL nitrobenzene.

Tube 2: 3 mL 95% H_2SO_4 w/ 6 mL nitrobenzene.

Tube 1: 2 mL 95% H_2SO_4 w/ 6 mL nitrobenzene.

-Same tube layout used as in experiment 1

-Stable 3 phase behavior was achieved with tubes 1 and 2 but not with the others and only at ambient temperatures, not at the higher temperature settings observed. Three phase behavior wasn't observed with tubes 3, 4 or 5. Tubes 4 and 5 initially formed 2 phases in the absence of agitation but as the sulfonation reaction continued they ultimately formed one homogeneous aqueous phase.

Temperatures observed (set-points):

50 °C

60 °C

70 °C

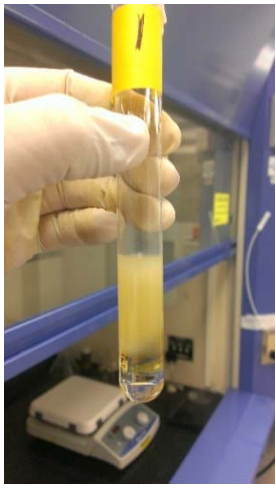
82 °C

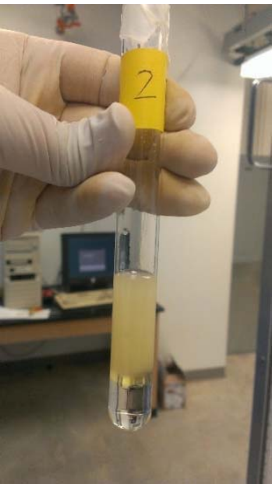
93 °C

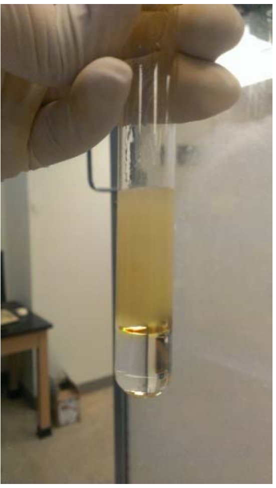
104 °C

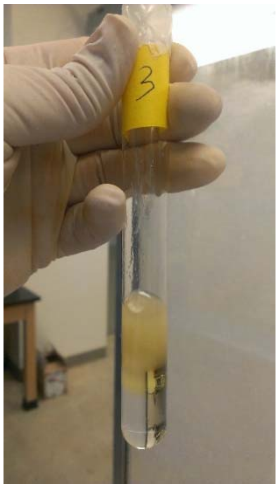
Tube	Initial Weight	Final Weight	Change
1	21.80 g	21.80 g	0.00 g
2	23.29 g	23.27 g	-0.02 g
3	22.48 g	22.48 g	0.00 g
4	24.47 g	24.47 g	0.00 g
5	23.30 g	23.29 g	-0.01 g

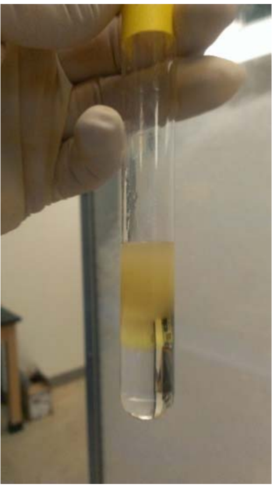
Ambient – Prerun after mixing

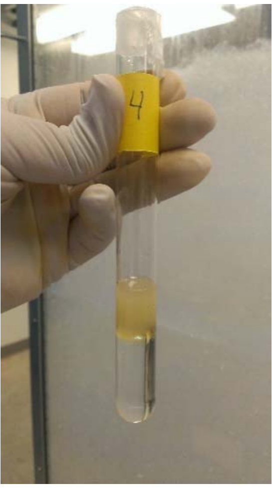


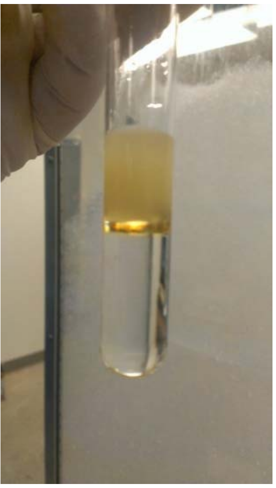


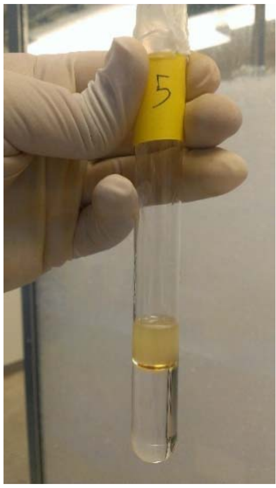




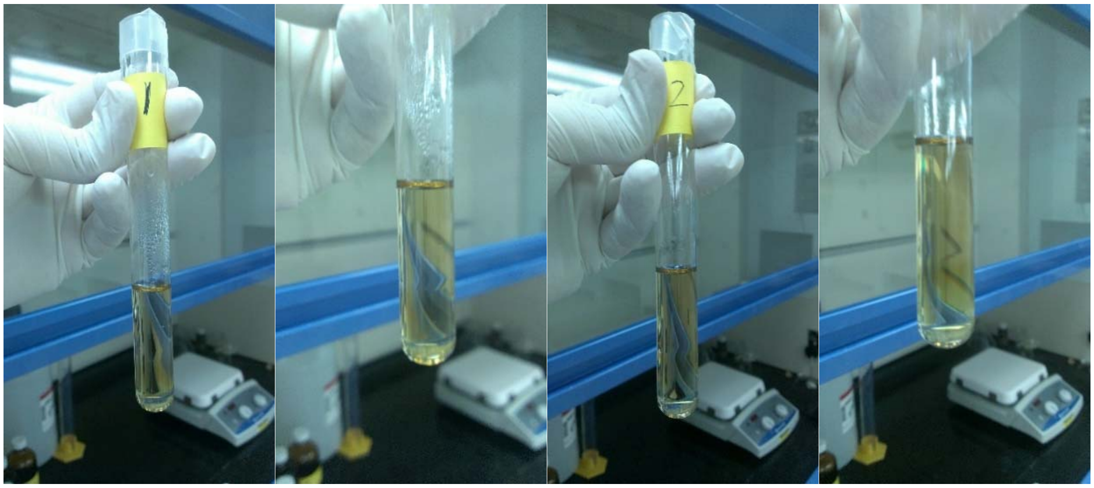


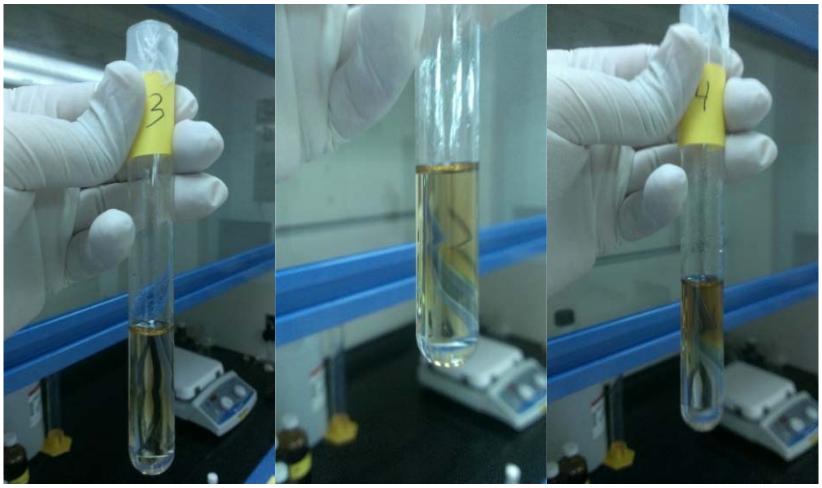


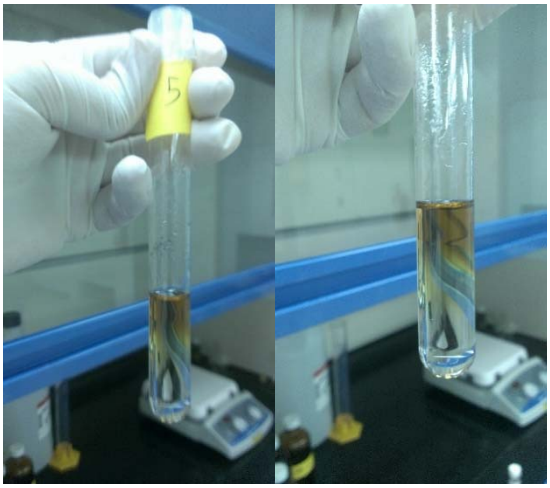




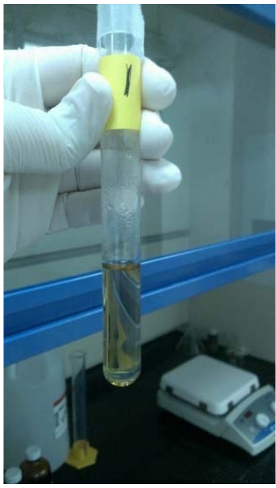
Ambient – Prerun after sitting:

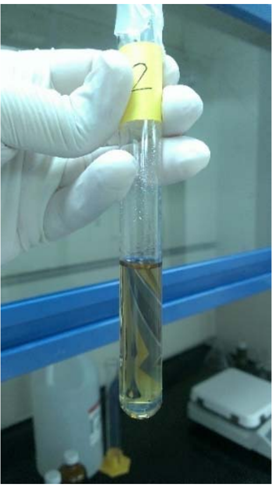


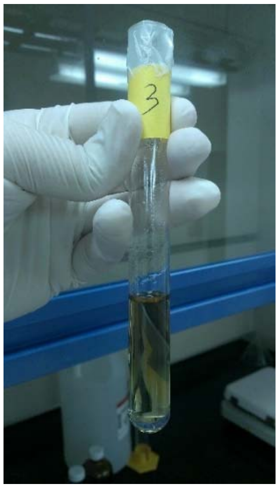


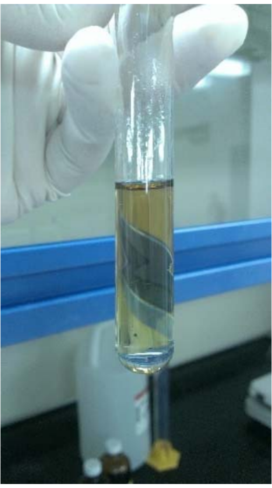


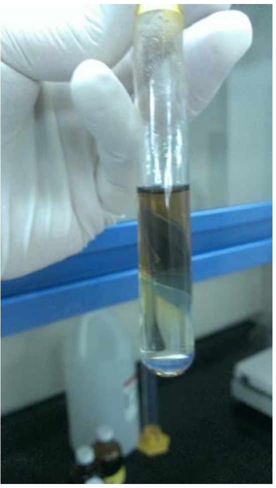
50 °C

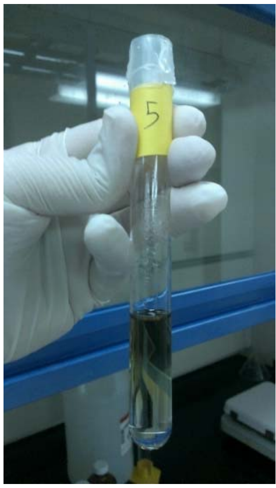


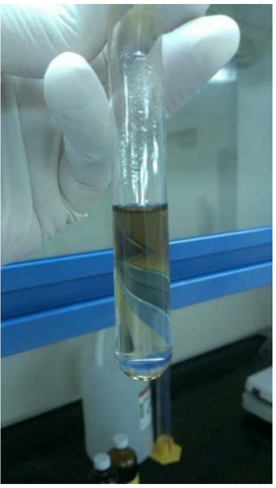




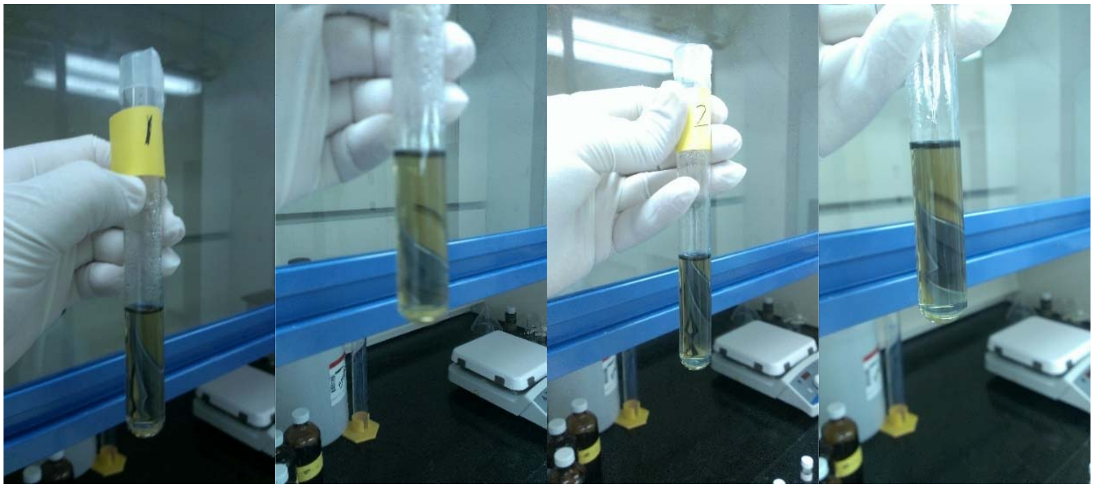


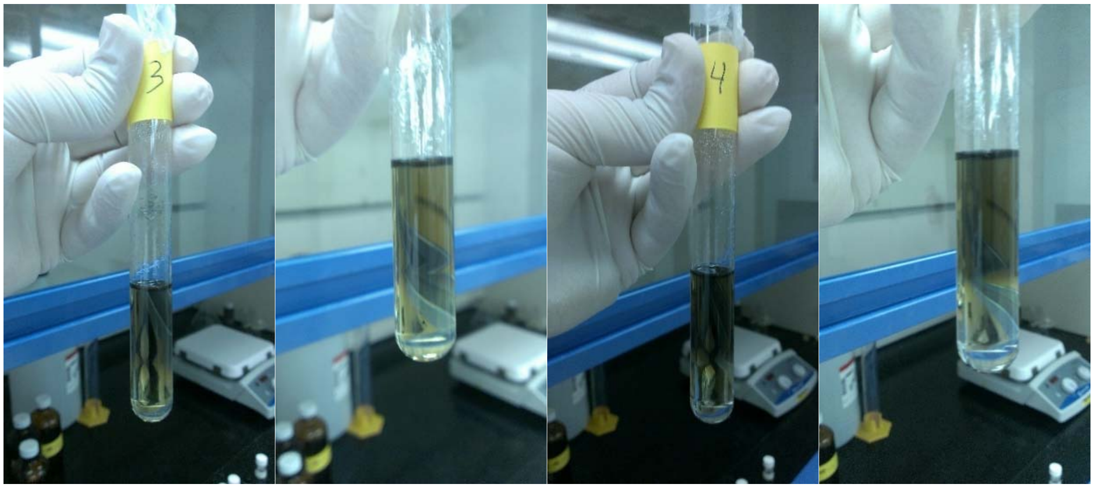


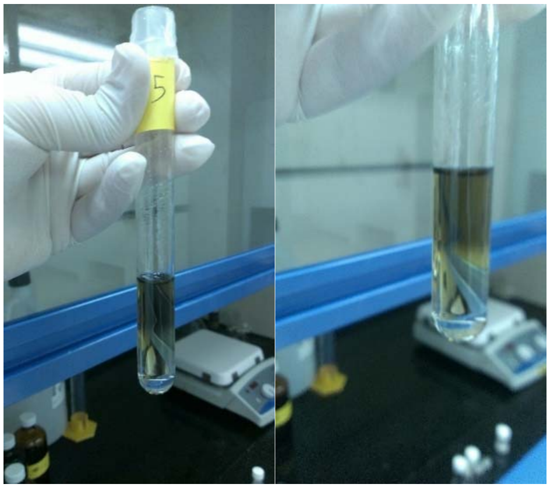




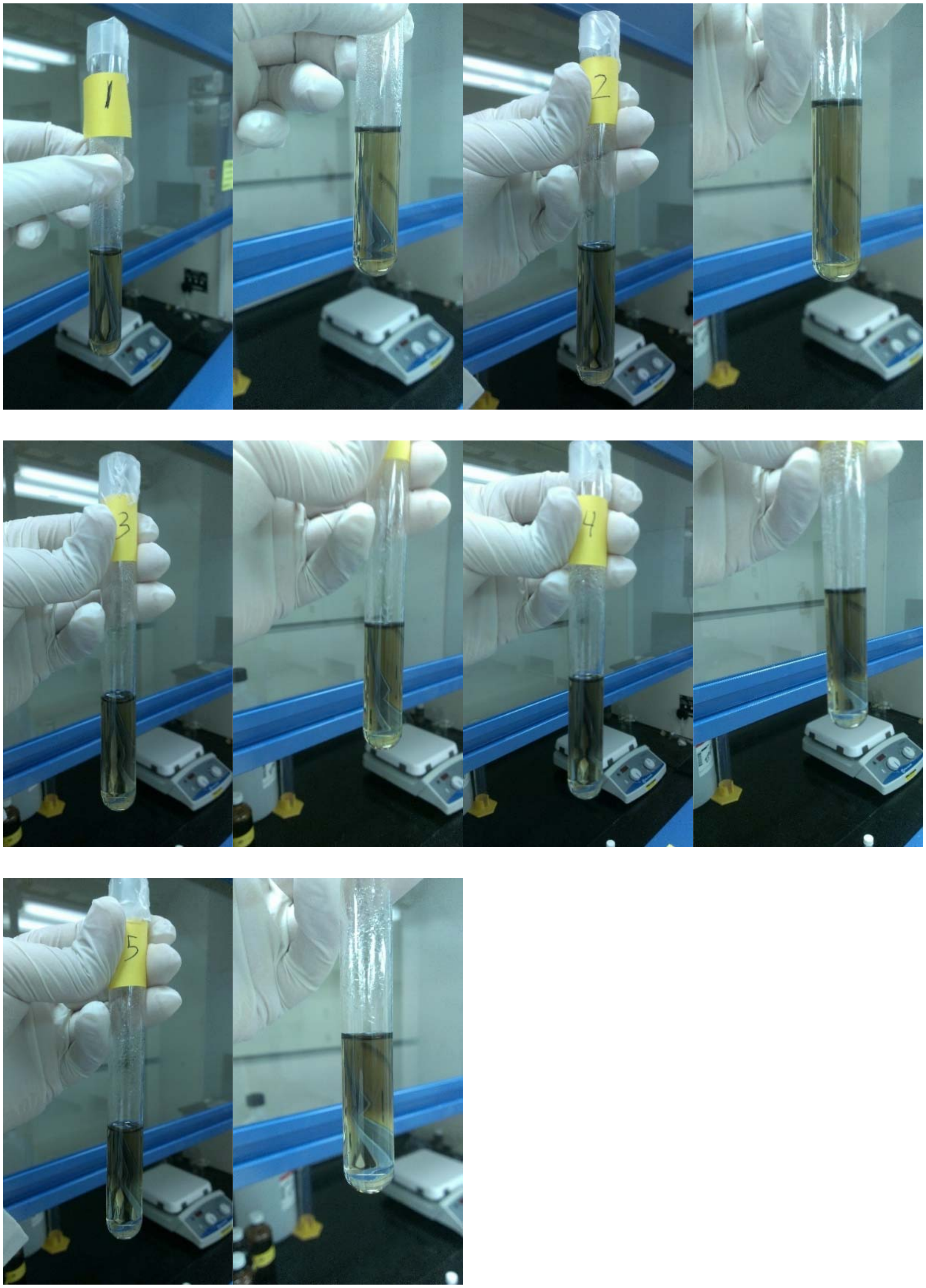
60 °C



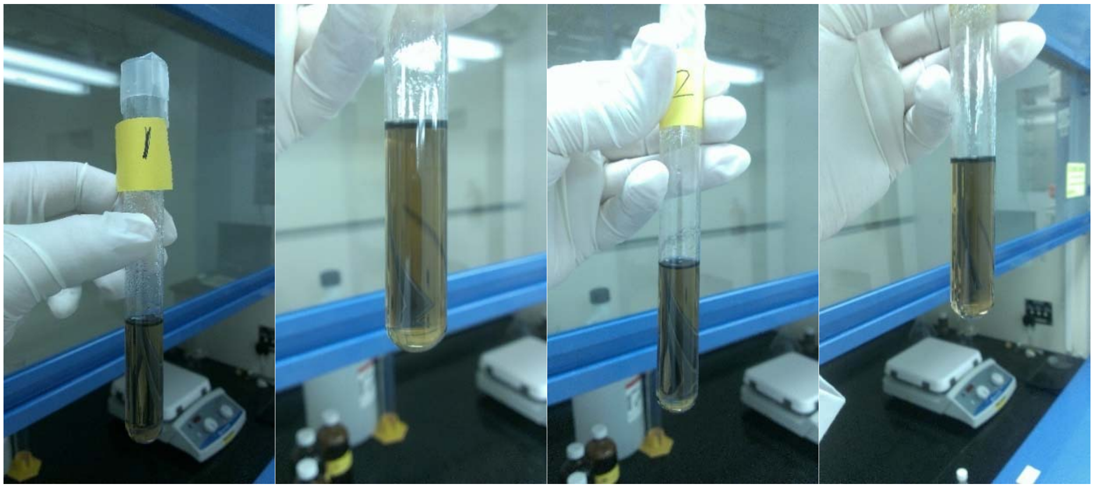


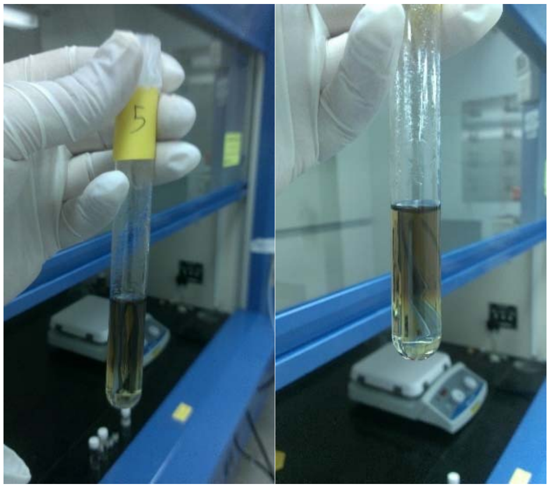


70 °C

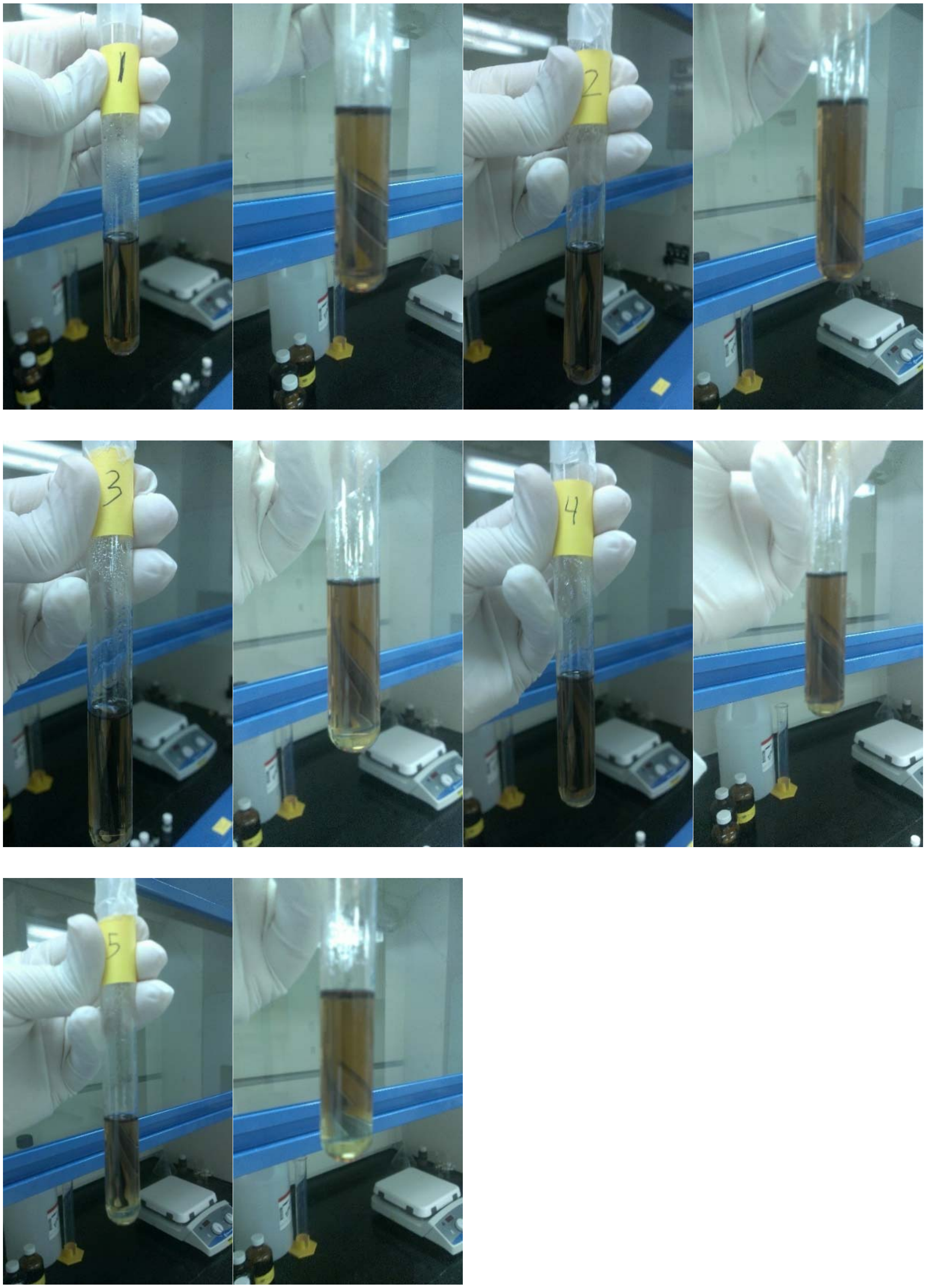


82 °C

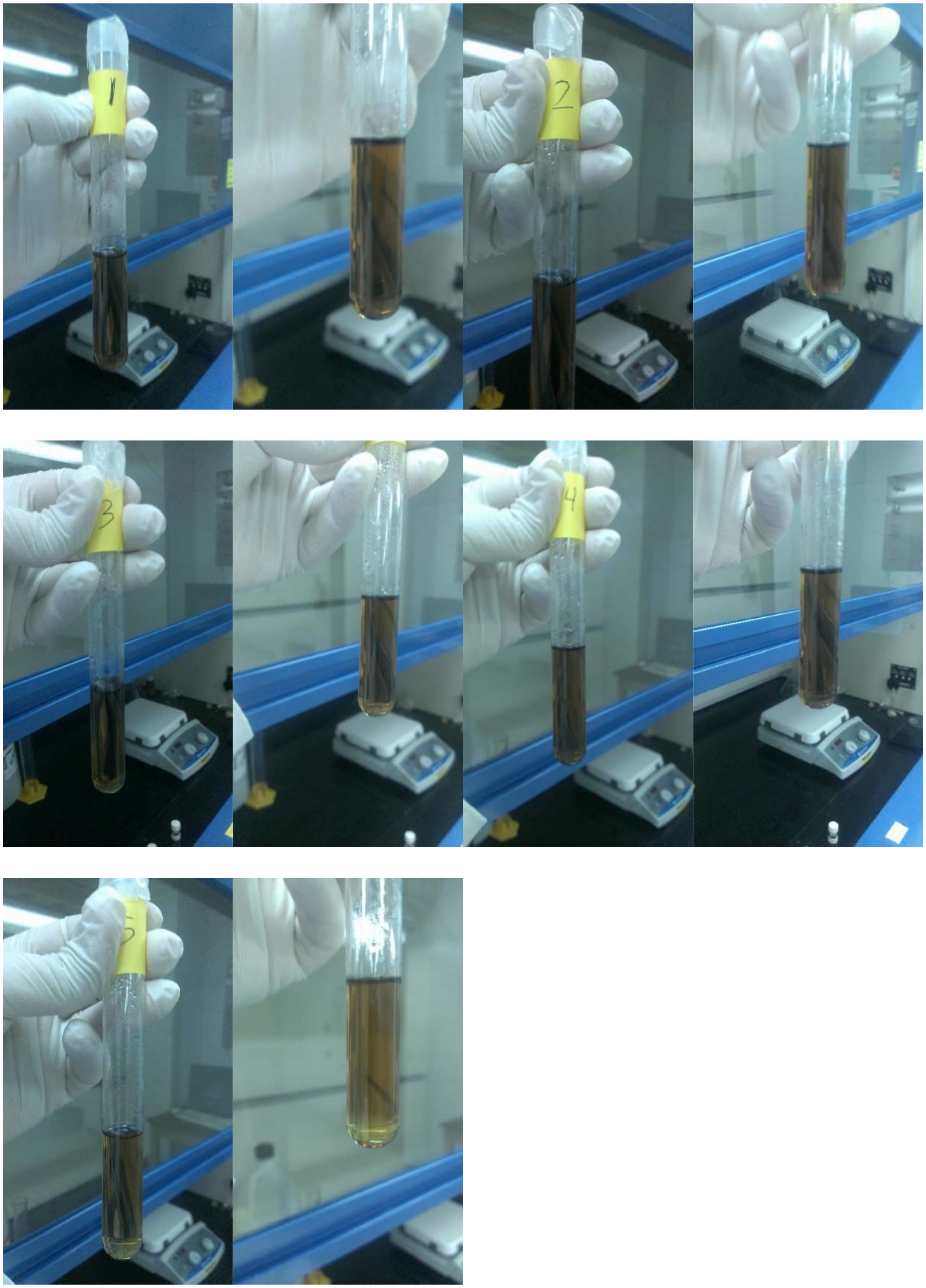




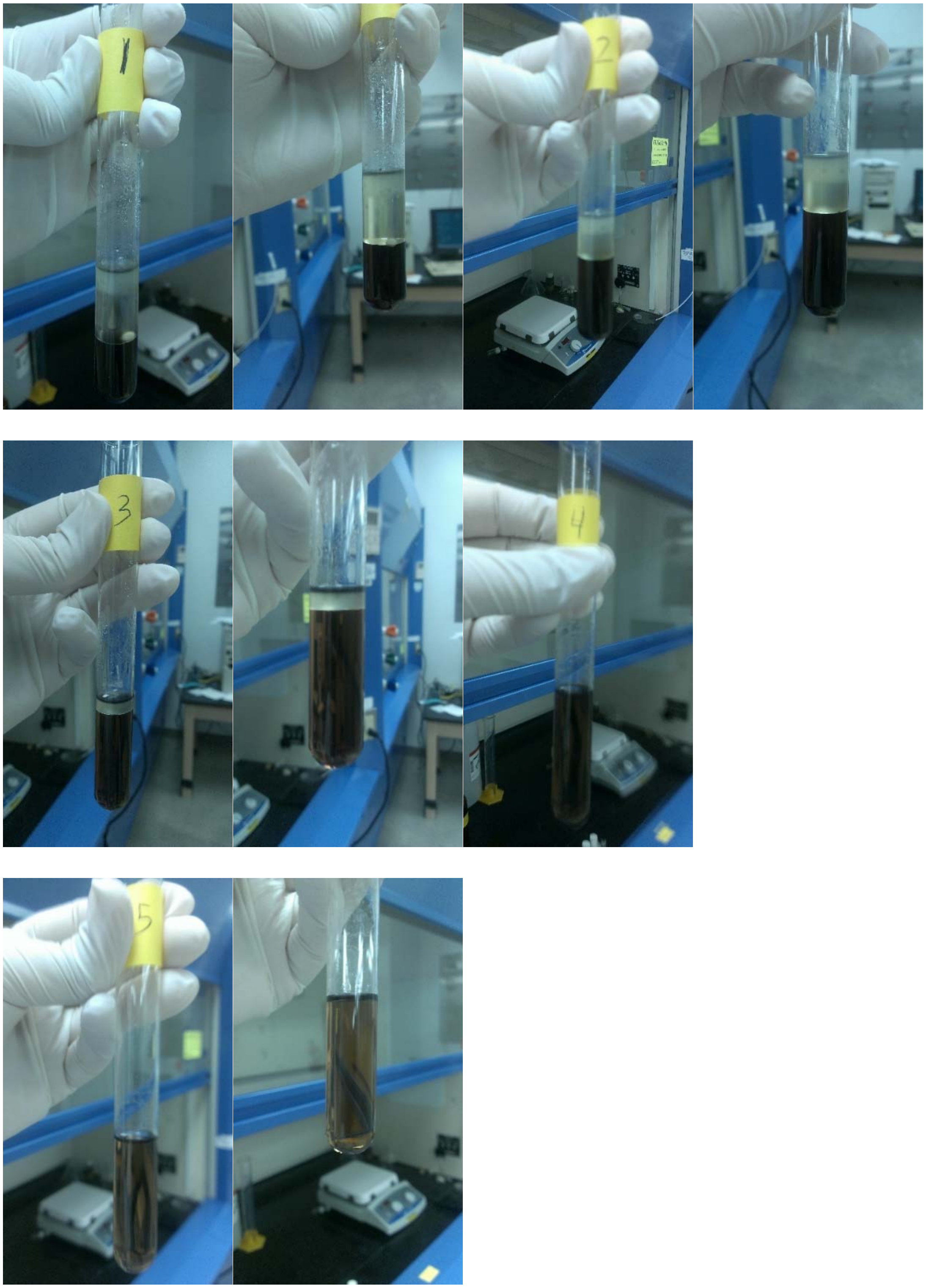
93 °C



104 °C



Ambient – Post Run



Experiment 5

2 nitrotoluene

Acid is 90% Sulfuric acid made by missing 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 4 mL water

Tube 1: 6 mL 90% H_2SO_4 w/ 2 mL 2 nitrotoluene.

Tube 2: 6 mL 90% H_2SO_4 w/ 3 mL 2 nitrotoluene.

Tube 3: 4 mL 90% H_2SO_4 w/ 4 mL 2 nitrotoluene.

Tube 4: 3 mL 90% H_2SO_4 w/ 6 mL 2 nitrotoluene.

Tube 5: 2 mL 90% H_2SO_4 w/ 6 mL 2 nitrotoluene.

-Same tube layout used as in experiment 1

Temperatures observed (set-points):

50 °C

60 °C

70 °C

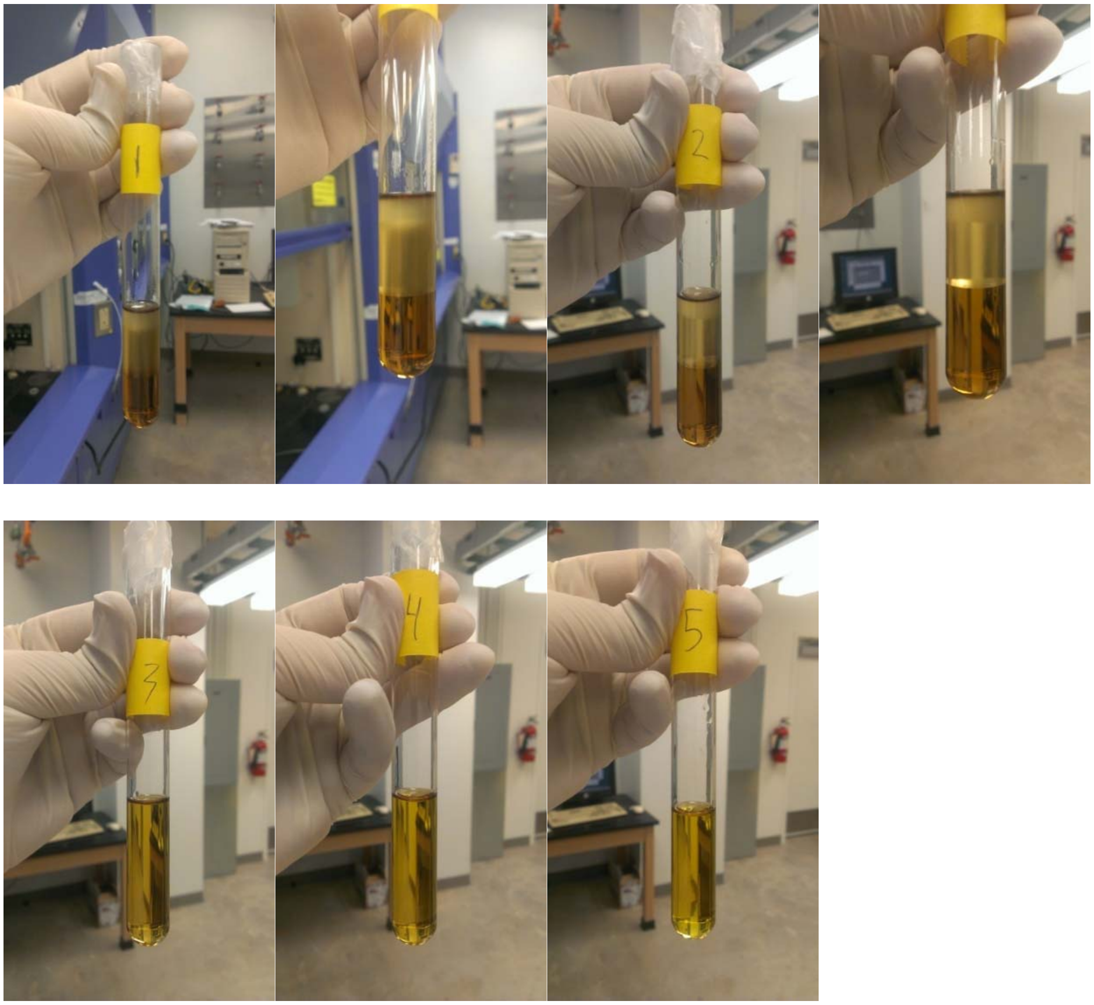
82 °C

93 °C

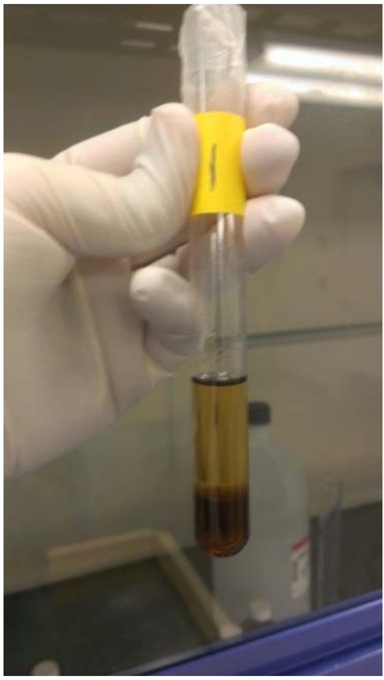
104 °C

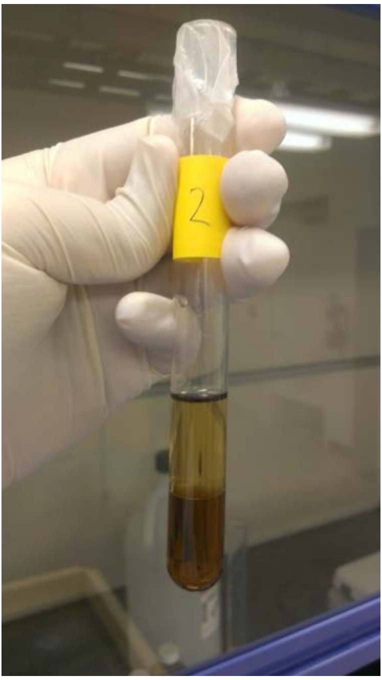
Tube	Initial Weight	Final Weight	Change
1	21.19 g	21.21 g	0.02 g
2	22.33 g	22.33 g	0.00 g
3	23.35 g	23.37 g	0.02 g
4	24.21 g	24.22 g	0.01 g
5	22.91 g	22.94 g	0.03 g

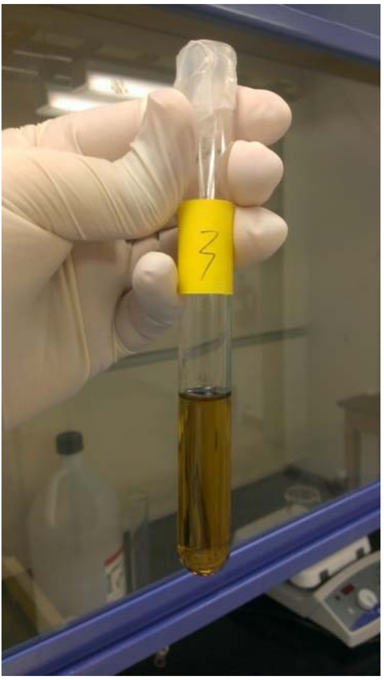
Ambient – Prerun

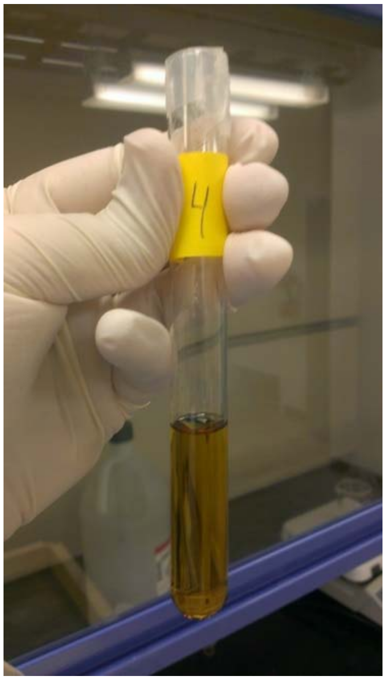


50 °C

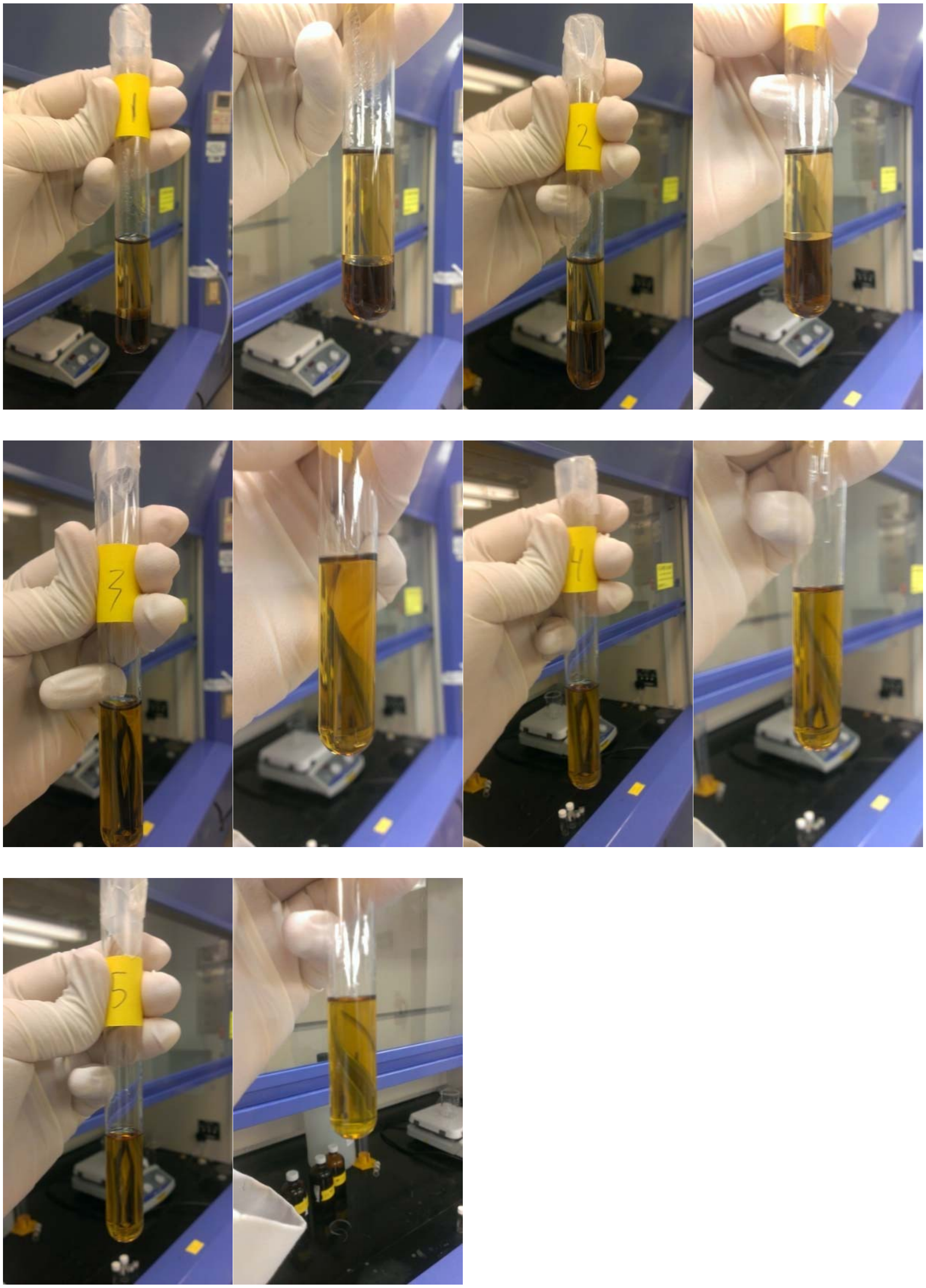




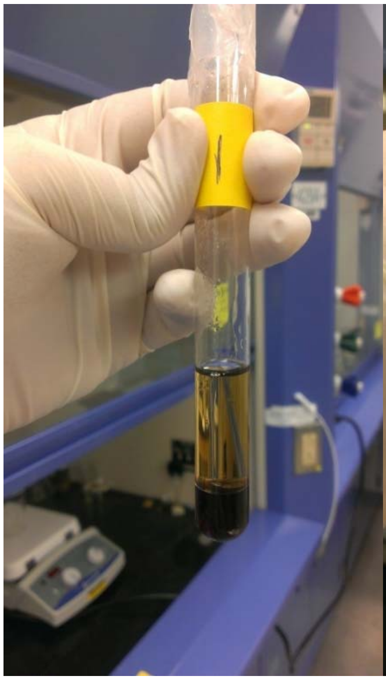


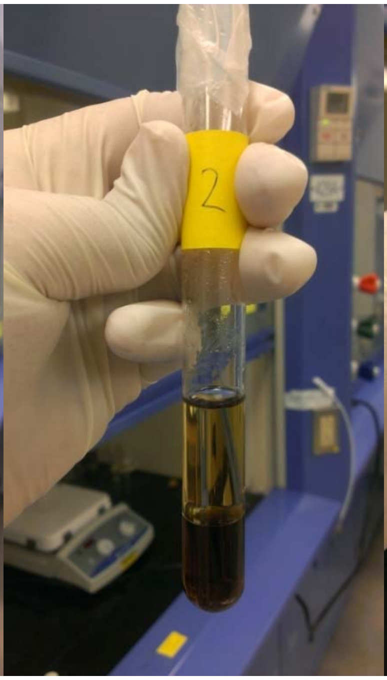


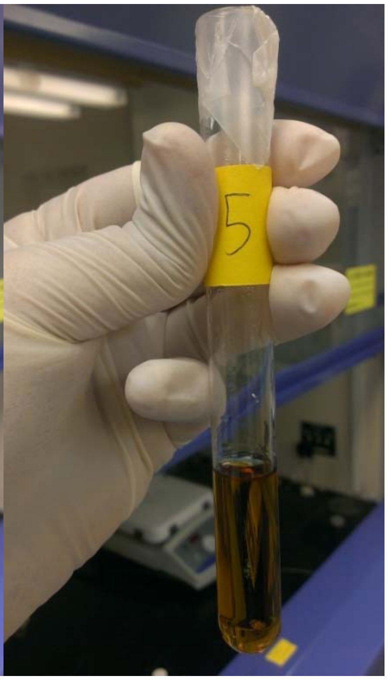
60 °C



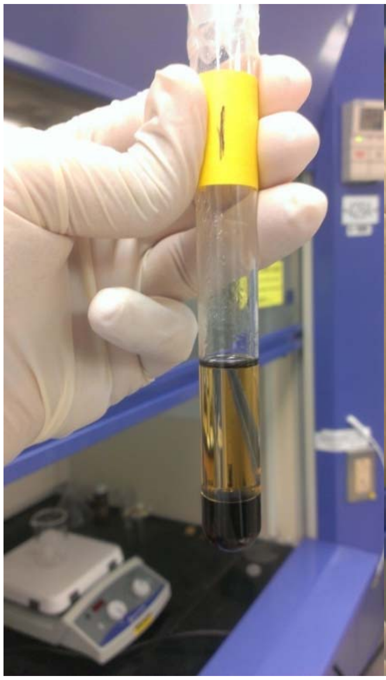
70 °C

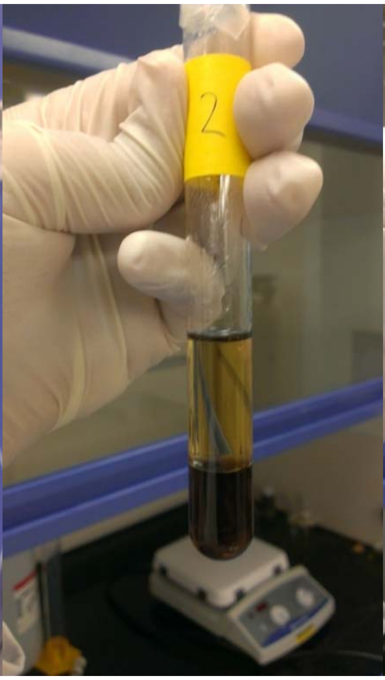


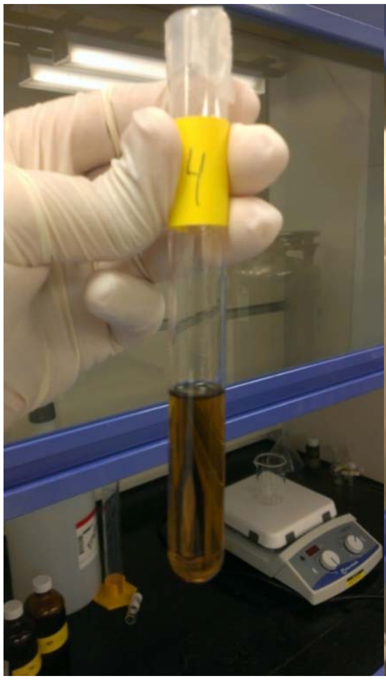




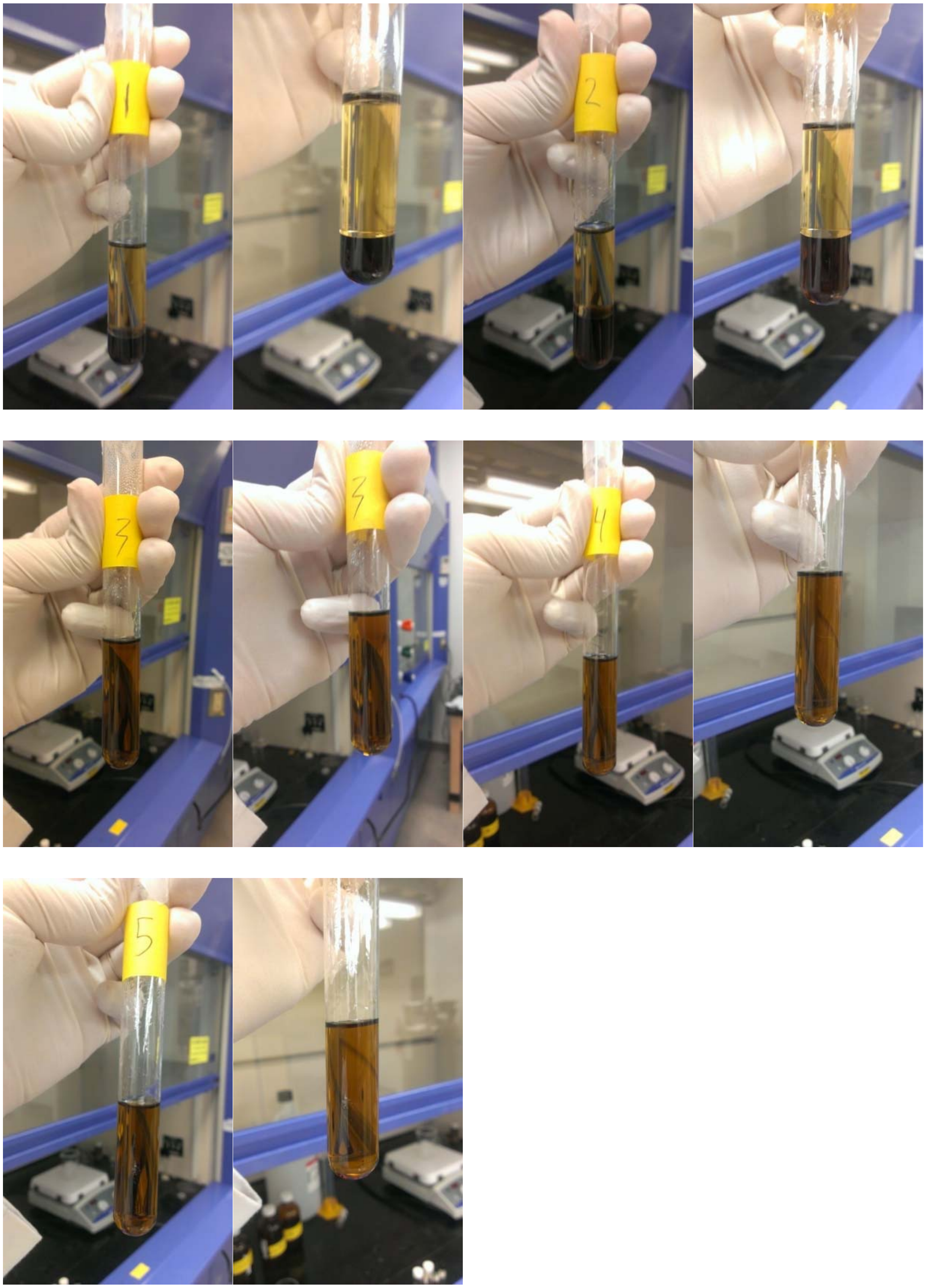
82 °C



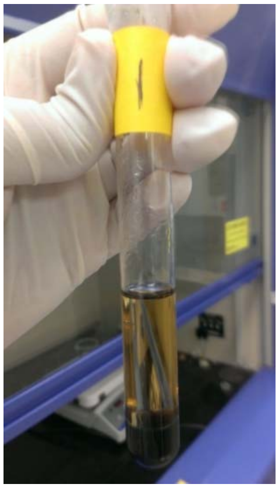


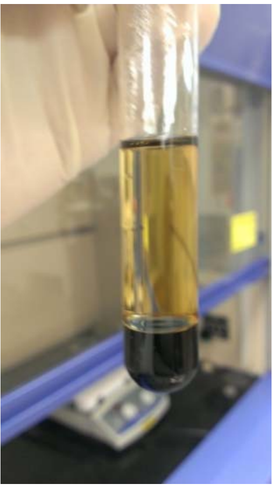


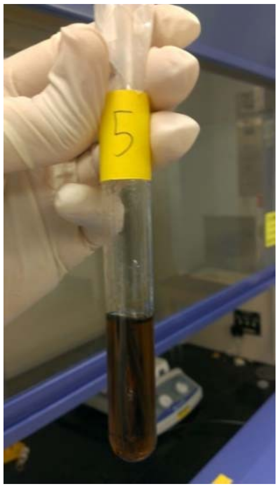
93 °C



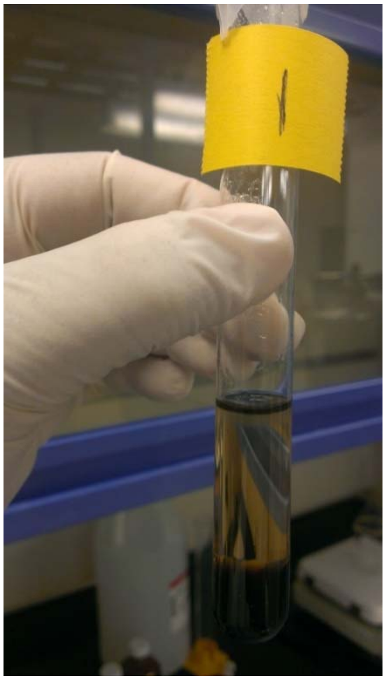
104 °C

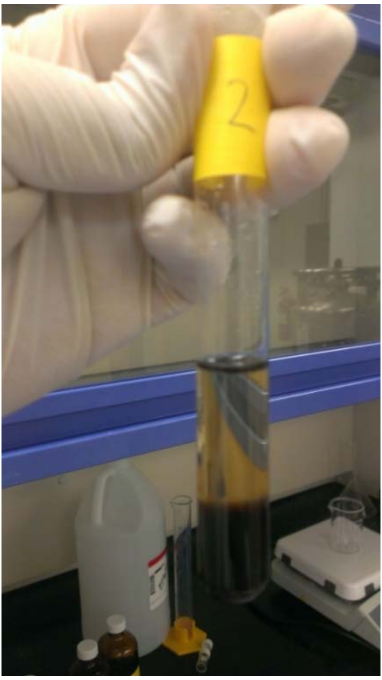


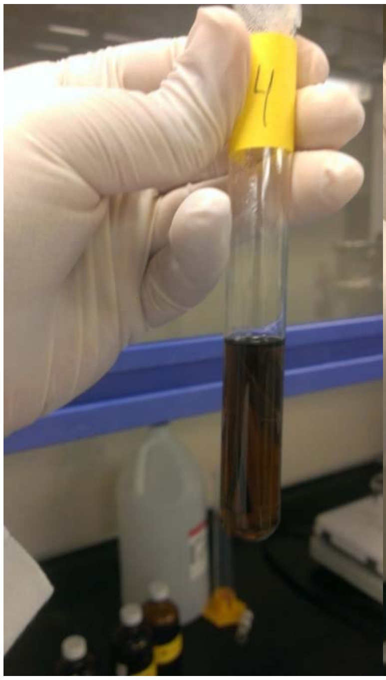


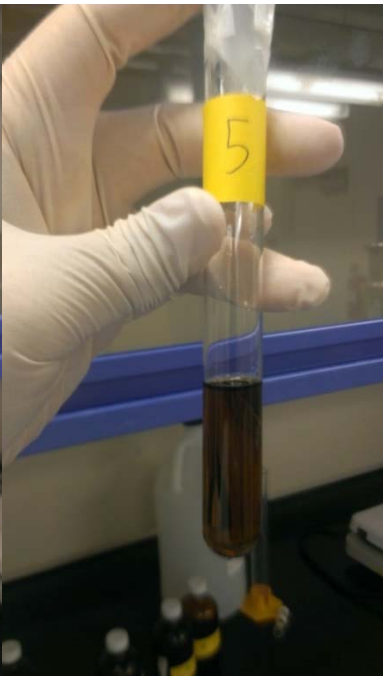


Ambient – Post Run









Experiment 6

2 nitrotoluene with 95% acid.

Acid is 95-98 wt% Sulfuric Acid (assumed 96 wt%)

Tube 5: 6 mL 95% H_2SO_4 w/ 2 mL 2 nitrotoluene.

Tube 4: 6 mL 95% H_2SO_4 w/ 3 mL 2 nitrotoluene.

Tube 3: 4 mL 95% H_2SO_4 w/ 4 mL 2 nitrotoluene.

Tube 2: 3 mL 95% H_2SO_4 w/ 6 mL 2 nitrotoluene.

Tube 1: 2 mL 95% H_2SO_4 w/ 6 mL 2 nitrotoluene.

Temperatures observed (set-points):

50 °C

60 °C

70 °C

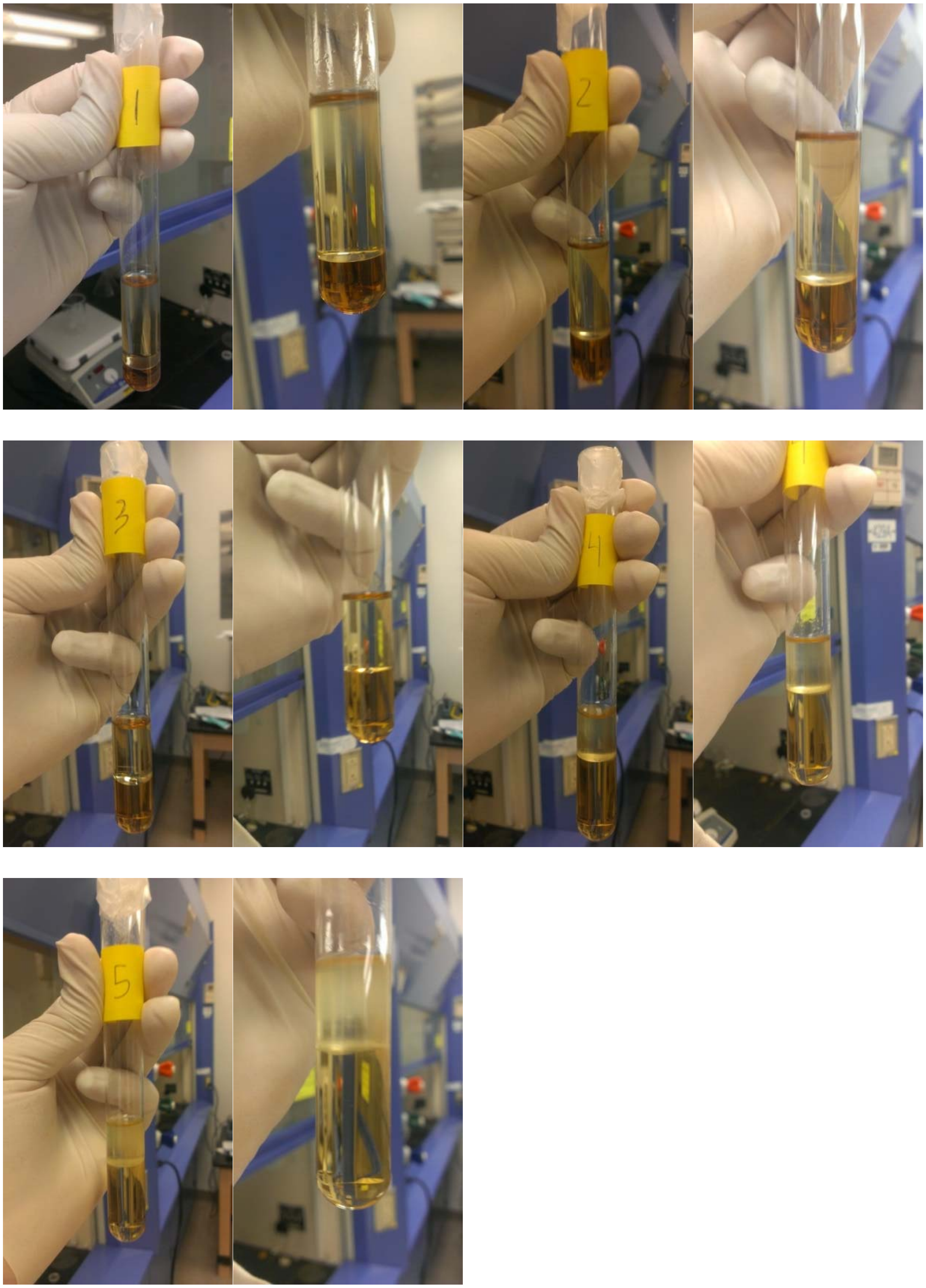
82 °C

93 °C

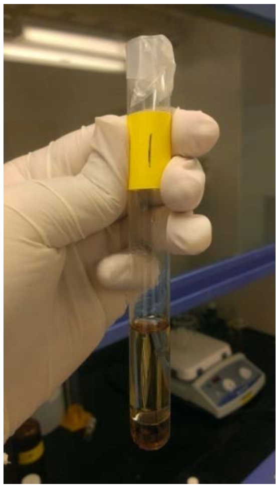
104 °C

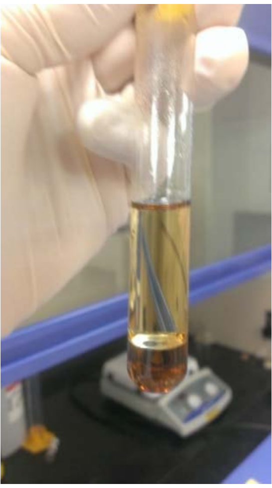
Tube	Initial Weight	Final Weight	Change
1	20.75 g	20.75 g	0.00 g
2	22.57 g	22.57 g	0.00 g
3	21.46 g	21.47 g	0.01 g
4	23.20 g	23.22 g	0.02 g
5	23.37 g	23.38 g	0.01 g

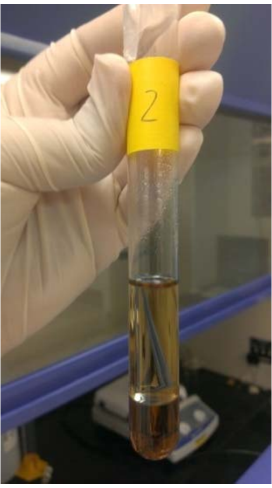
Ambient – Prerun

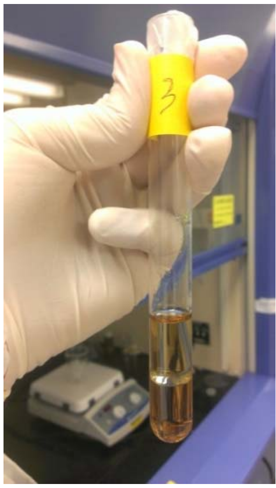


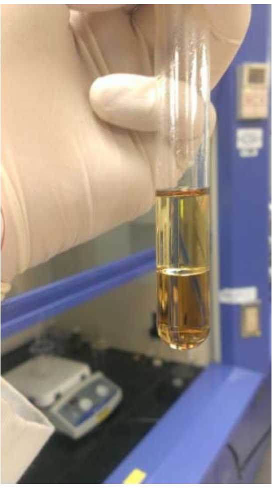
50 °C

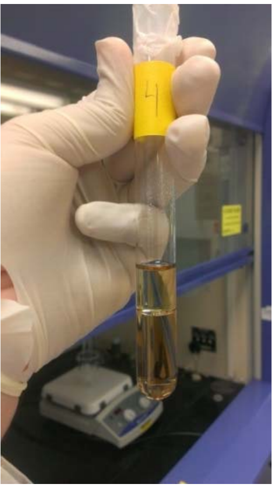


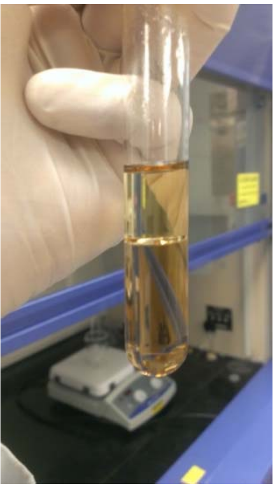


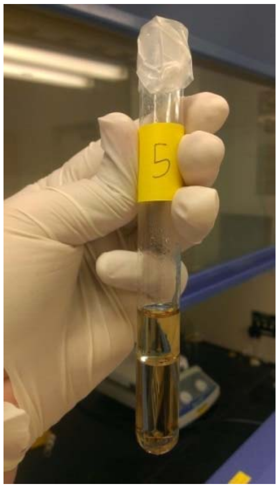


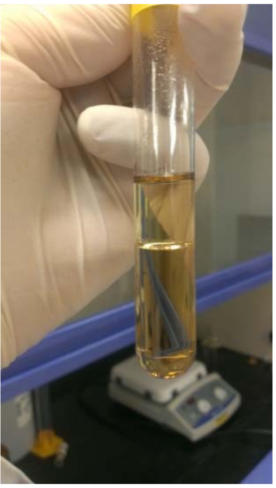




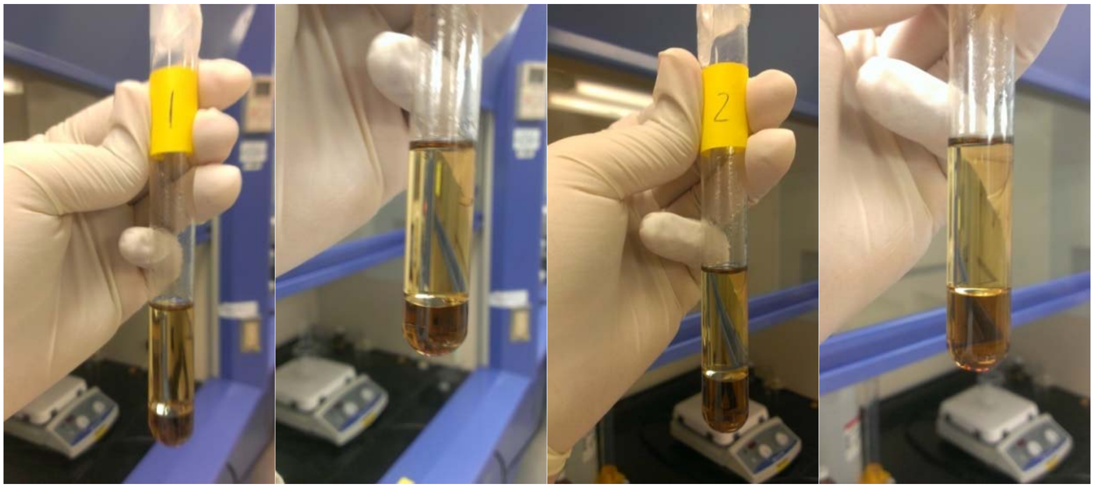


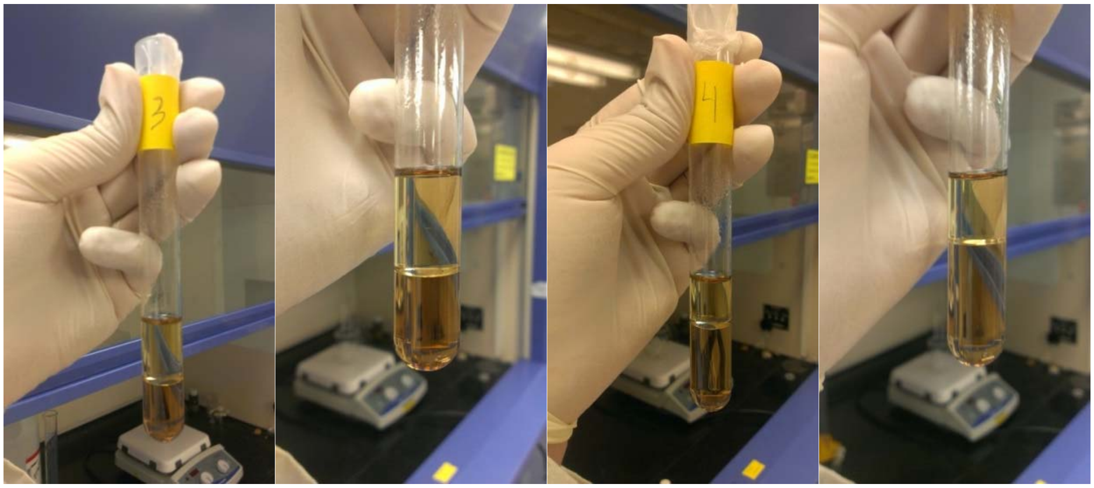


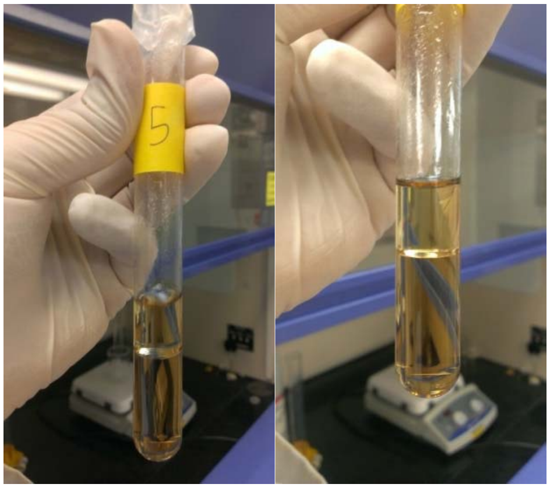




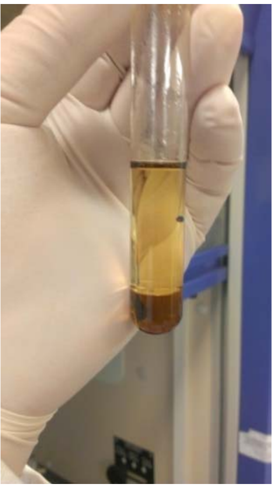
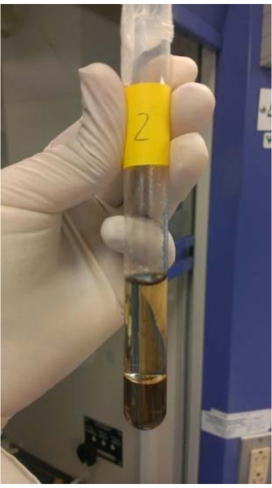
60 °C

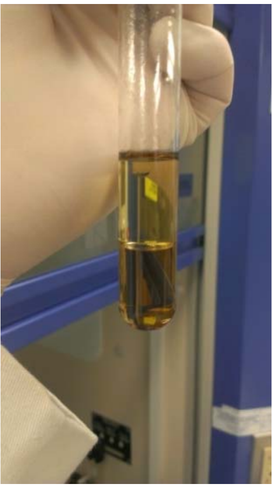


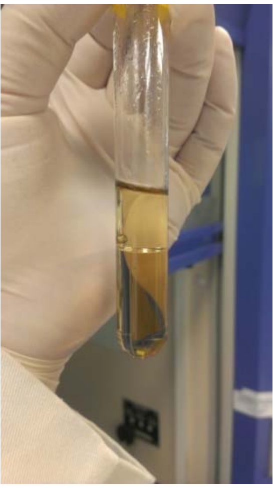
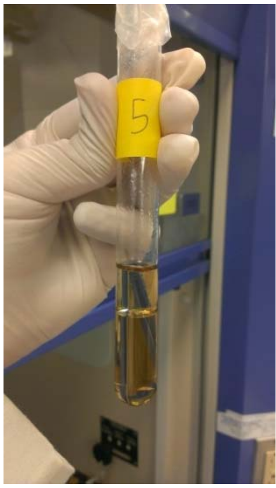


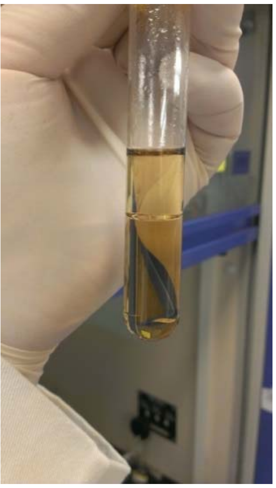


70 °C

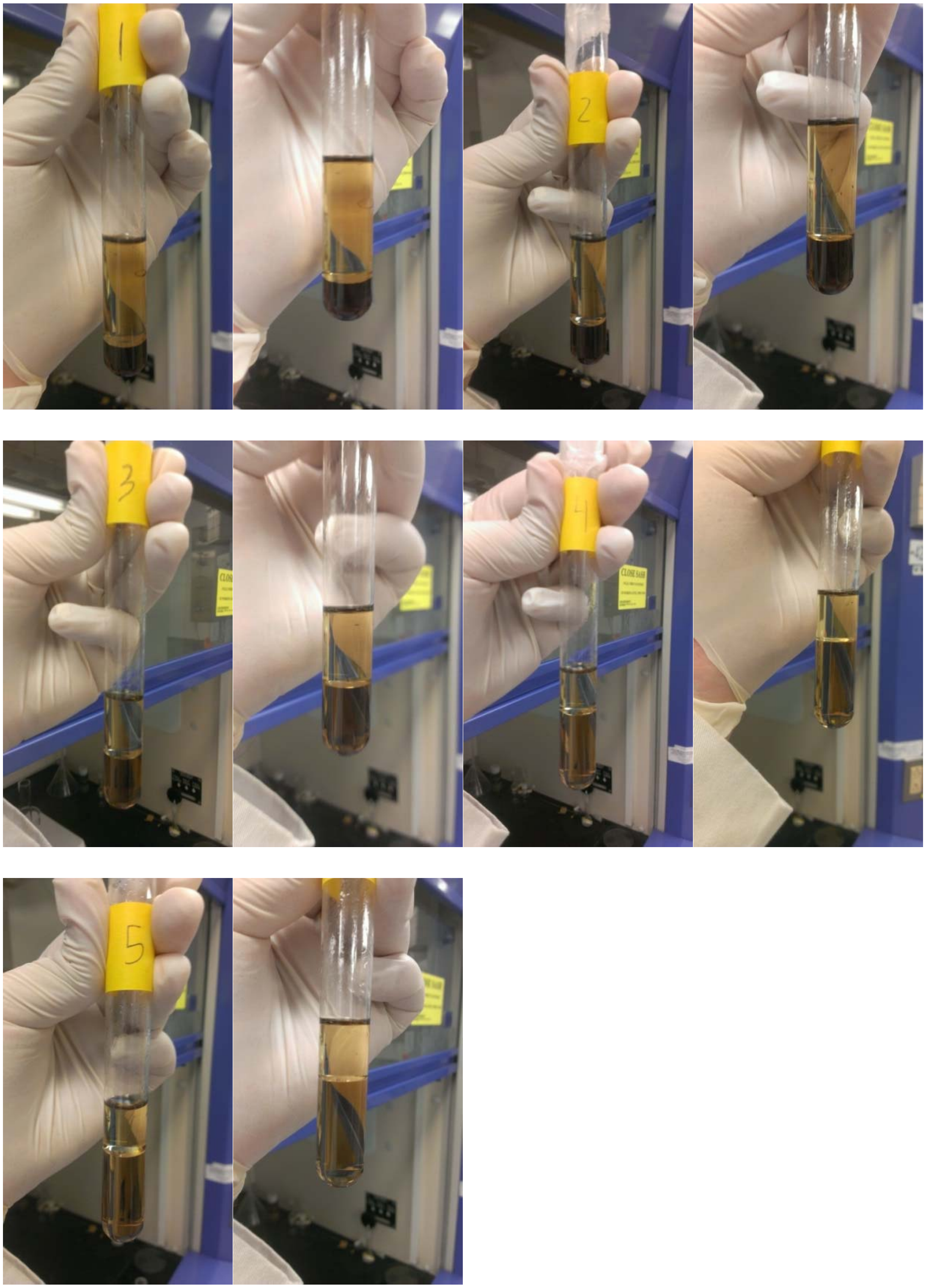



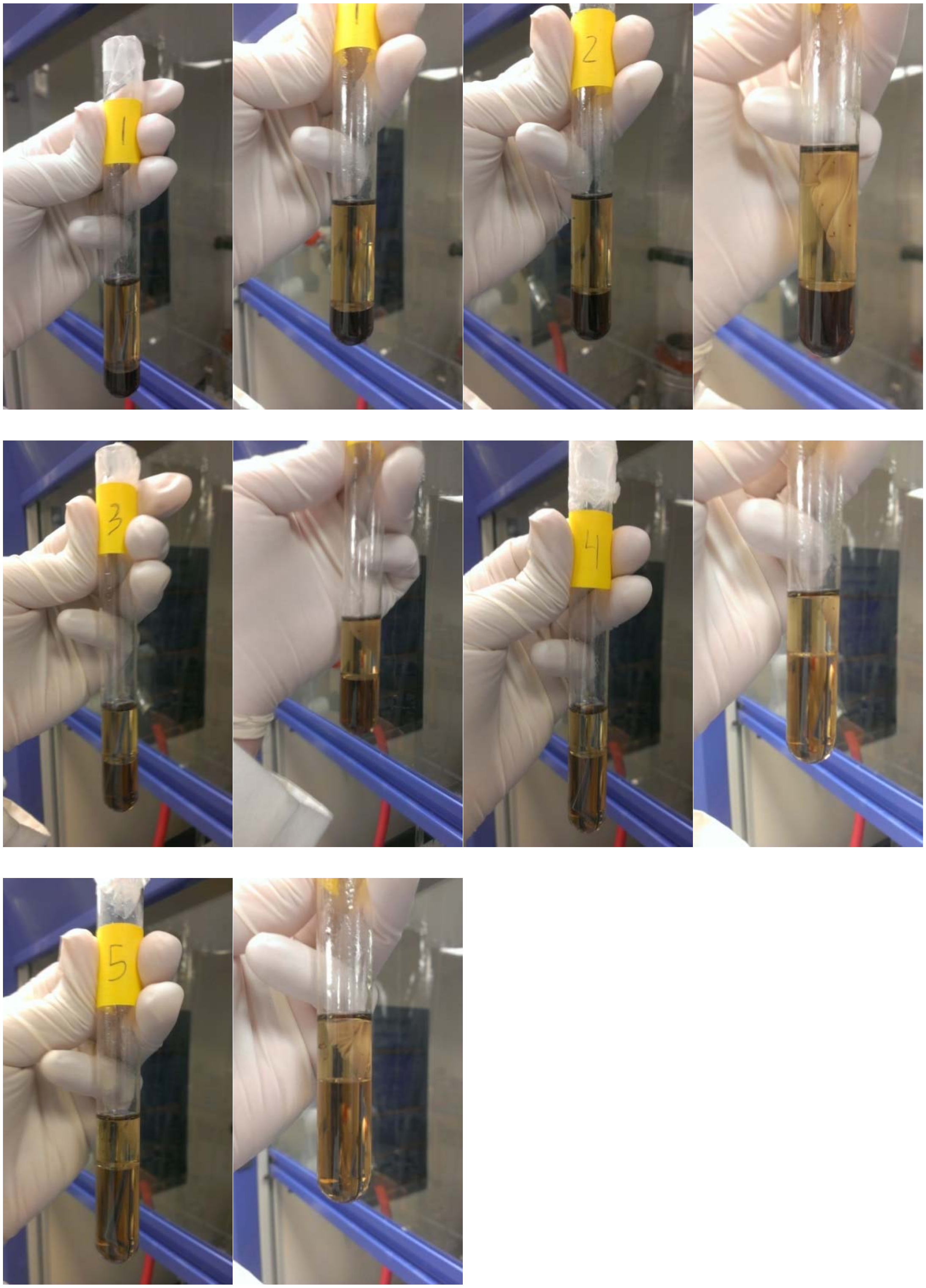






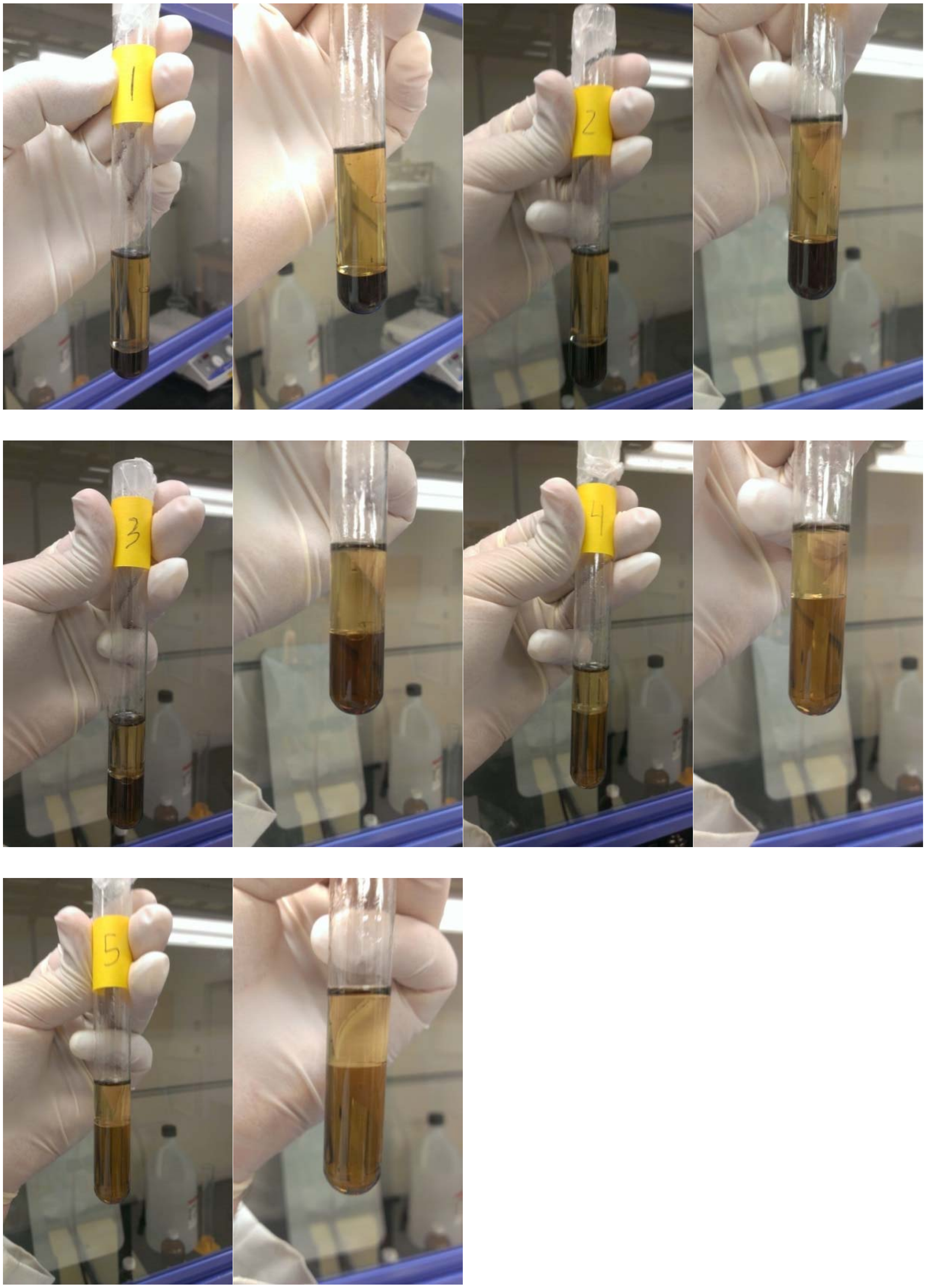
82 °C



93 °C

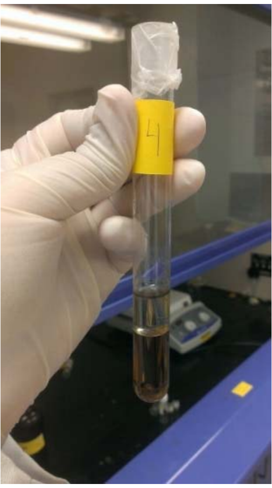


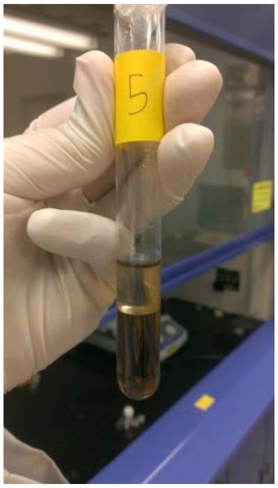
104 °C



Ambient – Post Run



Experiment 7

2-Nitrotoluene with 90% Sulfuric Acid.

Acid is 90% Sulfuric acid made by missing 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 4 mL water

Tube 1: 6 mL 90% H_2SO_4 w/ 2 mL 2-Nitrotoluene.

Tube 2: 6 mL 90% H_2SO_4 w/ 3 mL 2-Nitrotoluene.

Tube 3: 4 mL 90% H_2SO_4 w/ 4 mL 2-Nitrotoluene.

Tube 4: 3 mL 90% H_2SO_4 w/ 6 mL 2-Nitrotoluene.

Tube 5: 2 mL 90% H_2SO_4 w/ 6 mL 2-Nitrotoluene.

The most organic rich tube exhibited some apparent 3 phase behavior but none of the others did.

Temperatures observed (set-points):

50 °C

60 °C

70 °C

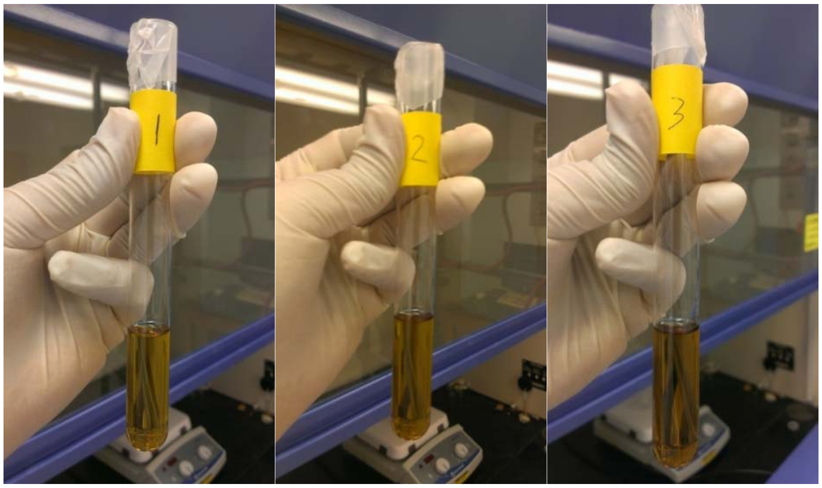
82 °C

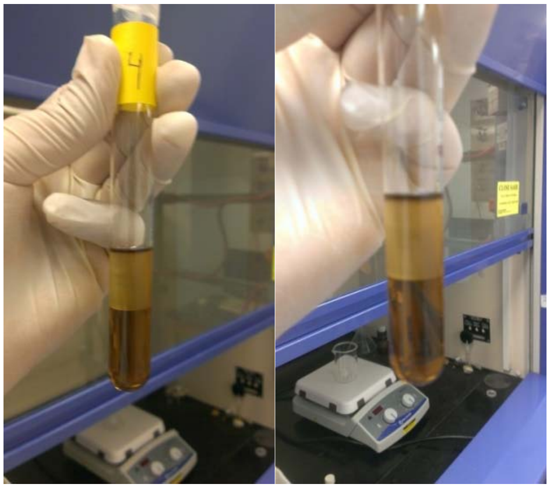
93 °C

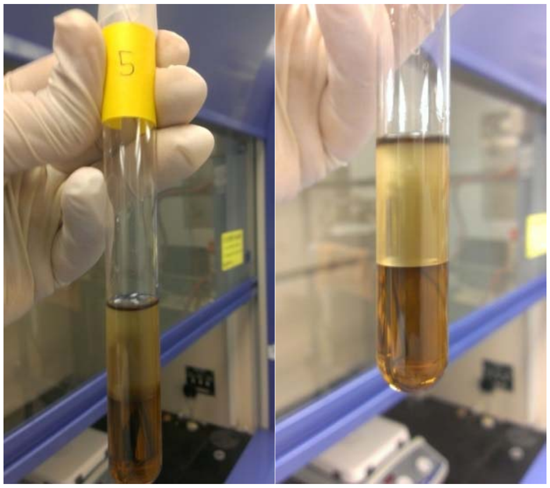
104 °C

Tube	Initial Weight	Final Weight	Change
1	22.53 g	22.54 g	0.01 g
2	23.46 g	23.46 g	0.00 g
3	22.33 g	22.33 g	0.00 g
4	22.39 g	22.39 g	0.00 g
5	22.39 g	22.41 g	0.02 g

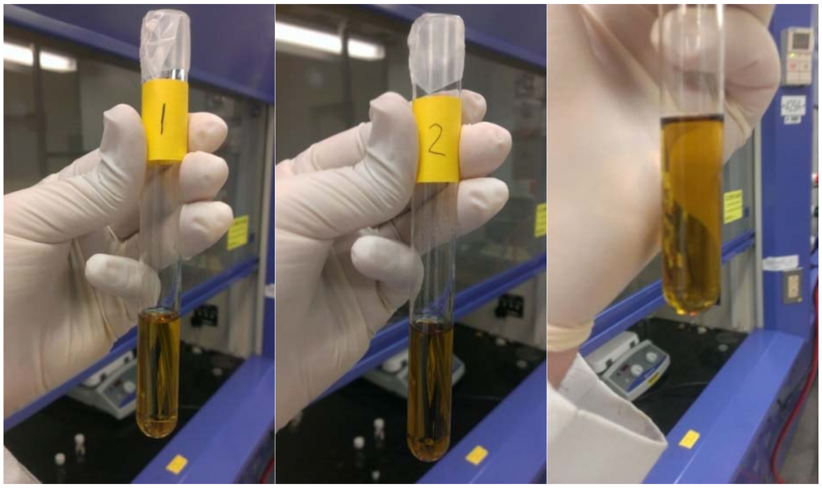
Ambient – Prerun

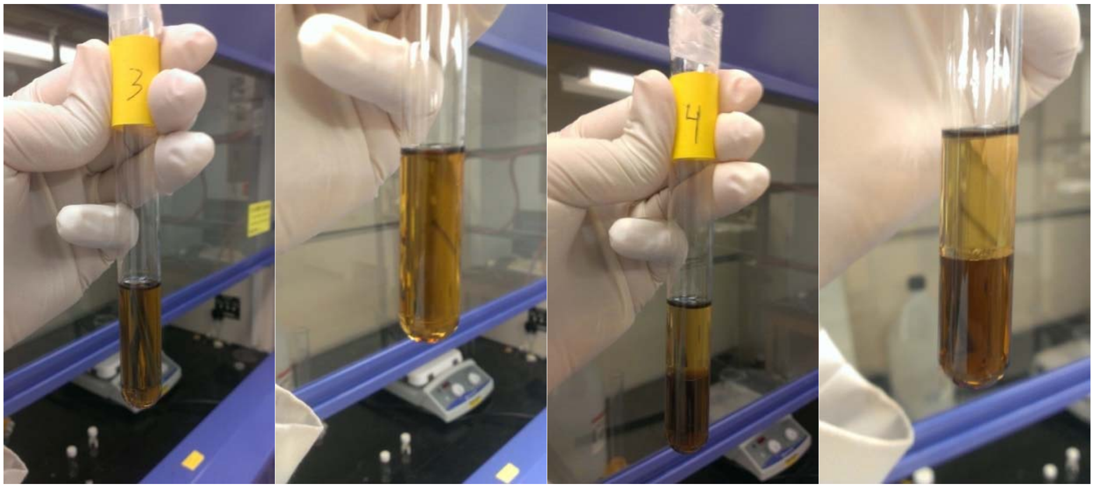


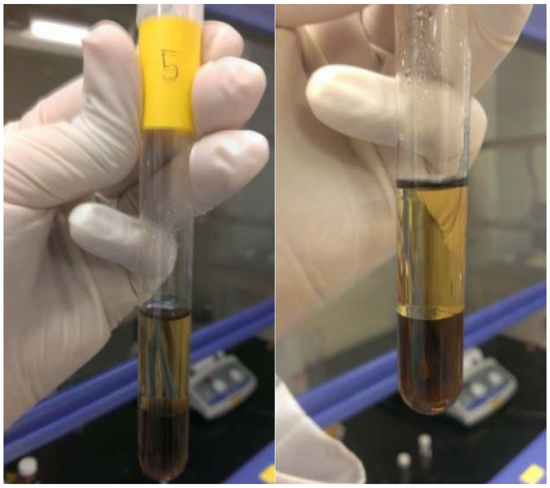




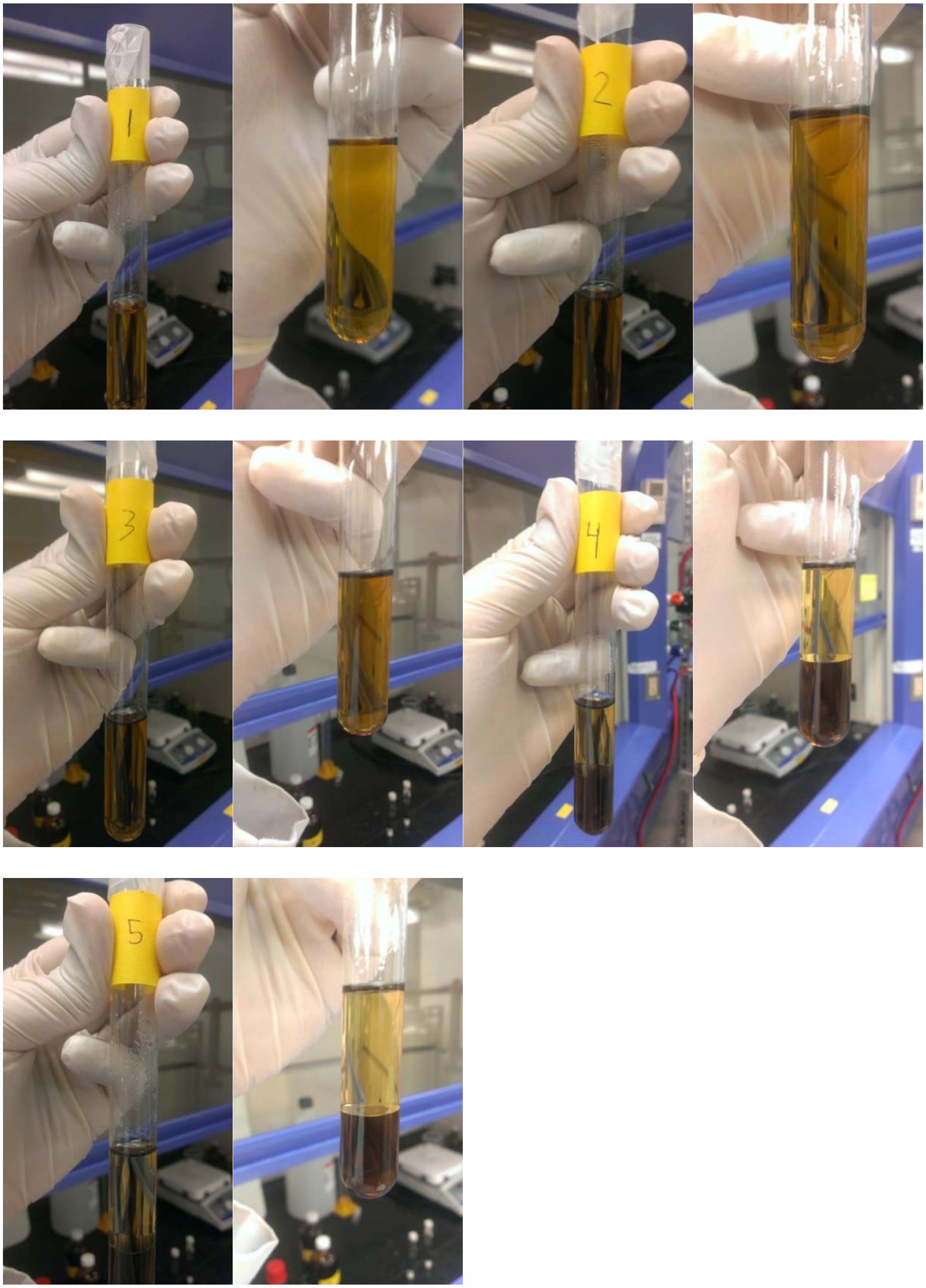
50 °C



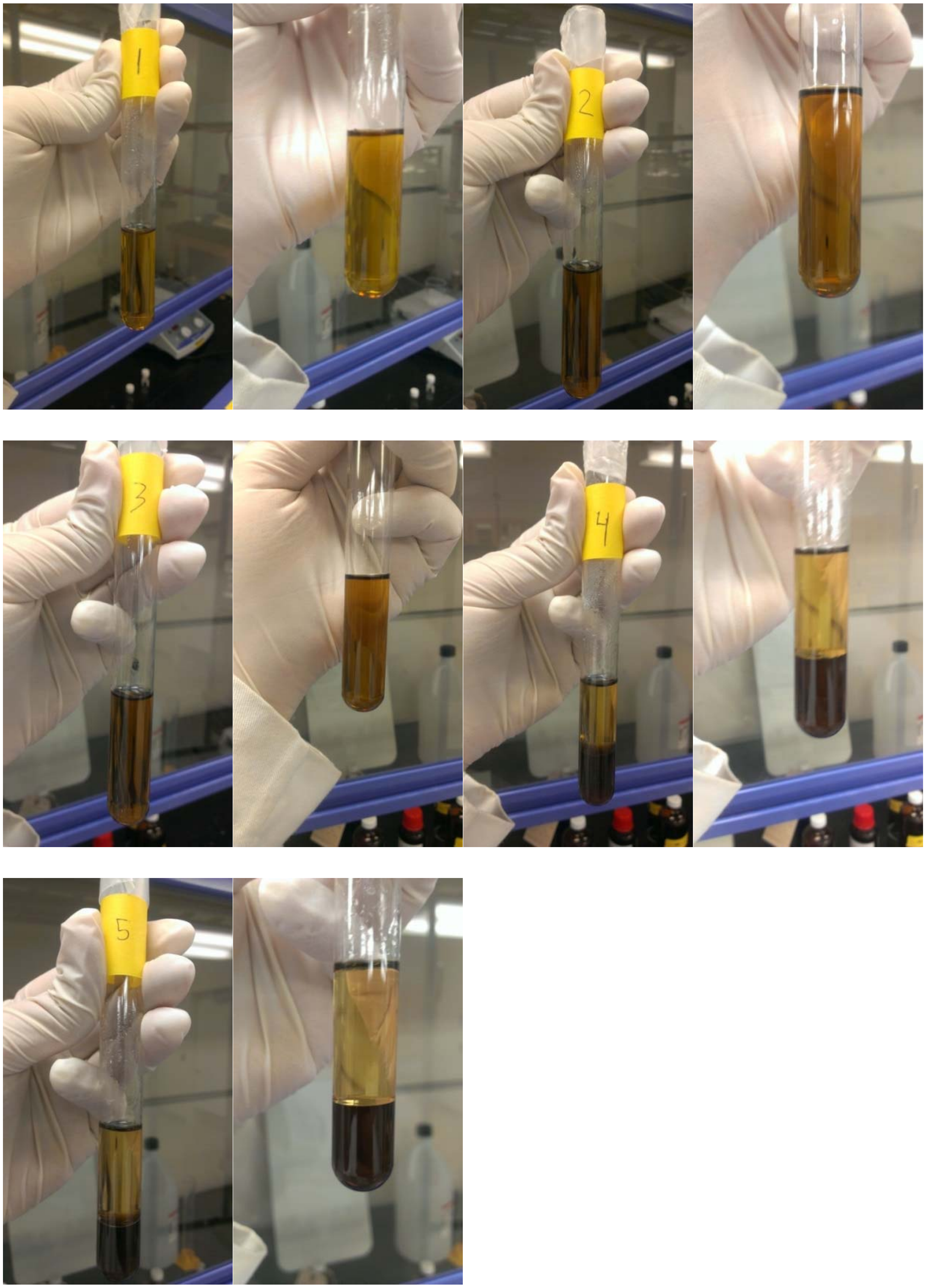




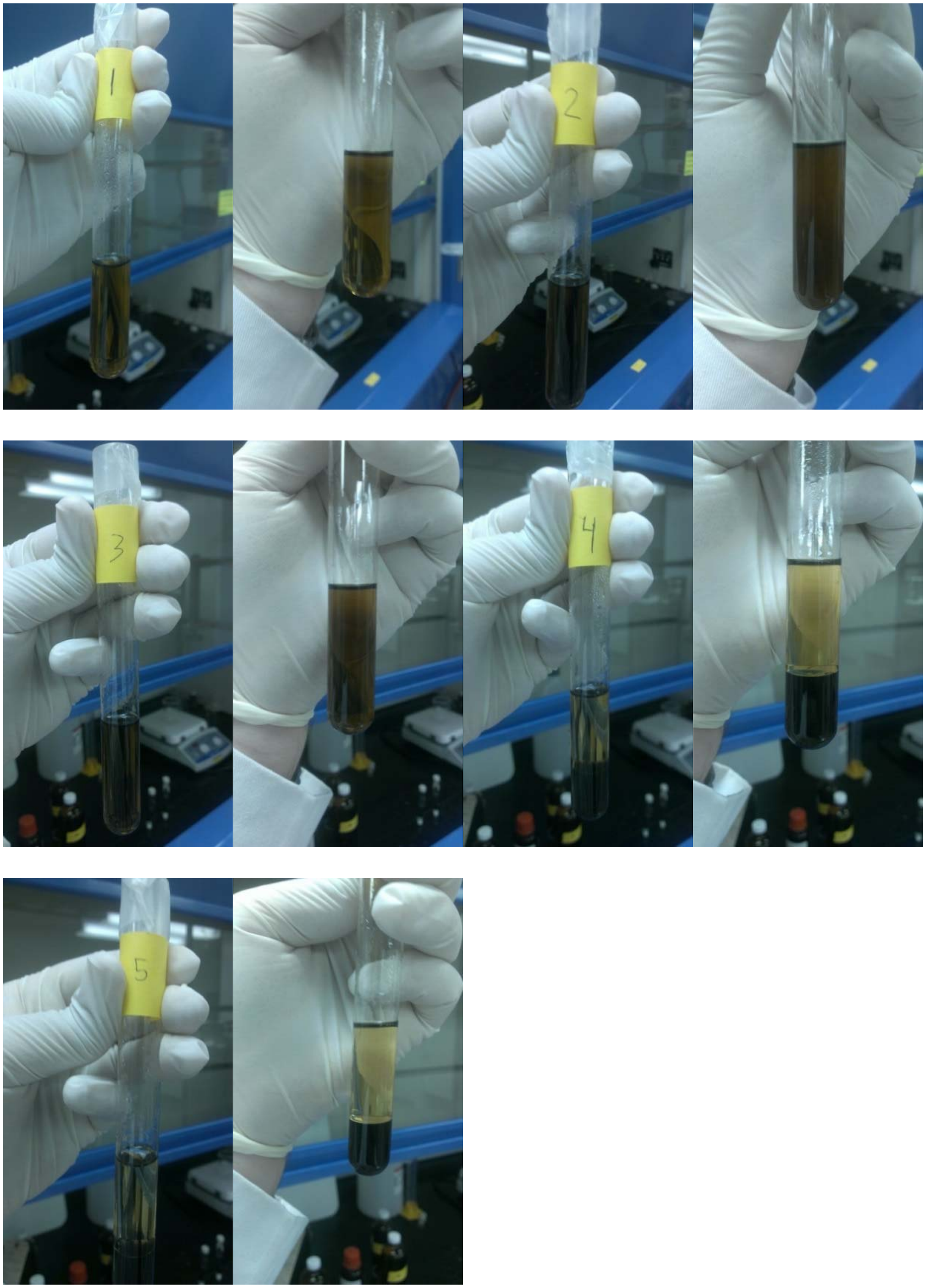
60 °C



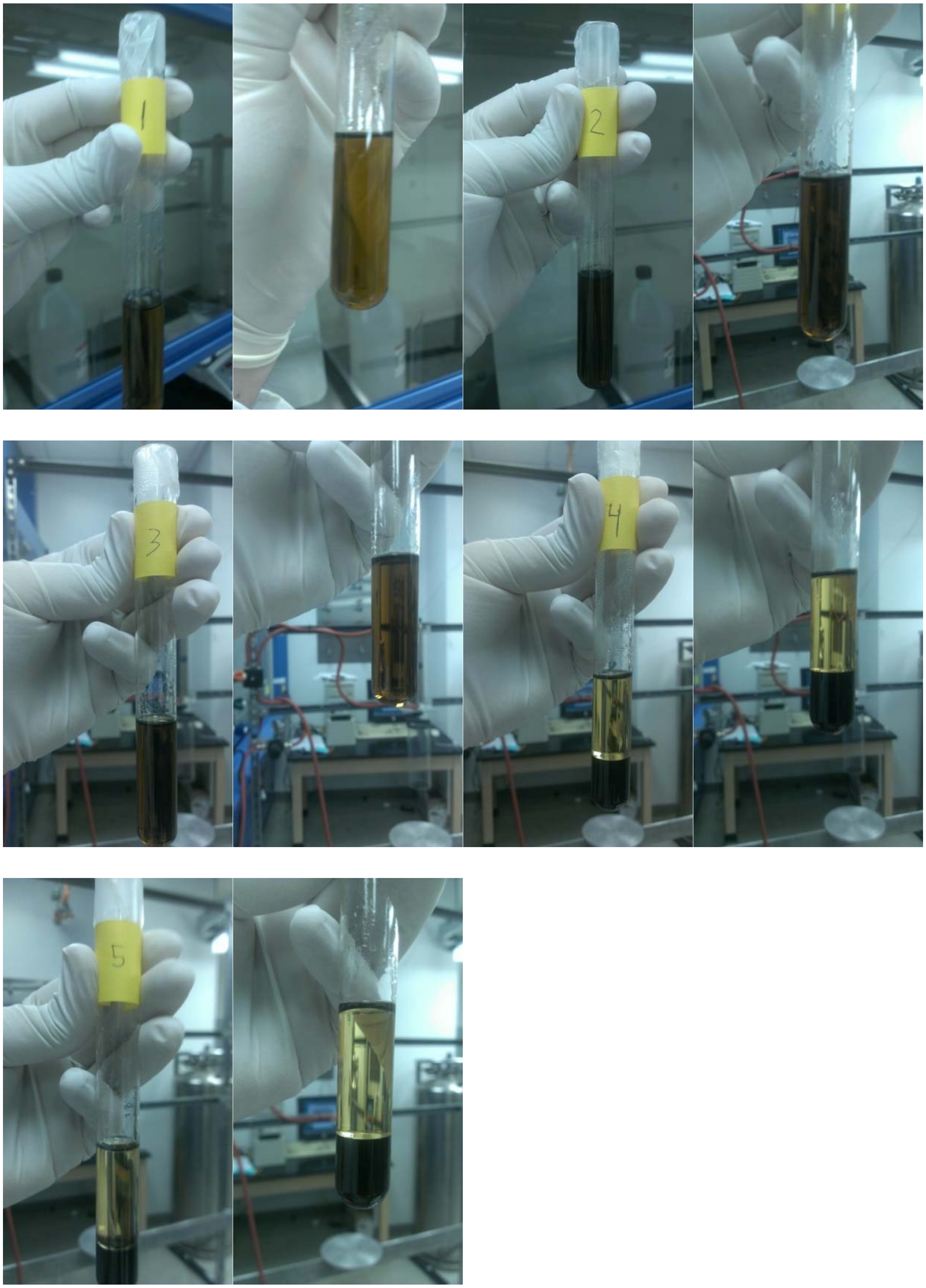
70 °C



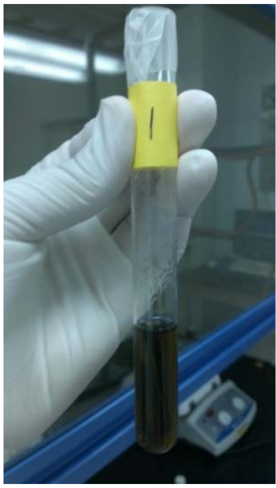
82 °C

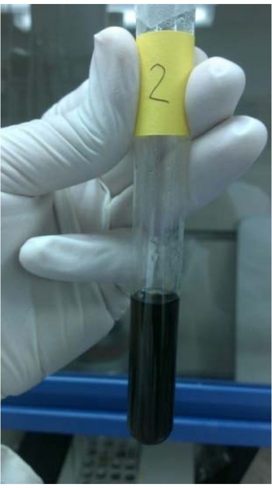


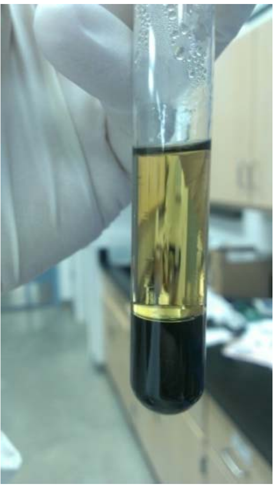
93 °C

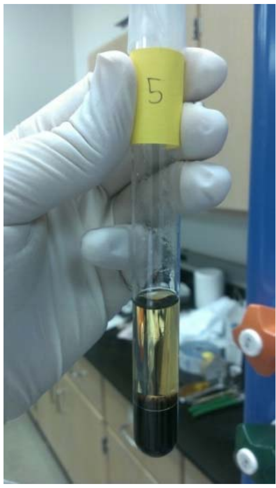


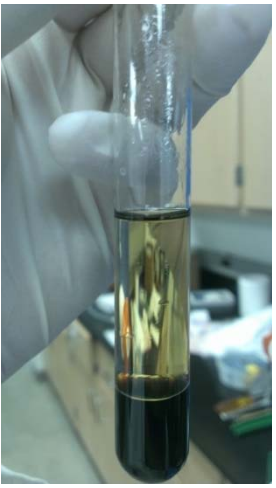
104 °C



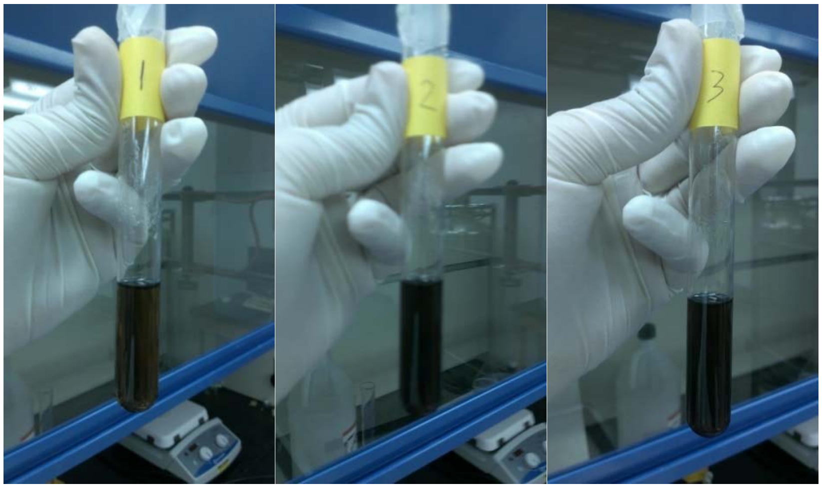


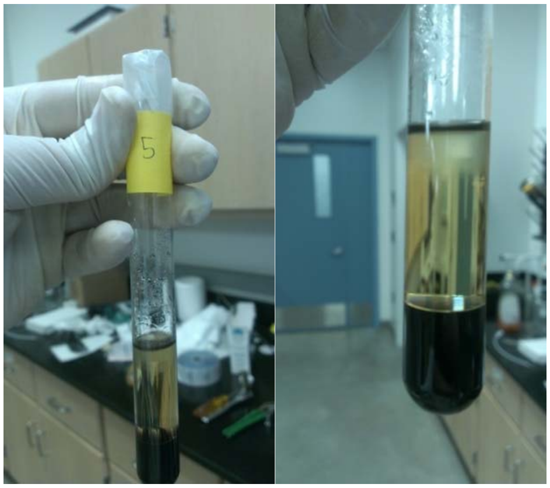






Ambient – Post Run





Experiment 8

3-Nitrotoluene with 95% Sulfuric Acid.

Acid is 95-98 wt% Sulfuric Acid (assumed 96 wt%)

Tube 1: 6 mL 95% H_2SO_4 w/ 2 mL 3-Nitrotoluene.

Tube 2: 6 mL 95% H_2SO_4 w/ 3 mL 3-Nitrotoluene.

Tube 3: 4 mL 95% H_2SO_4 w/ 4 mL 3-Nitrotoluene.

Tube 4: 3 mL 95% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

Tube 5: 2 mL 95% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

Temperatures observed (set-points):

50 °C

60 °C

70 °C

82 °C

93 °C

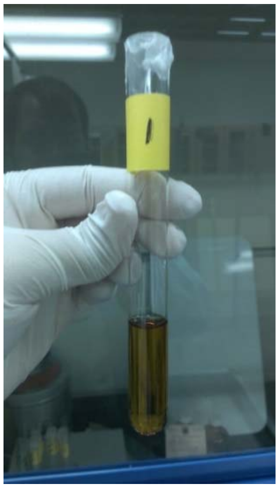
104 °C

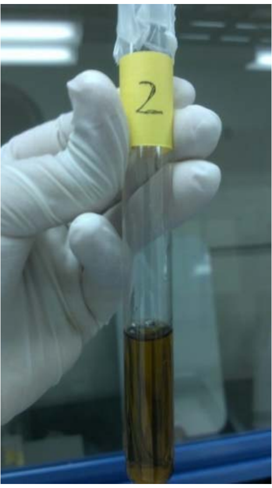
Ambient

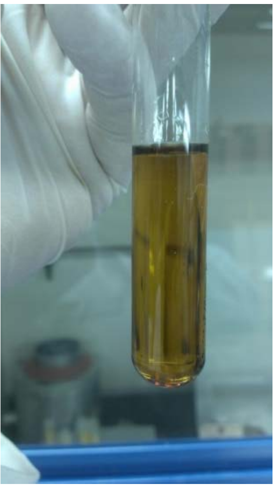
Tube	Initial Weight	Final Weight	Change
1	22.83 g	22.85 g	0.02 g
2	23.52 g	23.56 g	0.04 g
3	21.75 g	21.85 g	0.10 g
4	22.28 g	22.29 g	0.01 g
5	21.02 g	21.05 g	0.03 g

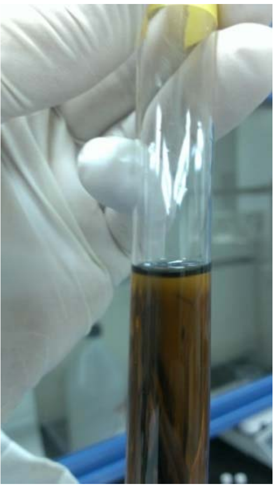
Three phases observed in tubes 4 and 5

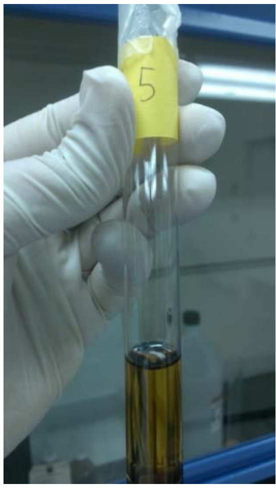
Ambient – Prerun



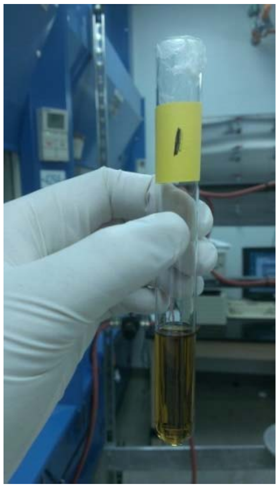


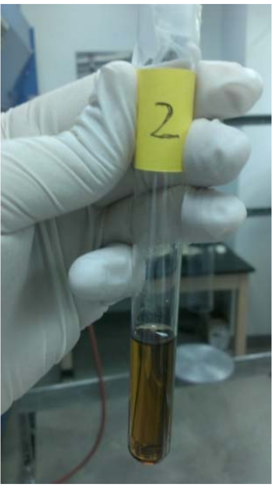


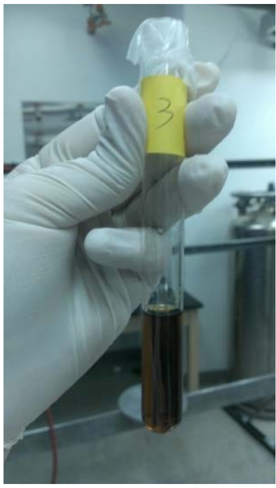


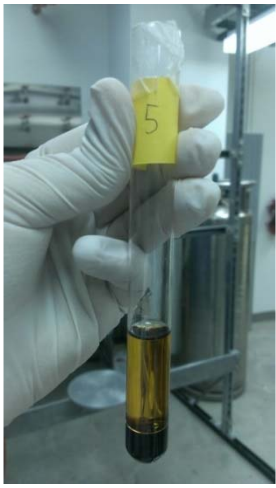


50 °C

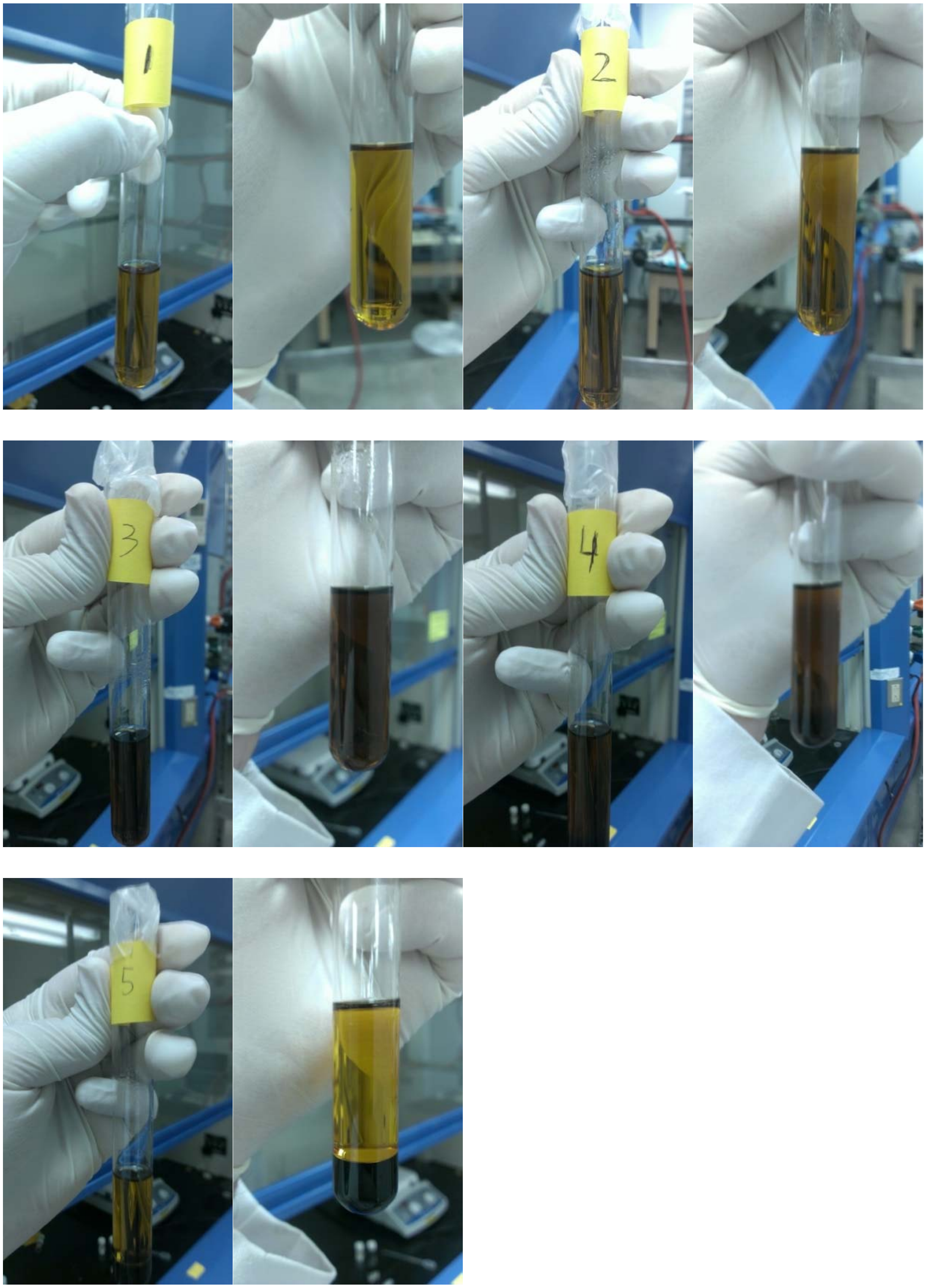




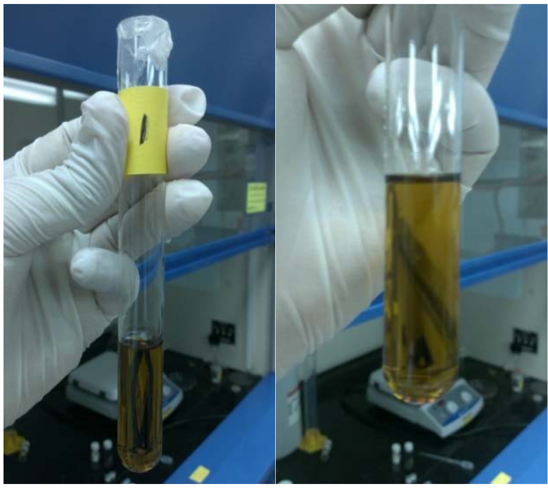


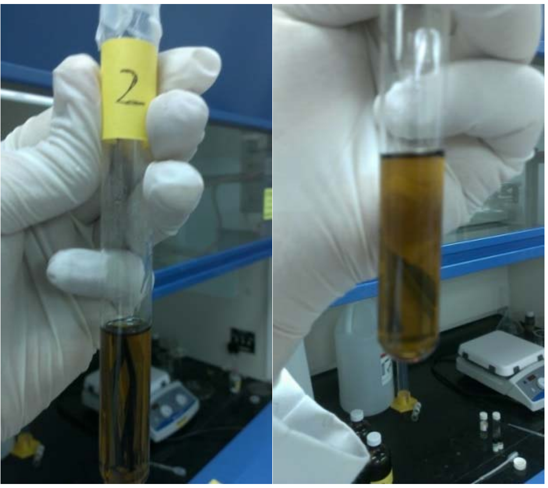


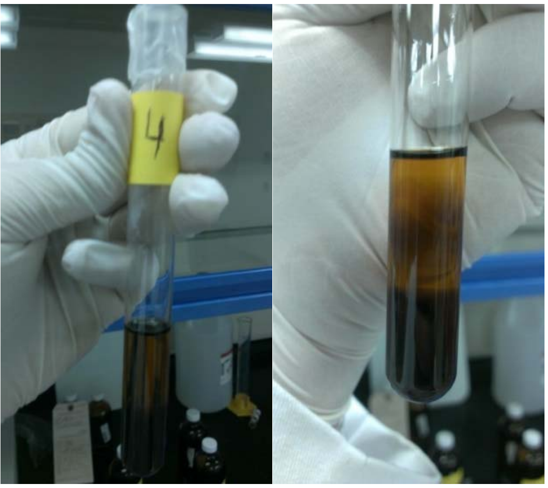
60 °C



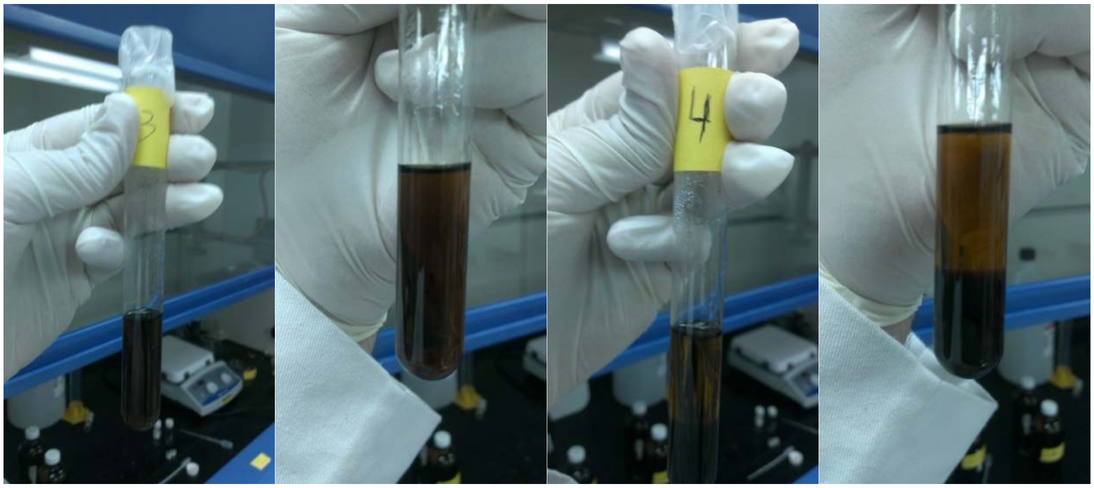
70 °C

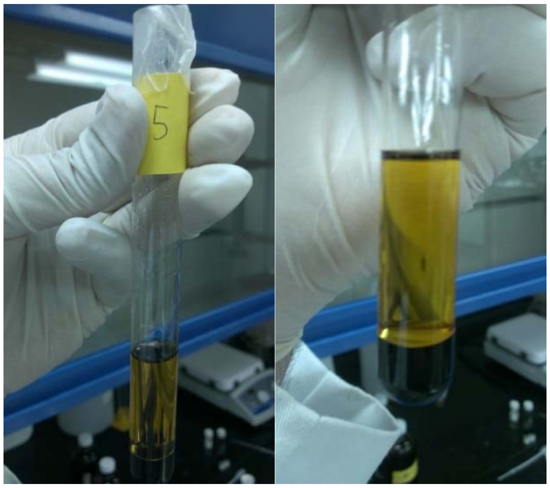




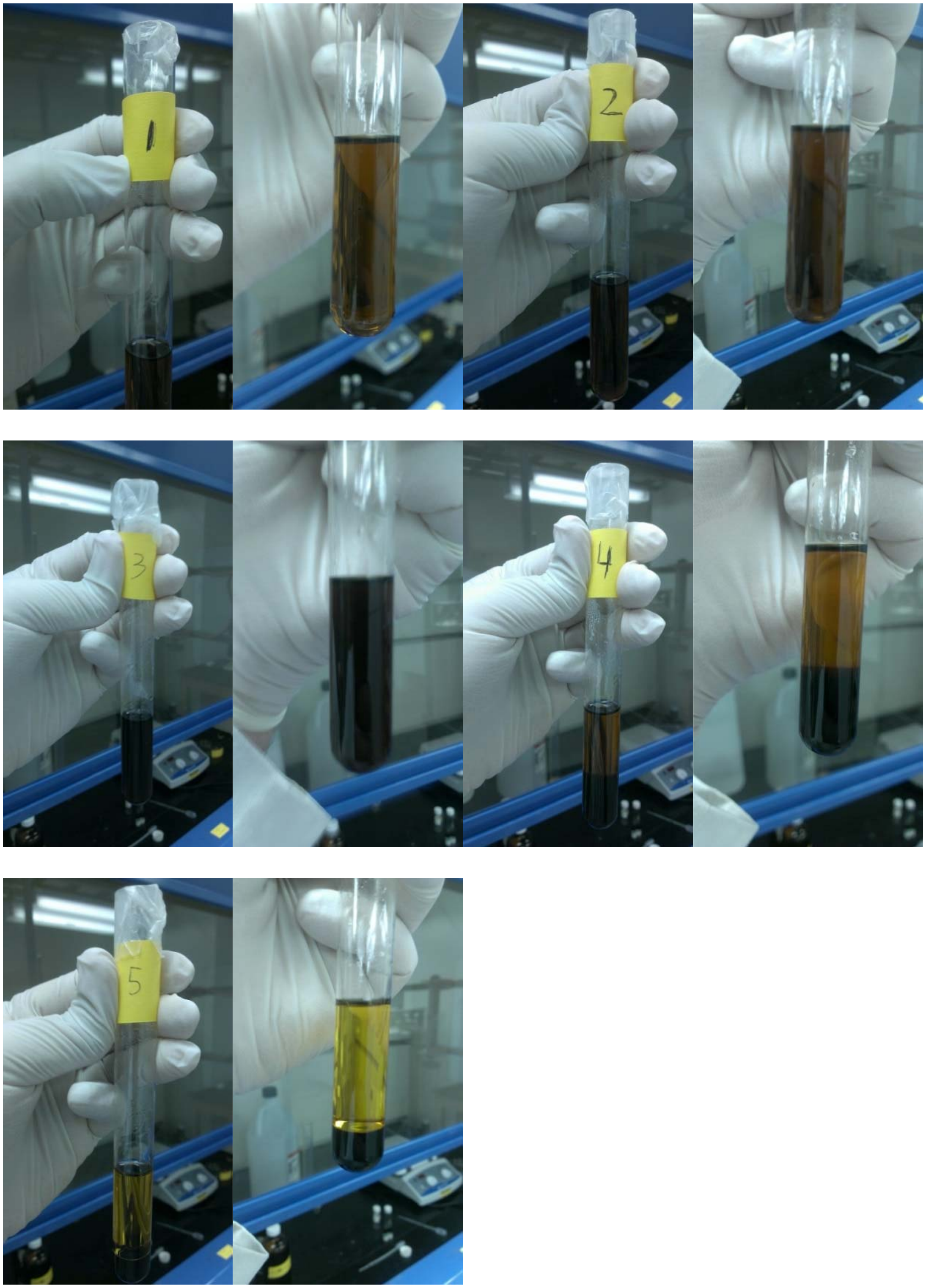


82 °C

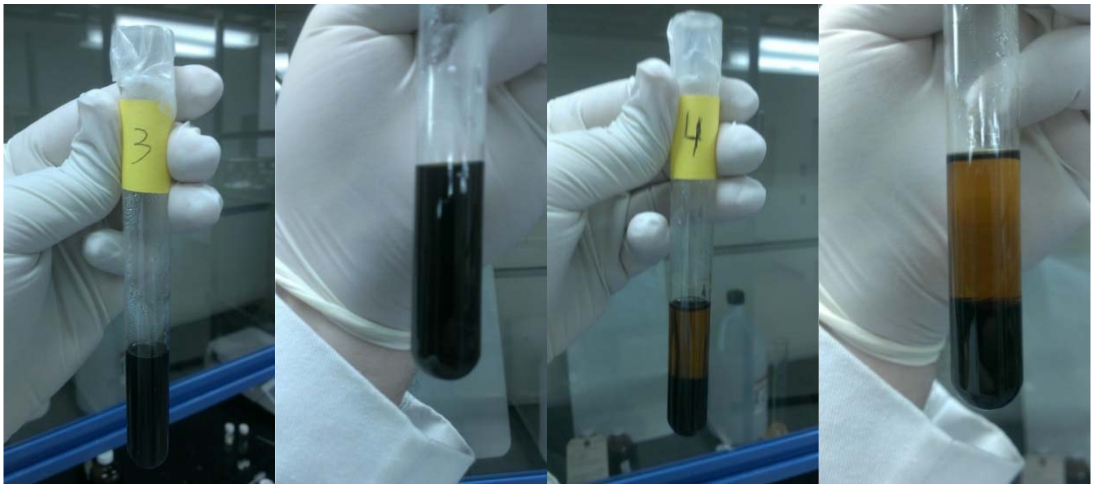


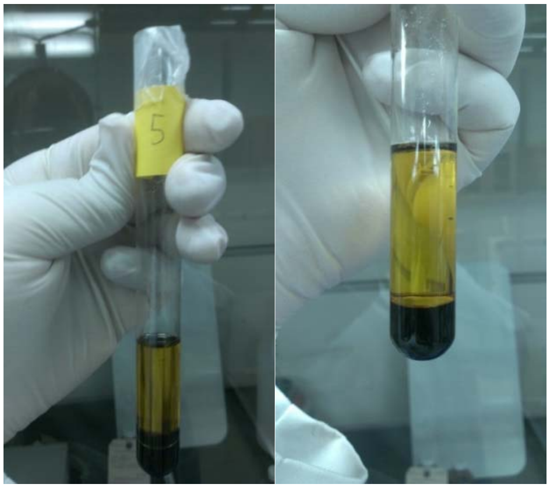


93 °C

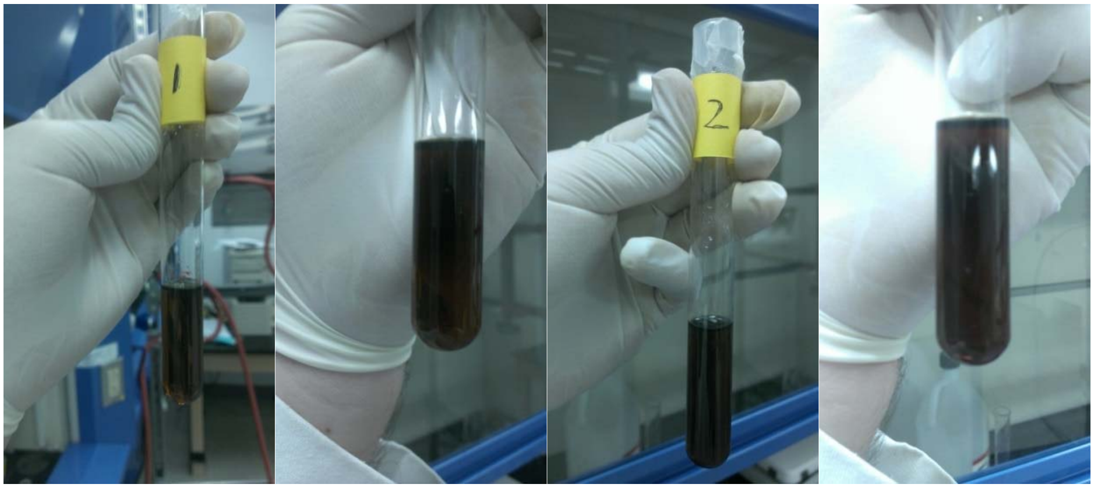


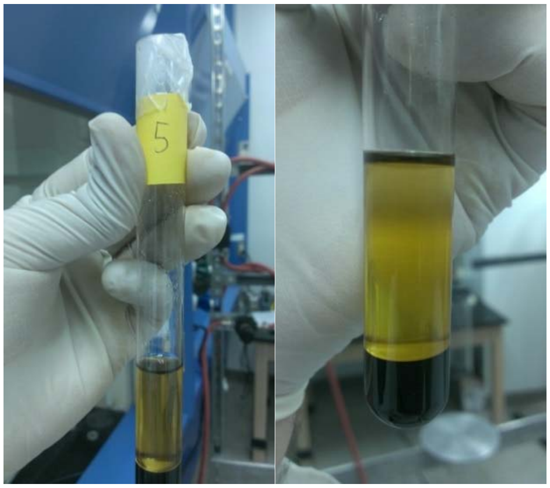
104 °C





Ambient – Post Run





Experiment 9

3-Nitrotoluene with 80% Sulfuric Acid.

Acid prepared by mixing 90 mL of 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 25 mL of water.

Tube 1: 6 mL 80% H_2SO_4 w/ 2 mL 3-Nitrotoluene.

Tube 2: 7 mL 80% H_2SO_4 w/ 3 mL 3-Nitrotoluene.

Tube 3: 4 mL 80% H_2SO_4 w/ 4 mL 3-Nitrotoluene.

Tube 4: 3 mL 80% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

Tube 5: 2 mL 80% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

Tubes 1 and 2 showed 3 phase behavior at ambient temperatures but not at higher temperatures.

Temperatures observed (set-points):

50 °C

60 °C

70 °C

82 °C

93 °C

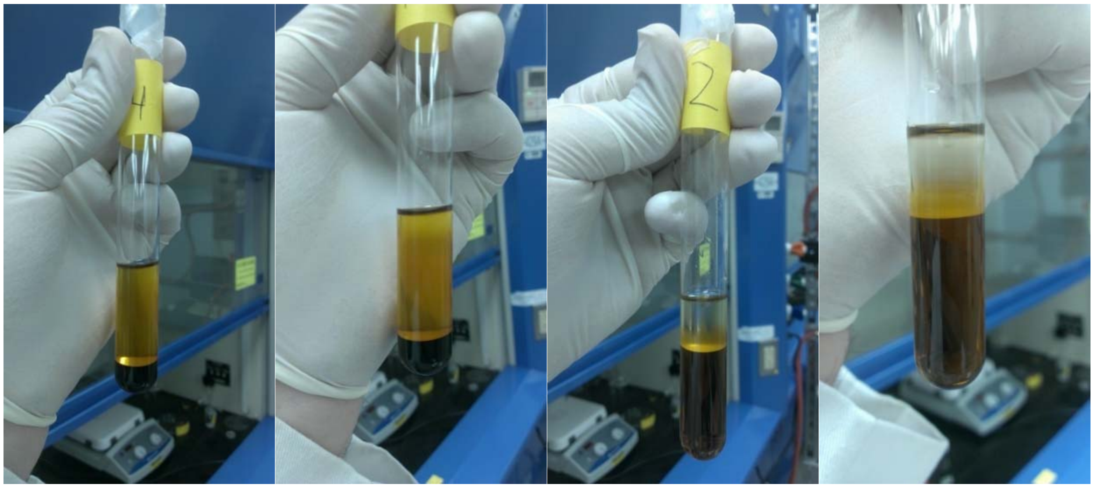
104 °C

Ambient

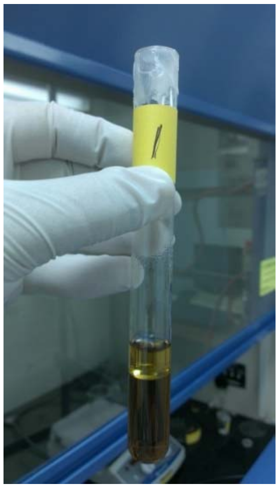
Tube	Initial Weight	Final Weight	Change
1	22.01 g	22.03 g	0.02 g
2	24.34 g	24.44 g	0.10 g
3	23.03 g	23.03 g	0.00 g
4	20.43 g	20.42 g	-0.01 g
5	21.98 g	21.97 g	-0.01 g

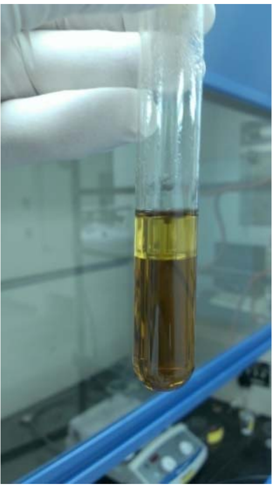
3 phase behavior seen in tube 2 before and after. 3 Phase behavior seen/suggested in 4 before but not after. Multi-phases apparent in tube 1 after heating but not really before.

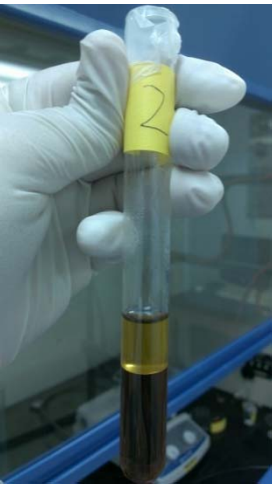
Ambient – Prerun after mixing

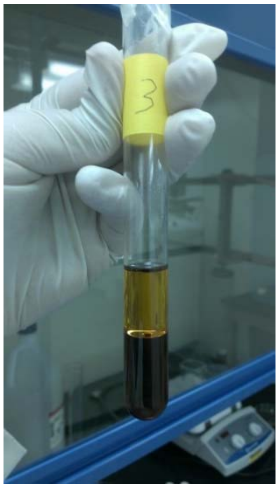

4
2

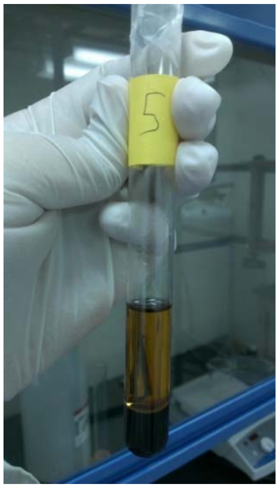
50 °C



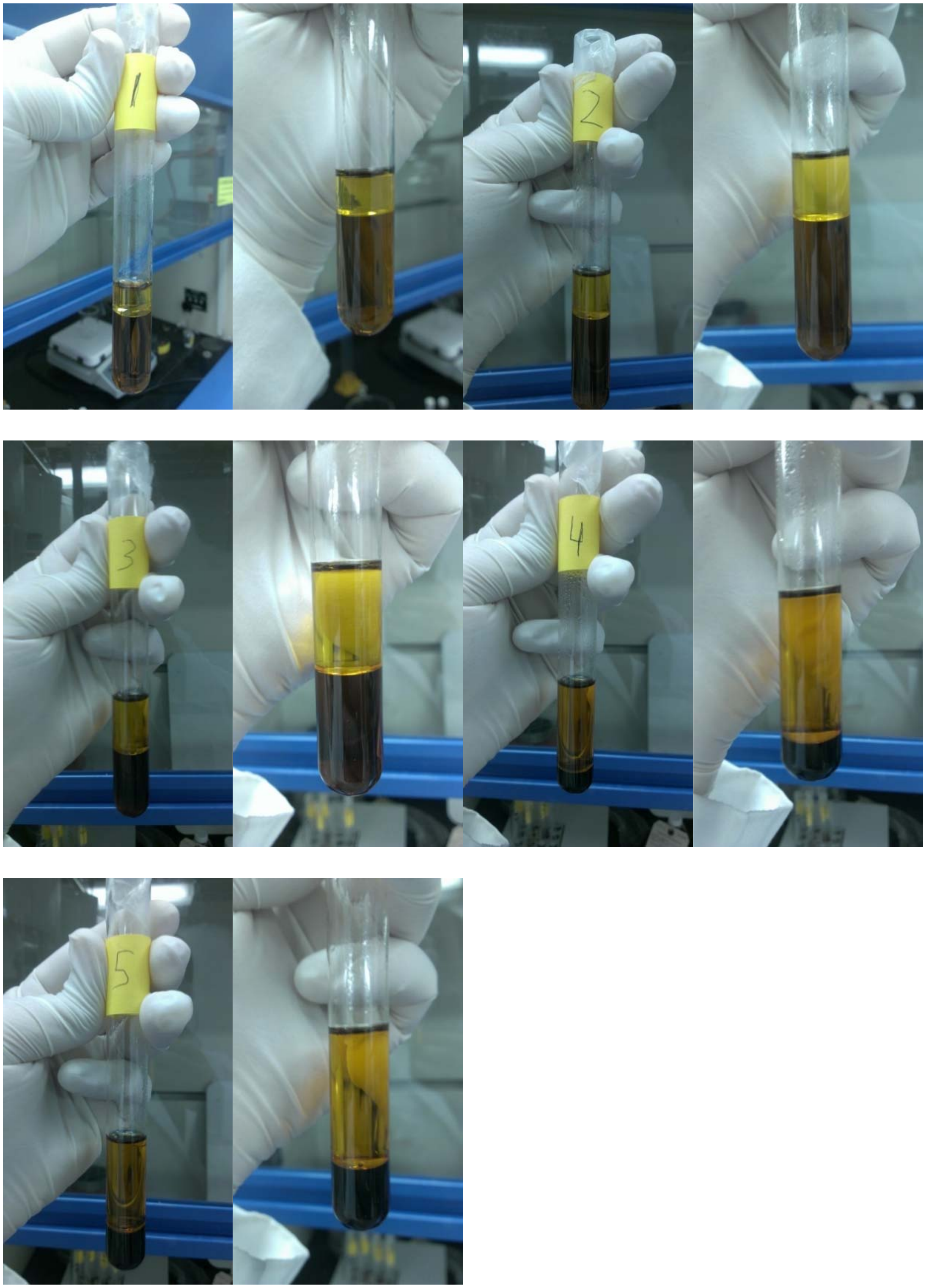




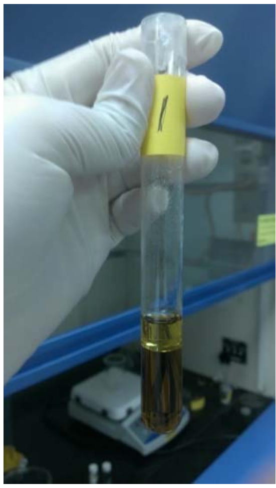


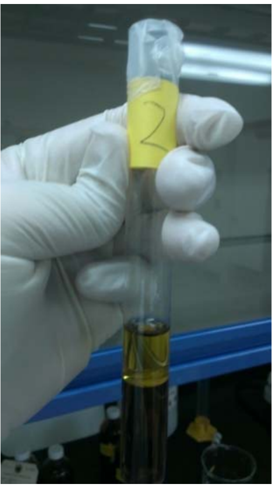


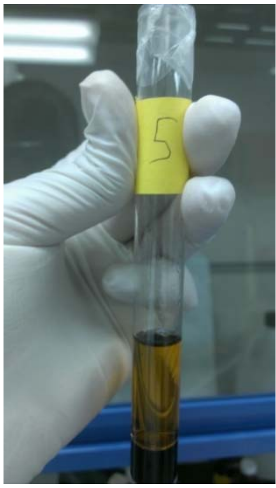
60 °C



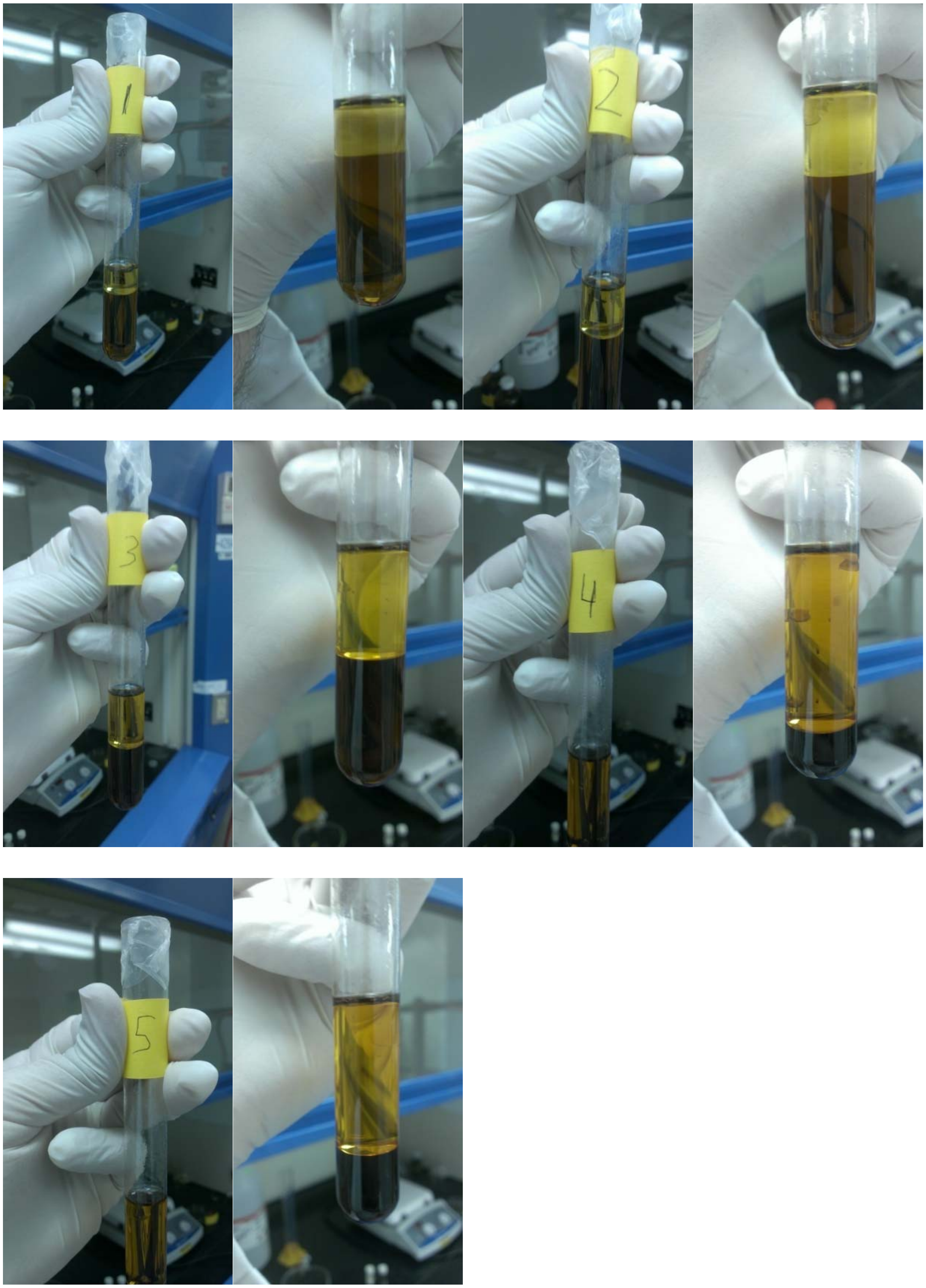
70 °C



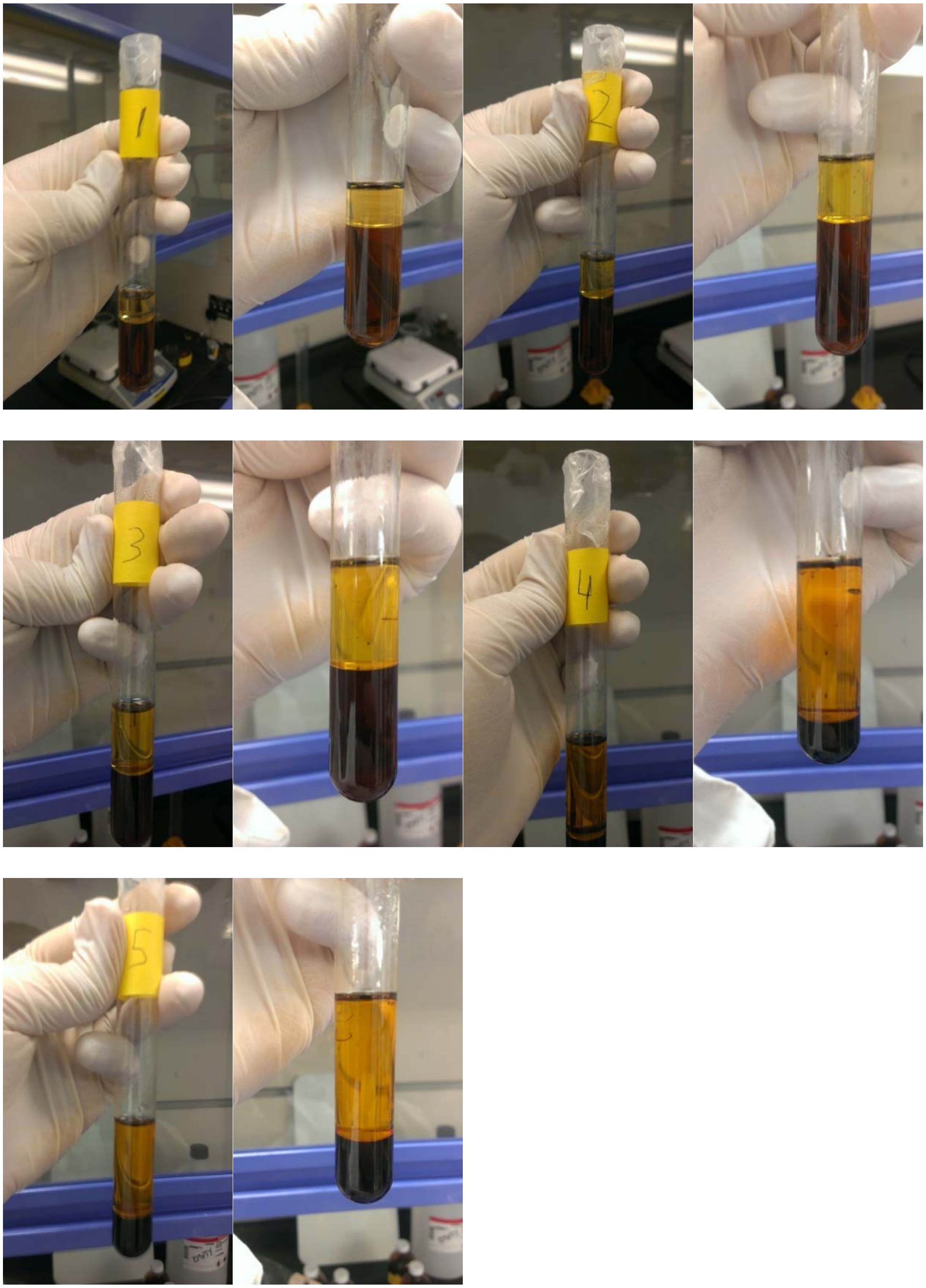




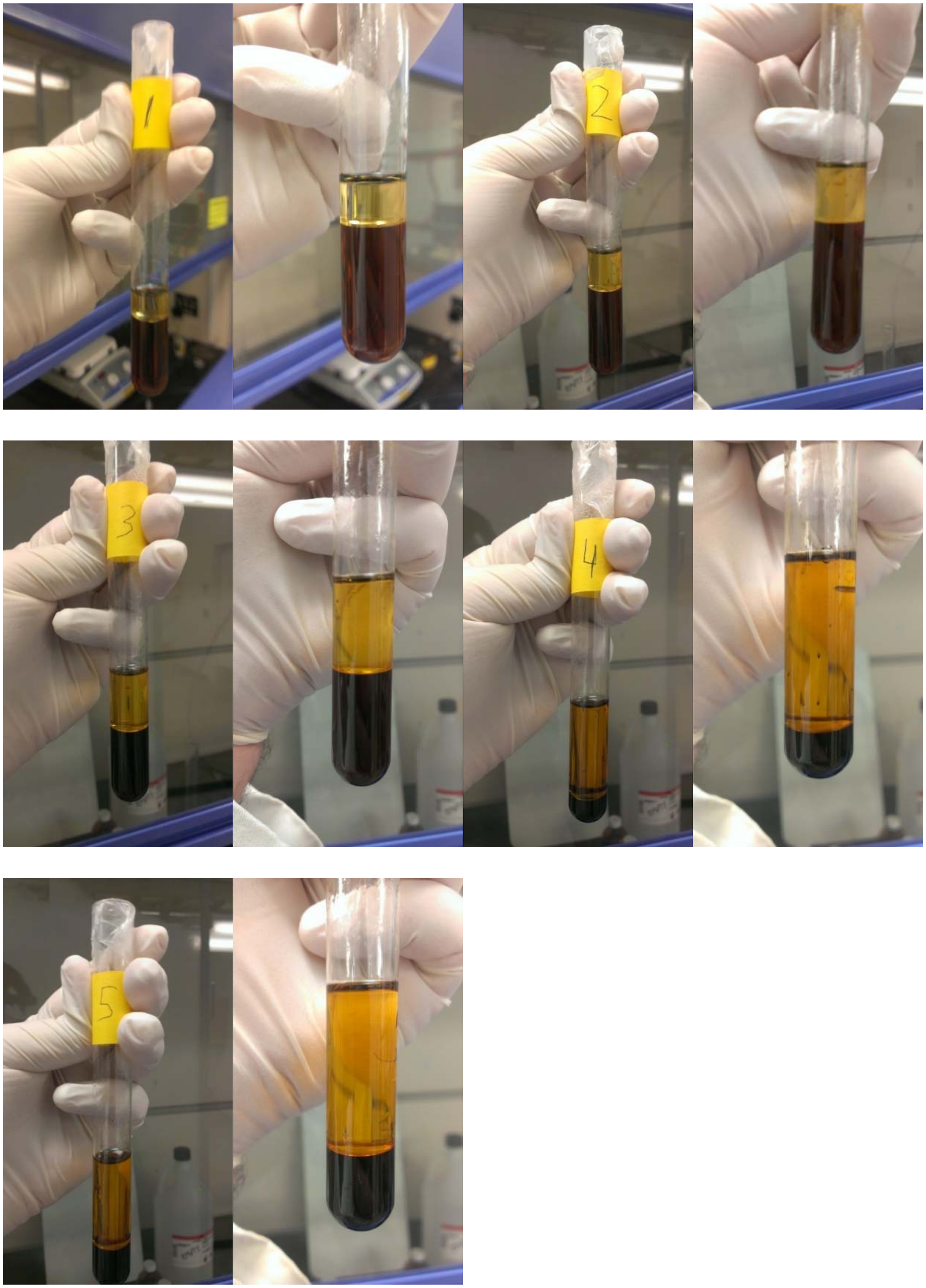
82 °C



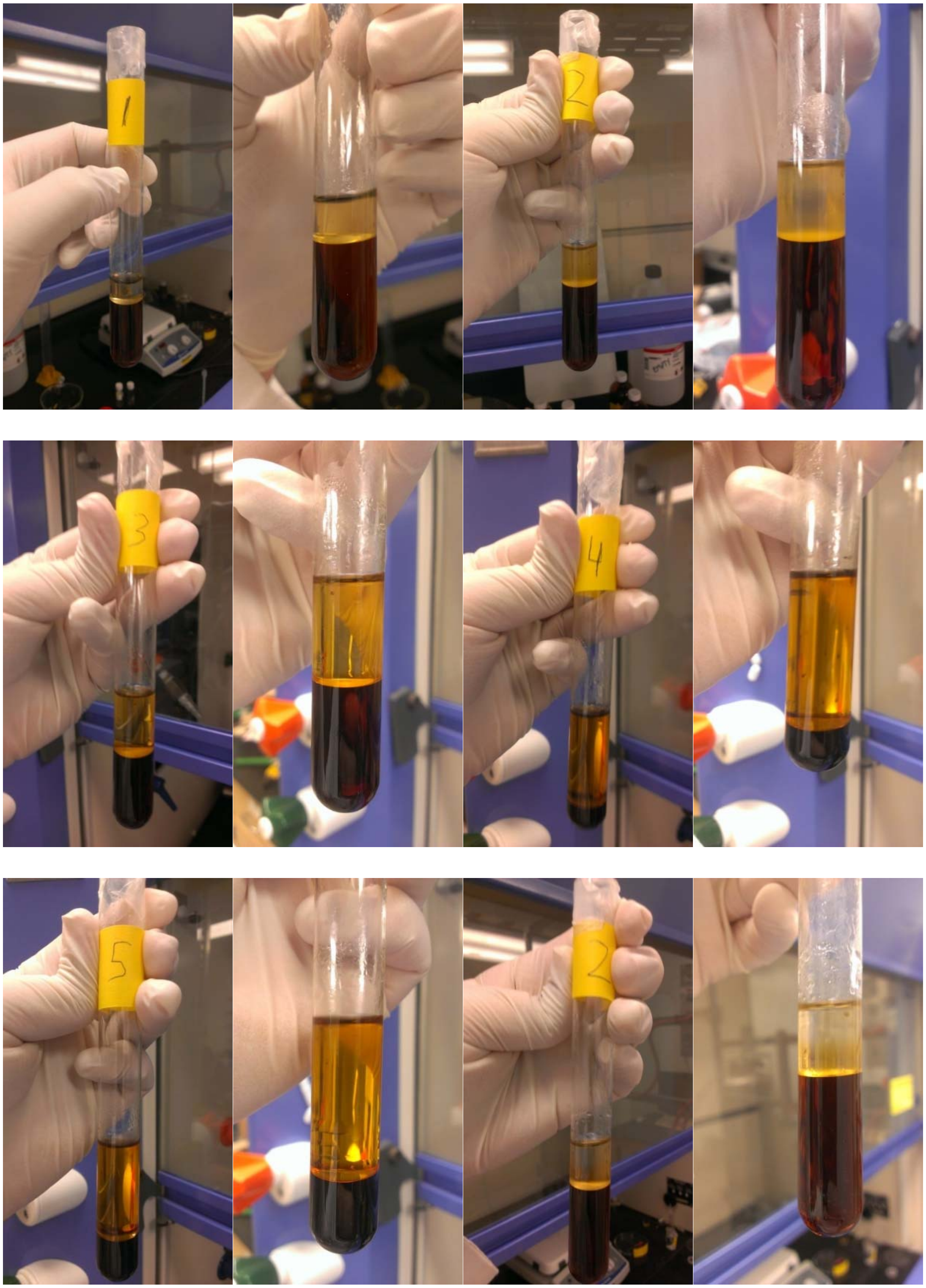
93 °C

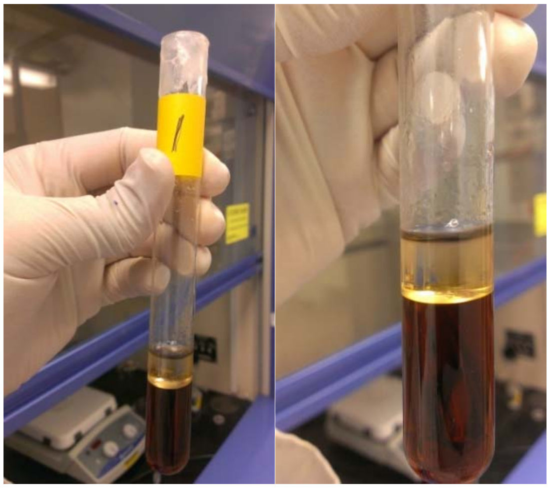


104 °C



Ambient – Post Run





Experiment 10

3-Nitrotoluene with 70% Sulfuric Acid.

Acid prepared by mixing 90 mL of 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 52 mL of water.

Tube 1: 6 mL 70% H_2SO_4 w/ 2 mL 3-Nitrotoluene.

Tube 2: 6 mL 70% H_2SO_4 w/ 3 mL 3-Nitrotoluene.

Tube 3: 4 mL 70% H_2SO_4 w/ 4 mL 3-Nitrotoluene.

Tube 4: 3 mL 70% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

Tube 5: 2 mL 70% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

Temperatures observed (set-points):

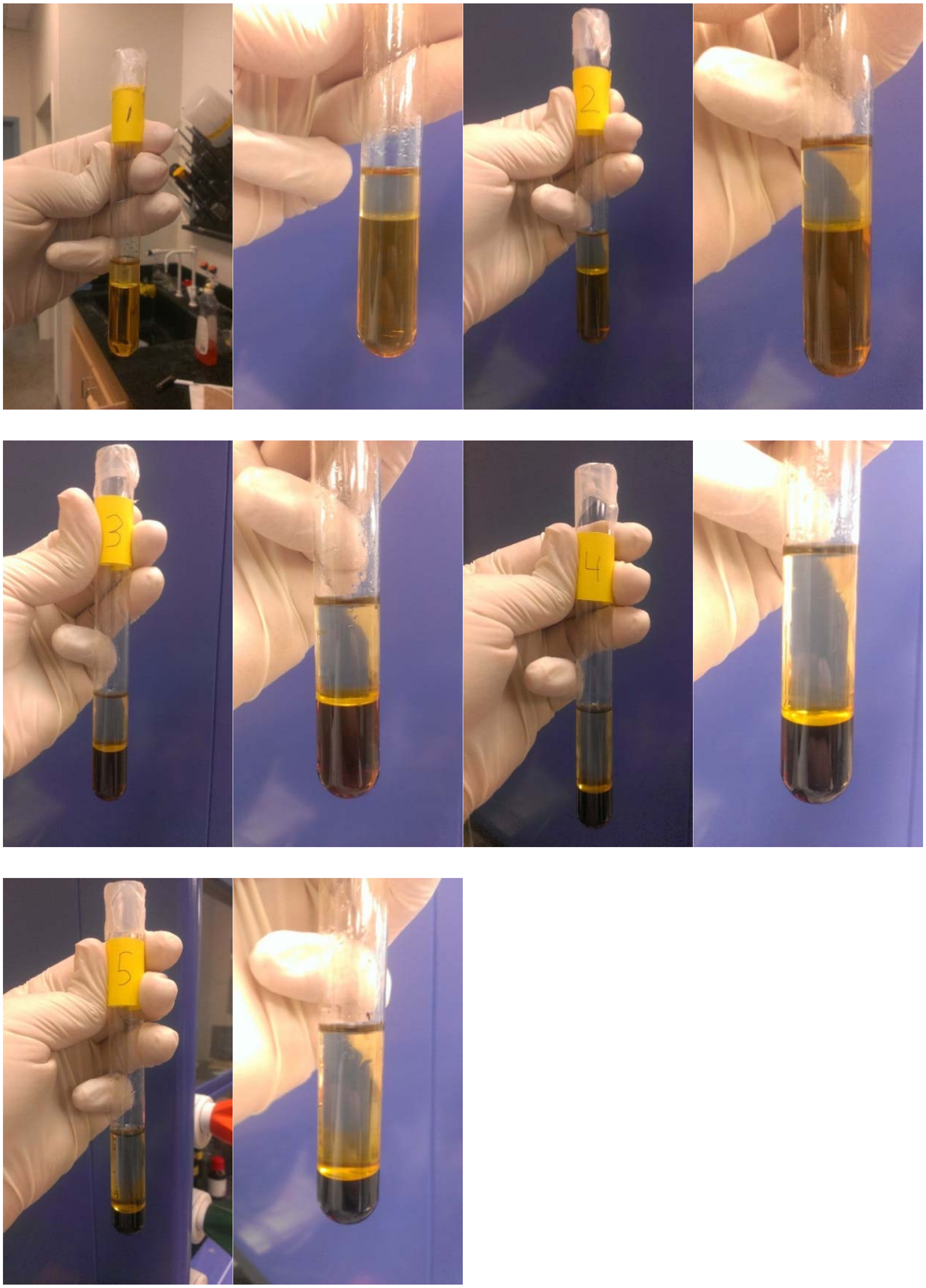
50 °C

Ambient

Tube	Initial Weight	Final Weight	Change
1	22.58 g	22.58 g	0.00 g
2	23.31 g	23.32 g	0.01 g
3	21.67 g	21.67 g	0.00 g
4	22.20 g	22.21 g	0.01 g
5	20.63 g	20.64 g	0.01 g

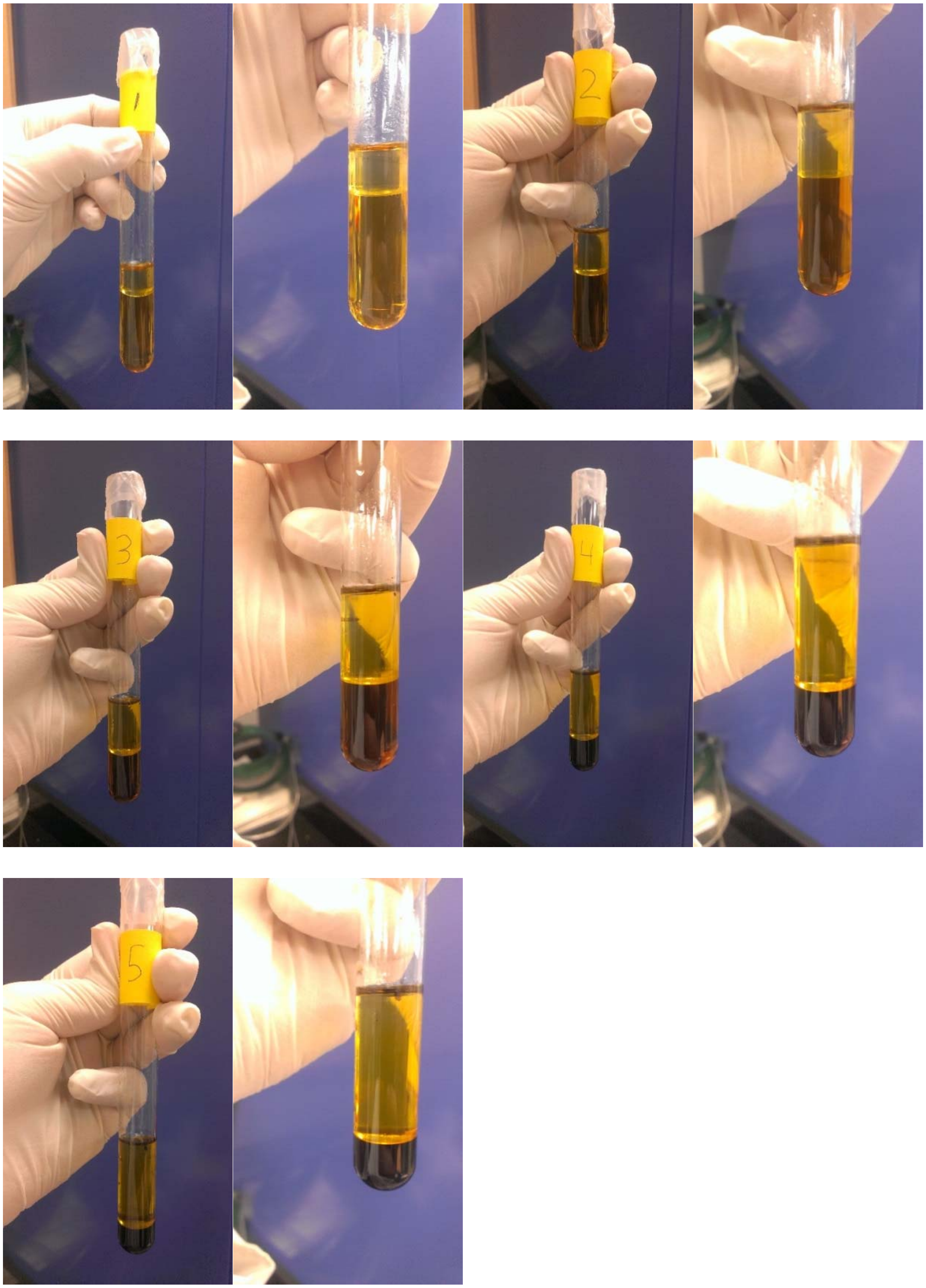
-The tube layout was the same as used in experiment 1

Ambient – Prerun after mixing



50 °C

Ambient – Post Run



Experiment 11

2-Nitrotoluene with 70% Sulfuric Acid.

Acid prepared by mixing 90 mL of 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 52 mL of water.

Tube 1: 6 mL 70% H_2SO_4 w/ 2 mL 2-Nitrotoluene.

Tube 2: 6 mL 70% H_2SO_4 w/ 3 mL 2-Nitrotoluene.

Tube 3: 4 mL 70% H_2SO_4 w/ 4 mL 2-Nitrotoluene.

Tube 4: 3 mL 70% H_2SO_4 w/ 6 mL2-Nitrotoluene.

Tube 5: 2 mL 70% H_2SO_4 w/ 6 mL2-Nitrotoluene.

Temperatures observed (set-points):

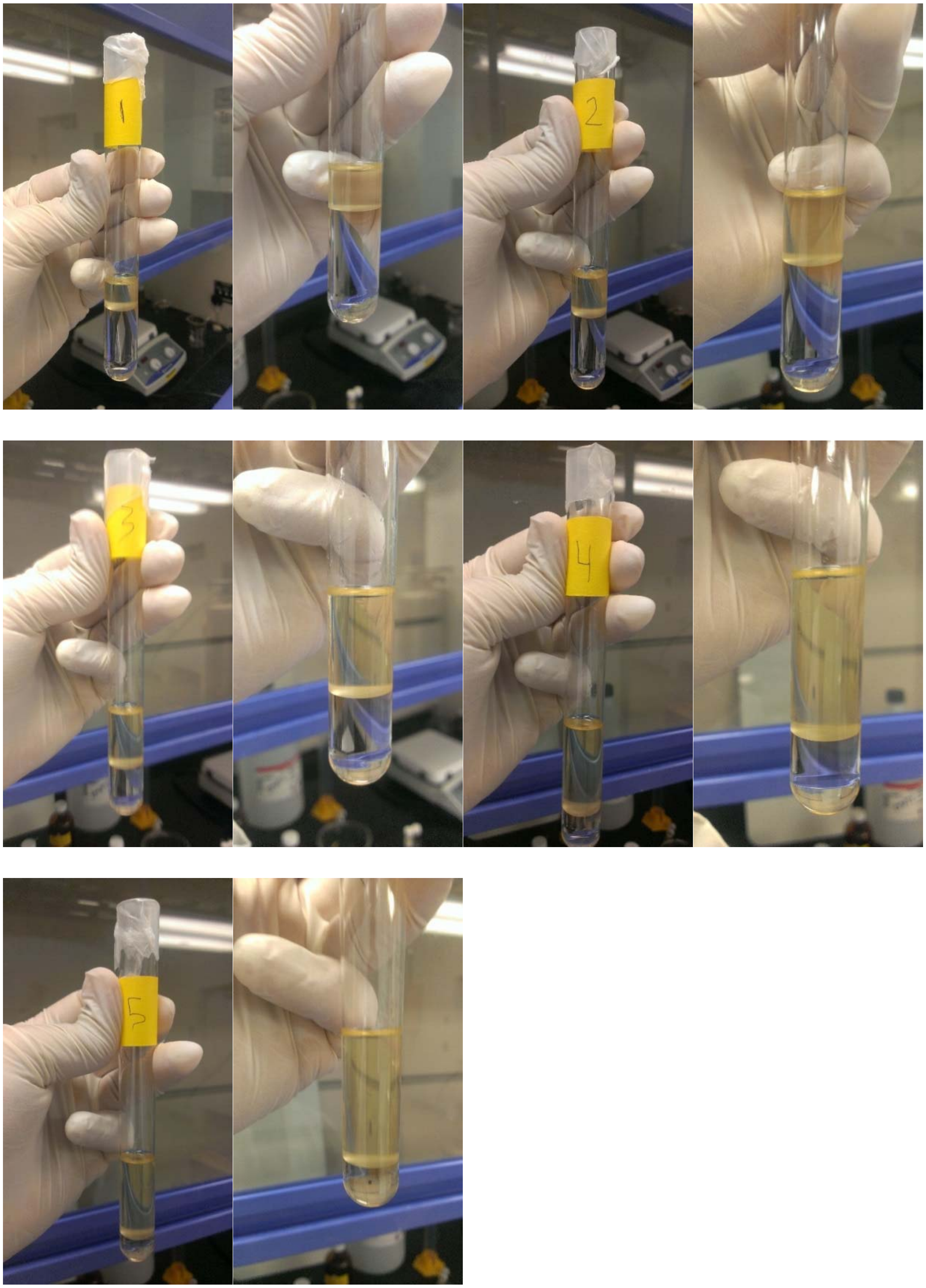
50 °C

Ambient

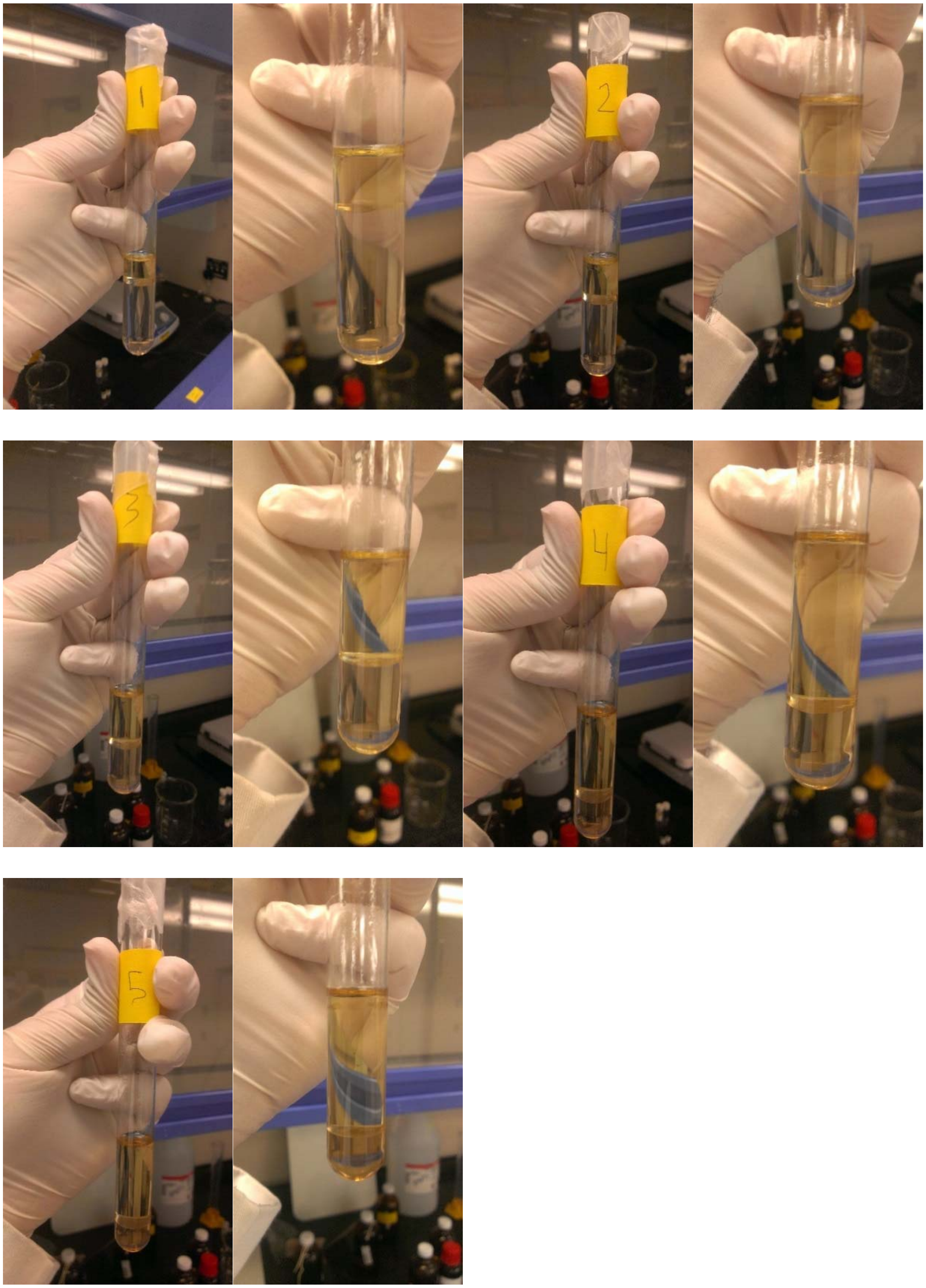
Tube	Initial Weight	Final Weight	Change
1	22.73 g	22.73 g	0.00 g
2	23.64 g	23.64 g	0.00 g
3	21.50 g	21.51 g	0.01 g
4	22.38 g	22.38 g	0.00 g
5	20.85 g	20.85 g	0.00 g

-The tube layout was the same as used in experiment 1

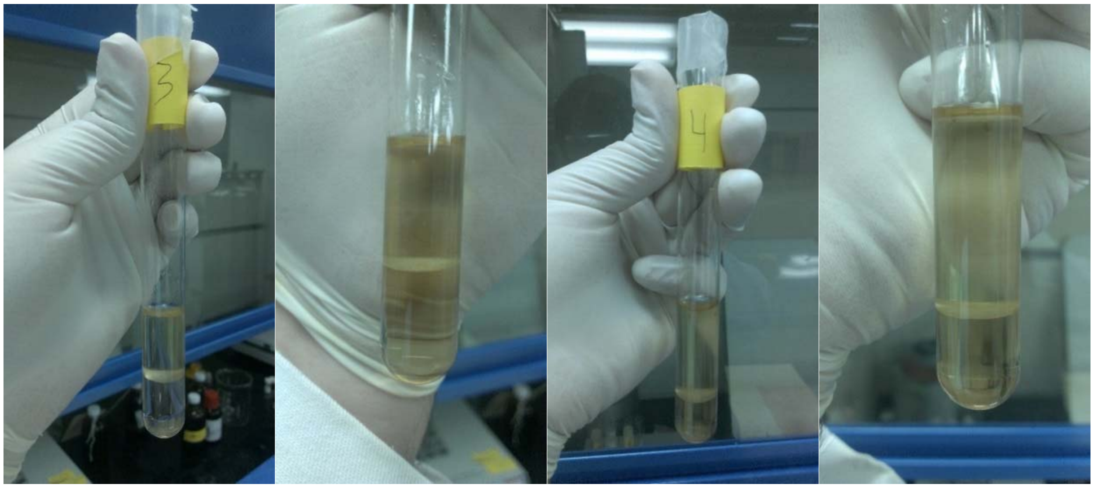
Ambient – Prerun after mixing

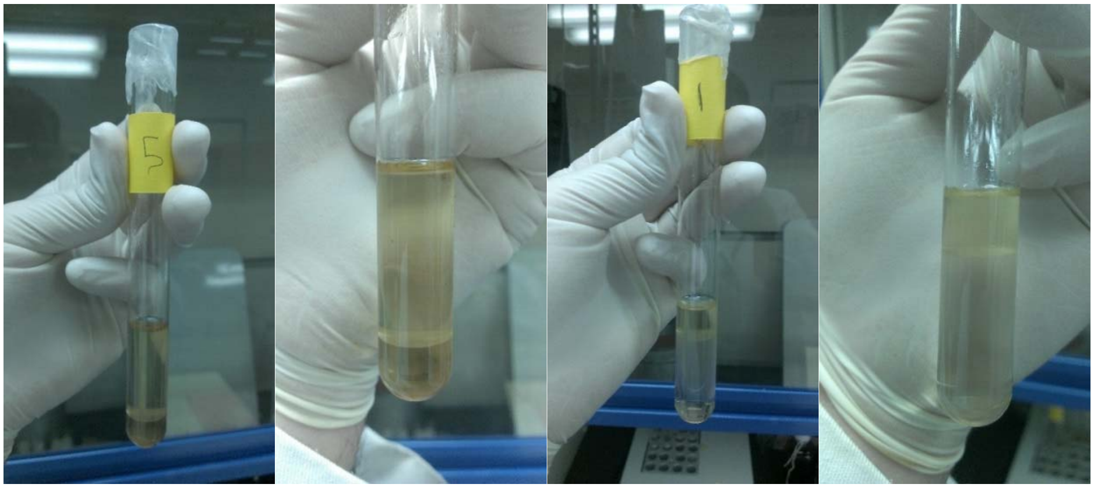


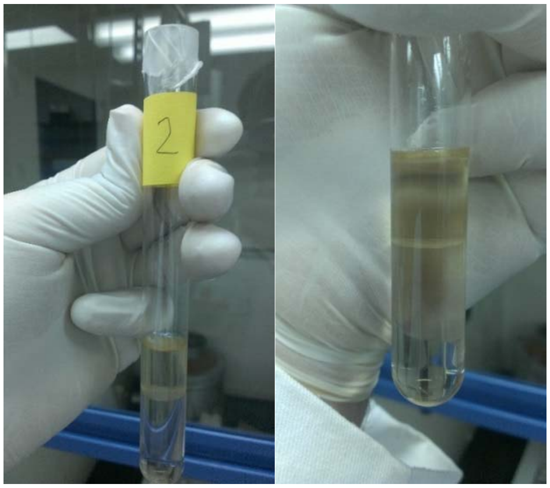
50 °C



Ambient – Post Run







Experiment 12

Experiment 12:

2-Nitrotoluene with 80% Sulfuric Acid.

Acid prepared by mixing 90 mL of 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 25 mL of water.

Tube 1: 6 mL 80% H_2SO_4 w/ 2 mL 2-Nitrotoluene.

Tube 2: 6 mL 80% H_2SO_4 w/ 3 mL 2-Nitrotoluene.

Tube 3: 4 mL 80% H_2SO_4 w/ 4 mL2-Nitrotoluene.

Tube 4: 3 mL 80% H_2SO_4 w/ 6 mL 2-Nitrotoluene.

Tube 5: 2 mL 80% H_2SO_4 w/ 6 mL 2-Nitrotoluene.

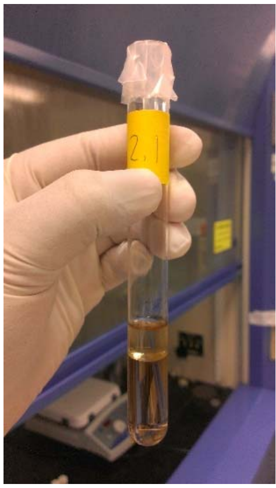
Temperatures observed (set-points):

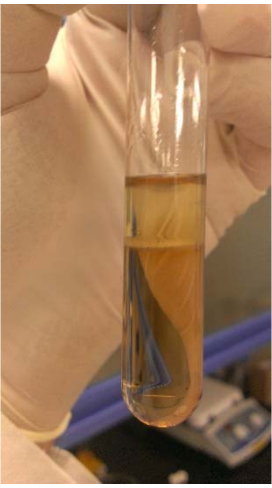
50 °C

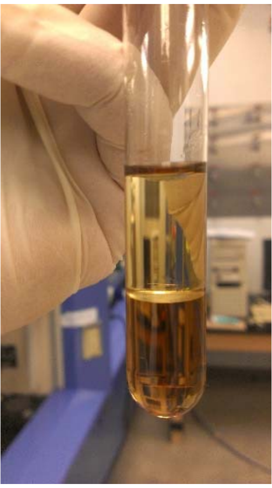
Ambient

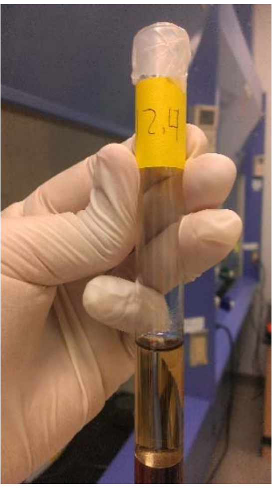
Tube	Initial Weight	Final Weight	Change
1	22.73 g	22.73 g	0.00 g
2	23.64 g	23.64 g	0.00 g
3	21.50 g	21.51 g	0.01 g
4	22.38 g	22.38 g	0.00 g
5	20.85 g	20.85 g	0.00 g

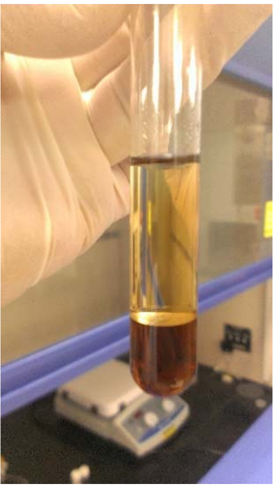
Pre-run Ambient

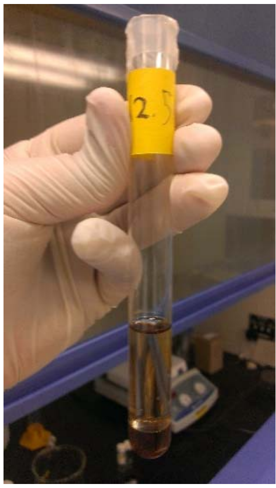




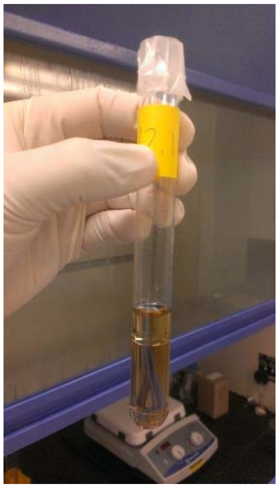


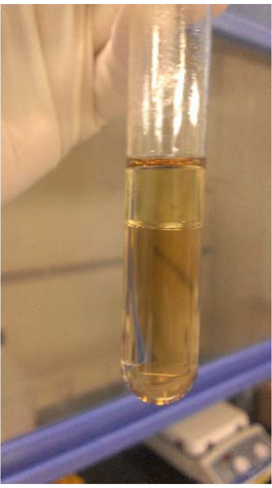


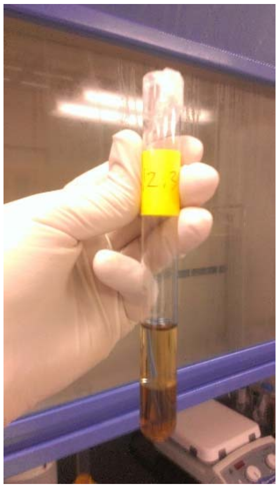


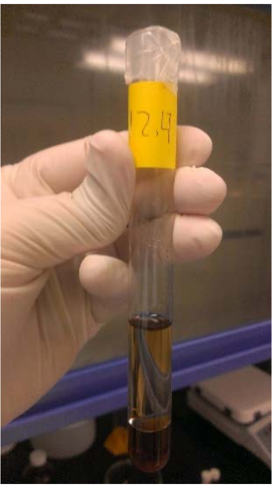


50°C









Post Run Ambient

Experiment 13

3-Nitrotoluene with 90% Sulfuric Acid.

Acid prepared by mixing 90 mL of 95-98 wt% Sulfuric Acid (assumed 96 wt%) with 4 mL of water.

Tube 1: 6 mL 90% H_2SO_4 w/ 2 mL 3-Nitrotoluene.

Tube 2: 6 mL 90% H_2SO_4 w/ 3 mL 3-Nitrotoluene.

Tube 3: 4 mL 90% H_2SO_4 w/ 4 mL 3-Nitrotoluene.

Tube 4: 3 mL 90% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

Tube 5: 2 mL 90% H_2SO_4 w/ 6 mL 3-Nitrotoluene.

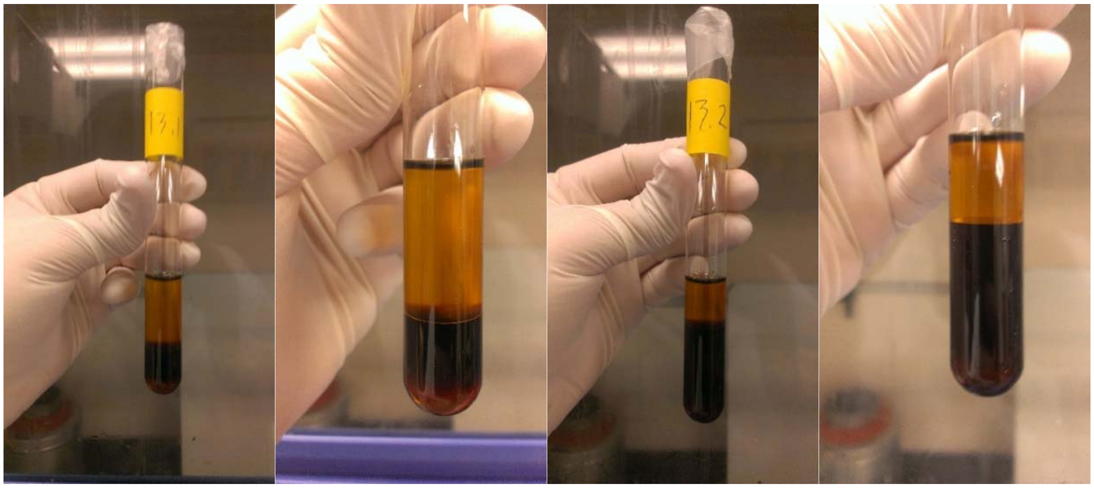
Temperatures observed (set-points):

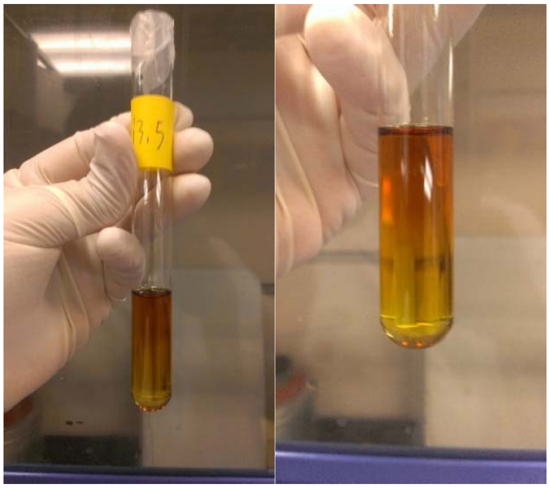
50 °C

60°C

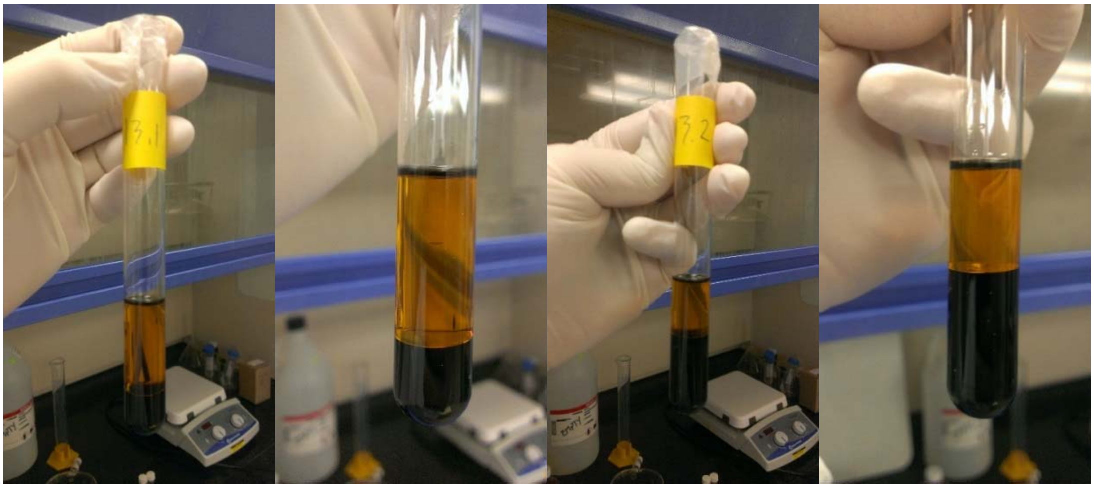
Ambient

Ambient – Prerun after mixing

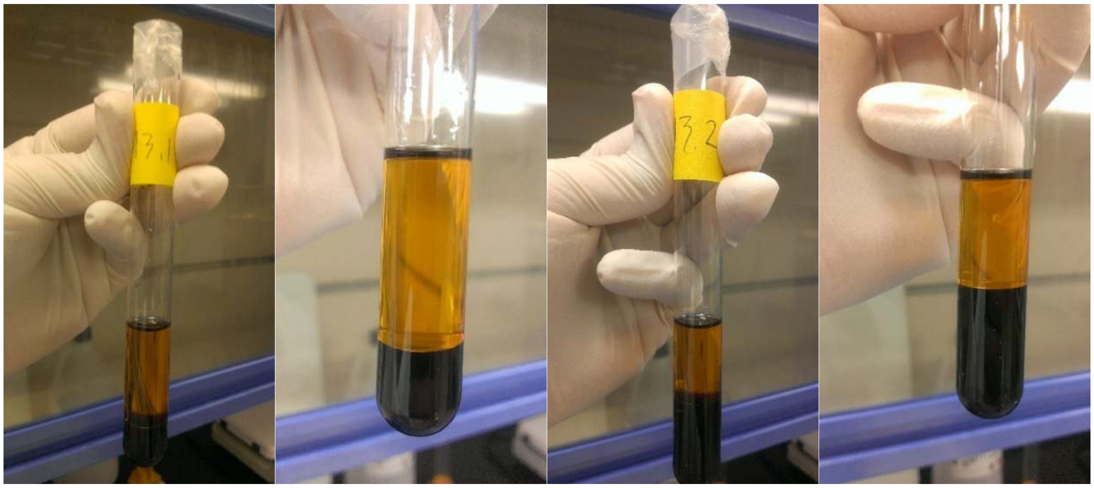


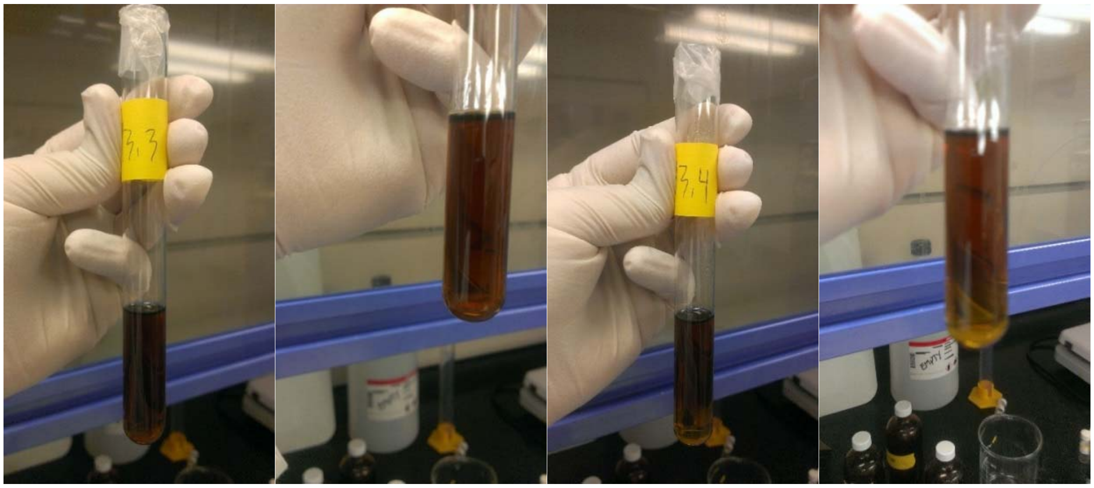


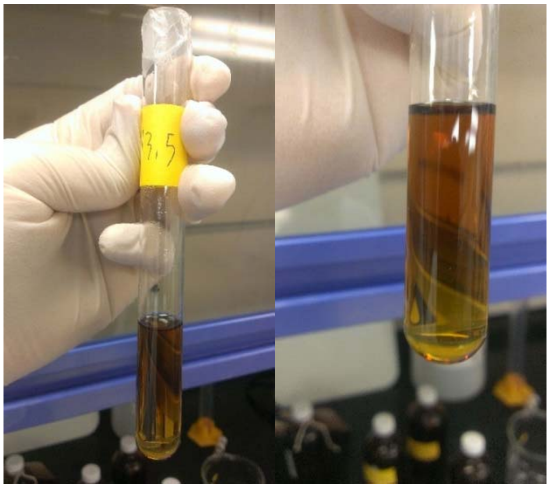
50 °C



60 °C







Ambient – Post Run