

School of Chemistry

# Masters Research Project

Title: Kolbe – Schmitt screening reaction conditions using supercritical carbon dioxide

Student's name: Mei Yao Young

Student ID Number: 20311571

Supervisor(s): Prof. Steve Howdle, Dr. Vincenzo Taresco

I hereby certify that this project report is my own work:

Student's signature: M. Young

This project is signed under a non-disclosure agreement with Lubrizol.

**Table of Contents**

**Abstract** ..... 3

**1. Introduction** ..... 4

**1.1 Lubrication** ..... 4
**1.1.1 Mechanism of film formation of boundary lubrication** ..... 5
**1.1.2 Lubricant** ..... 8
**1.1.3 Lubricant Additives** ..... 9

**1.2 Emulsion** ..... 14

**1.3 Kolbe-Schmitt Reaction** ..... 17
**1.3.1 Background** ..... 17
**1.3.2 Applications of Kolbe – Schmitt reaction** ..... 19
**1.3.3 Improvements of Kolbe – Schmitt reaction** ..... 20
**1.3.4 Mechanism of Kolbe – Schmitt reaction** ..... 28

**1.4 Supercritical Fluids** ..... 33
**1.4.1 Supercritical and liquid carbon dioxide** ..... 35
**1.4.2 Solubility in $scCO_2$** ..... 39
**1.4.3 Extraction** ..... 41

**2. Experimental** ..... 44

**2.1 High pressure equipment and setup** ..... 44

**2.2 Materials** ..... 47

**2.3 Superbase surfactant Characterisation** ..... 48

**2.4 Experimental procedure** ..... 49
**2.4.1 The effect of temperature on the Kolbe-Schmitt reaction of sodium alkyl phenolate at high pressure.** ..... 58
**2.4.2 The effect of pressure on the Kolbe-Schmitt reaction of sodium alkyl phenolate** ..... 61
**2.4.3 Synthesis of sodium alkyl salicylate in $scCO_2$ with promoters** ..... 63
**2.4.4 Synthesis of calcium alkyl salicylate in $scCO_2$** ..... 70
**2.4.5 Synthesis of calcium alkyl salicylate in $scCO_2$ with promoters** ..... 75
**2.4.6 Kolbe-Schmitt reaction performed under Ultrasonication** ..... 79
**2.4.7 Emulsion Stability** ..... 83

**3. Conclusion and future work** ..... 85

**4. References** ..... 87

**5. Appendixes** ..... 90

## Abstract

Salicylic acid derivatives from phenols with $CO_2$ are synthesised in the industry by a base-promoted Kolbe–Schmitt carboxylation reaction, however the mechanism is still unclear. Numerous studies and investigations were conducted on finding methods to improve the reaction conditions of the Kolbe – Schmitt reaction as well as increasing the product yield. This thesis is centred on the Kolbe – Schmitt screening reaction conditions using supercritical $CO_2$ for the synthesis of over-based detergents. The synthesis of sodium alkyl salicylate from sodium alkyl phenolate and $CO_2$ under several parameters ranging from reaction time, high temperatures, the use of promoters and two $CO_2$ pressure – supercritical and gaseous. The promising parameters were then applied to the synthesis of calcium alkyl salicylate from calcium alkyl phenolate and $CO_2$. The overall aim is to synthesise calcium alkyl salicylate directly by Kolbe – Schmitt reaction by using the optimal parameters used in synthesising sodium alkyl salicylate.

# 1. Introduction

## 1.1 Lubrication

A lubricant is a material that is used to reduce friction and wear between contacting surfaces in order to permit relative motion of solid entities.[1] Lubrication is the process of applying lubricants and lubrication chemicals to moving mechanical parts in order to reduce friction. Lubricant applications, when applied correctly, extend the life and efficiency of machinery while also lowering long-term expenditures in terms of energy usage, maintenance, and operating temperatures. A lubricant's primary function is to provide a coating that separates two surfaces that roll or glide against one another, reducing friction and eliminating wear. As a result, the frictional force opposing the rubbing motion is low because these coatings minimise the contact between the rubbing surfaces and shear easily.[2] Other important functions include removing heat from the friction zone (cooling) and protecting the friction components from damage and corrosion. The lubricant has a number of secondary functions that must be carried out correctly in order for it to be used in the lubrication process. The lubricant must be easy to handle in all weather conditions, it must maintain its physical and chemical properties, i.e., it must not break down or polymerise during use, it must be safe to be exposed to and the environment, it must not produce or emit toxic components and it must be easy to process and dispose of after use, among other requirements.

In engines, lubrication is principally responsible for the prevention of wear and the maintenance of performance and efficiency. Lubricants are required to comply with these objectives by effectively protecting parts, lubricating moving parts, and controlling frictional properties.[3] They also need to protect surfaces and oilways from corrosion, stay cool and permit operating at extreme temperatures.[3] Boundary lubrication refers to a method for reducing wear and friction between surfaces when fluid film formation is not possible.[4] There are several mechanisms that are involved in boundary lubrication, which frequently work simultaneously.[4] In their general approach, all mechanisms aim at counteracting the general causes of friction and wear, reduction of energy required to shear asperity junctions, as well as ploughing.

### 1.1.1 Mechanism of film formation of boundary lubrication

The several mechanisms are:

i) Formation of a layer of molecules adsorbed by Van der Waals forces[1]. In order to form such layers a molecule must have a polar end which attaches to the metal (attachment via more than more polar group is also possible) and a non-polar end which associates with the oil solution. These layers provide a low shear strength layer that allows motion without friction and reduces wear. Their effectiveness depends on their individual chemical and physical structures as well as the temperature and load ranges around which they operate.[4] (Figure1)

ii) Oil component reacting with metal surfaces produce relatively thick high viscosity layers that can become globular or continuous after formation. This film has a hydrodynamic effect even at low speeds and can link to the surface by van der Waals forces. These films are less effective under high contact loads.[4] (Figure 2)

iii) Smoothing and a thin reacted layer. Oil components, such as soap, chemically attack exposed clean metal surfaces, resulting in a thin chemically altered layer. Chemical film formation does not occur to any significant depth, and abrasion soothes asperities. Because of this, as well as the film's low shear strength, adhesion is reduced, and thus ploughing is reduced. The formation of these films is frequently necessitated by moderate temperatures.[4] (Figure 3)

iv) Thick reacted inorganic layers. When active oil components react with metal surfaces, thick reacted low shear strength inorganic films, such as sulphides, form on the sliding surfaces. This surface layer restricts adhesion but must be reformed as soon as possible or scuffing will occur. Only at high temperatures and loads do these films form.[4] (Figure 4)

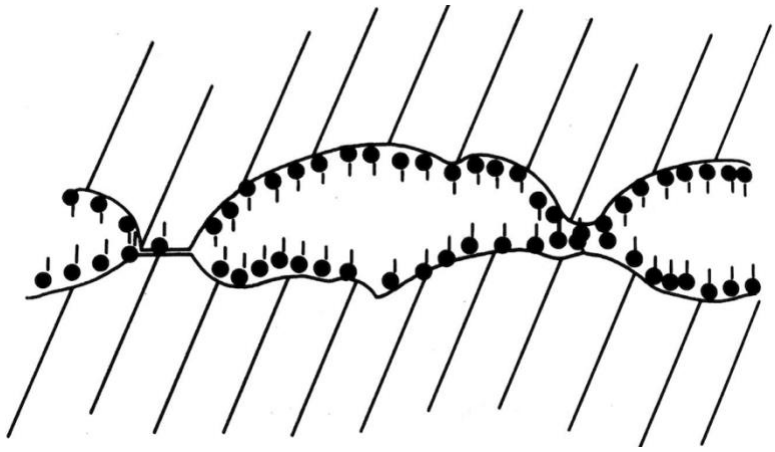


Figure 1: Van der Waals adsorption [4]

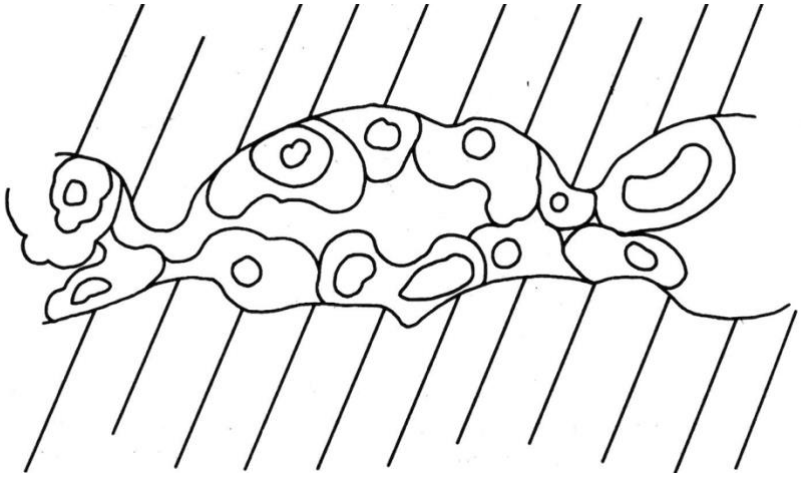


Figure 2: High-viscosity layer formation [4]

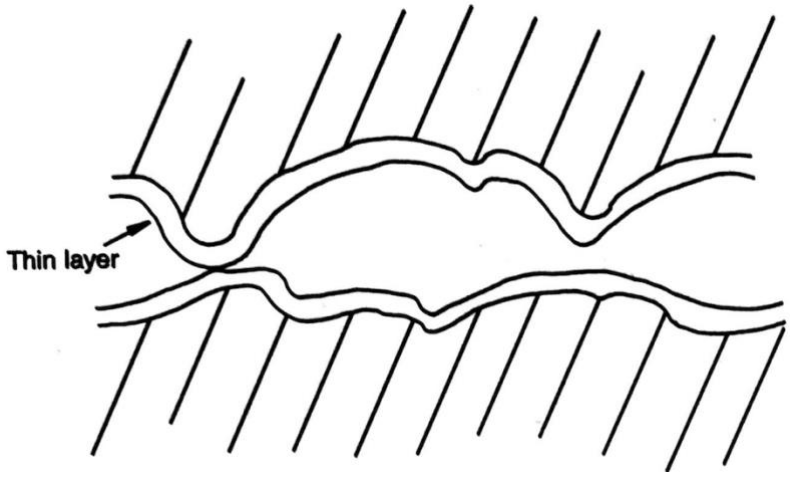



Figure 3: Thin reacted layer and smoothing [4]

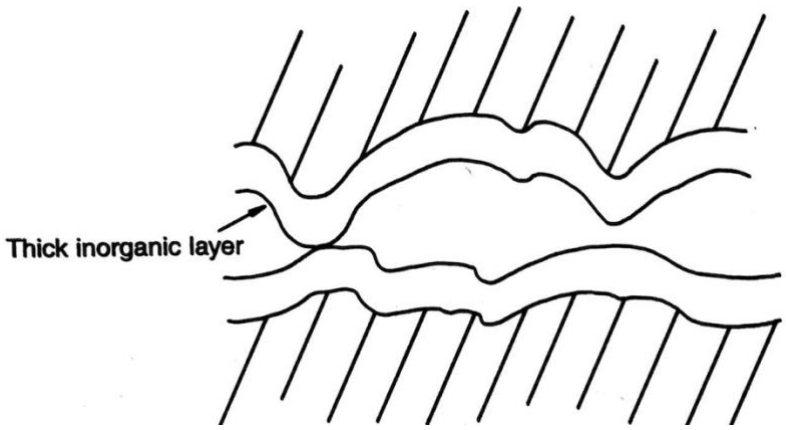



Figure 4: Thick reacted inorganic layer [4]

### 1.1.2 Lubricant

Lubricants prevent rusting by removing wear debris, carrying frictional heat away, and removing wear debris. The base oil plus one or more additives are the most fundamental components of a lubricant formulation. The base oil might be a single component (for example, refined petroleum with a specific distillation range) or a mixture of various base oils with different viscosity classes and chemistry. Alkaline (over-based) detergents, dispersants, antioxidants, corrosion inhibitors, pour point depressants, anti-wear, and severe pressure additives are some of the additives utilised in lubricant formulation. Each component is chosen with care to ensure that the lubricant can perform its primary and secondary functions properly for the duration of its service life.

The lubricant formulations can be used as both an oil-based fluid and a water-based fluid. In oil-based fluids, the lubricant formulation, which includes base oil and additives, is used as-is or diluted with the appropriate base oil prior to application. The lubricant formulation is dispersed in water to form oil-water mixtures (emulsions, microemulsions, micellar solutions) with varying degrees of stability in water-based fluids. Water-based fluids have a number of advantages over oil-based fluids, including superior cooling, low cost, and low greenhouse gas emissions. The emulsifier (also known as a surfactant or detergent) is an important additive in water-based formulations because it allows the oil formulation to be mixed with the water while also controlling the stability of the resulting emulsion.

The base oil is the first ingredient chosen for lubricant formulation because it accounts for the greatest proportion of the formulation (60-99%).[5] The viscosity of the base oil at the temperature of application is the most important, it must match the viscosity requirement for the process. The viscosity of the base oil influences the thickness of the lubricant film formed during the tribological process, and thus the outcome of the lubrication process. Other important base oil properties include viscosity index (VI), pour point, cloud point, flash point, and so on.[5]

In many cases, the base stock oil blends alone would struggle to meet the requirements for formulating a lubricant that adequately performs its primary and secondary functions while remaining cost competitive. In such cases, additives are used to optimise the formulation. Additives perform two broad functions: the first is to enhance the properties of the base oil to

the value required for the formulation, such as viscosity, pour point, and others; the second is to provide the formulation with critical properties that the base oil alone cannot provide. Friction, wear, corrosion resistance, bio resistance, and other characteristics are examples.[5] The number of additives required to optimise the lubricant formulation is determined by the type of lubricant formulation (oil- or water-based) and application. Simple formulations have one to three additives, whereas complex formulations, such as engine oils, can have up to ten additives.

### 1.1.3 Lubricant Additives

Lubricant additives are compounds or mixtures, when incorporated in base lubricating fluid, supplement its natural characteristics, and improve their field service performance in existing applications. Almost all lubricants contain additives to enhance their performance in amounts ranging between 5-25% wt.[6] These additives will be required in the future to maintain oil consumption control over the life of the equipment, while also providing a high level of thermal stability and enhancing low temperature fluidity.[3] The need to control sludge, soot, and general engine deposits will be more pronounced for dispersants. Similarly, detergents will play an important role in deposit reduction and will need to provide the proper sulphated and total base number (TBN) balance to meet the needs of new engines and emerging fuel types.[3]

Lubrication additives play a significant role in reducing the build-up of hazardous deposits on lubricated parts. Organic components in mineral oils and lubricants are prone to oxidation, especially at high temperatures and in the presence of air and metals. Consequently, because of this degradation, sludge and other insoluble deposits form and the fluid thickens. As a result, the additive pack must be oxidation stable as well as rust and corrosion resistant.[7]

Numerous additives have been developed to reduce the acidity of the products of sulfurous combustion of filthy fuel and to avoid the aggregation of soot and wear particles from combustion. Particle clumping can seriously harm engines by obstructing oil supply lines or even filters. The terms "detergent" and "dispersant" are used to describe additives that prevent the onset of any of these negative side effects.

The detergent and dispersant additives are the most commonly discussed types of additives. The incorporation of detergent and dispersant additives into a lubricant as surface-active agents (surfactants) is critical to preventing harmful carbon and sludge deposits, and deposits in critical areas of the engine would lead to engine shutdown and repair by dispersing engine sludge deposits at low temperatures and detergents at high temperatures.[3]

Furthermore, the basic functions of a lubricant are related to proper oil flow properties, which detergent and dispersant additives help to maintain by minimising oil thickening and thus maintaining viscosity stability and flow properties, as well as the containment of carbon sludge deposits that clog oil lines and result in lack of oil flow and subsequent engine failure.[8]

Originally, the term "detergents" meant substances with cleaning capabilities similar to those found in laundry detergents, but their primary function appears to be the dispersion of particulate debris, such as abrasive wear and soot particles, rather than the removal of existing dirt.[9] Daily detergents are water soluble, whereas lubricant detergents and dispersant additives are oil soluble.[8] Because both additives keep insoluble combustion debris and oil oxidation products dispersed within the lubricant and neutralise acids formed from fuel combustion products, the terms "dispersants" and "detergents" are frequently used interchangeably.[8] Dispersants are used to control low-temperature engine sludge deposits while detergents are used to control high-temperature engine varnish and lacquer deposits. Sludge deposits in certain engine parts may necessitate engine shutdown and repair.[8]
There are two types of detergent/dispersant additives: mild and over-based/alkaline additives. The majority of mild detergent/dispersant additives are composed of simple hydrocarbons or ashless chemicals (burnt compounds with no residual oxides). They are used to disperse soot (carbon) and other wear particles.

Calcium, barium, or zinc salts of sulphonic, phenolic, or salicylic acids are over-based detergent/dispersant additives. The term "over-based" refers to the use of excessive amounts of alkali in the manufacturing process of these additives. Dispersants and detergents account for 2% to 15% of all additives.[10] These compounds retain oil-insoluble combustion by-products in suspension and prevent the oxidation products from aggregating into solid particles.

Typically, they are metal-containing compounds with a significant hydrocarbon part and a hydrophilic area (Figure 5). The tail part of the polar group can operate as a solubilizer in the base oil, allowing pollutants to be linked together. The surfactants used to prepare over-based detergents have an amphiphilic structure. The polar head group may be a benzene sulfonate, phenate, salicylate, or phosphonate, which commonly binds to a calcium, magnesium, or sodium metal cation.[10] [11] While the metal carbonate functions as a neutralising agent, and the diluent oil acts as a compatible agent, the surfactants act as a dispersing agent. The phrase "over based" indicates that the amount of colloidal metal carbonate in the particle cores is larger than what is required to neutralise the surfactant acid; otherwise, it is referred to as "neutral" or "low basicity," indicating that the over based detergents have a greater capacity for acid neutralisation than their neutral salts.[10]

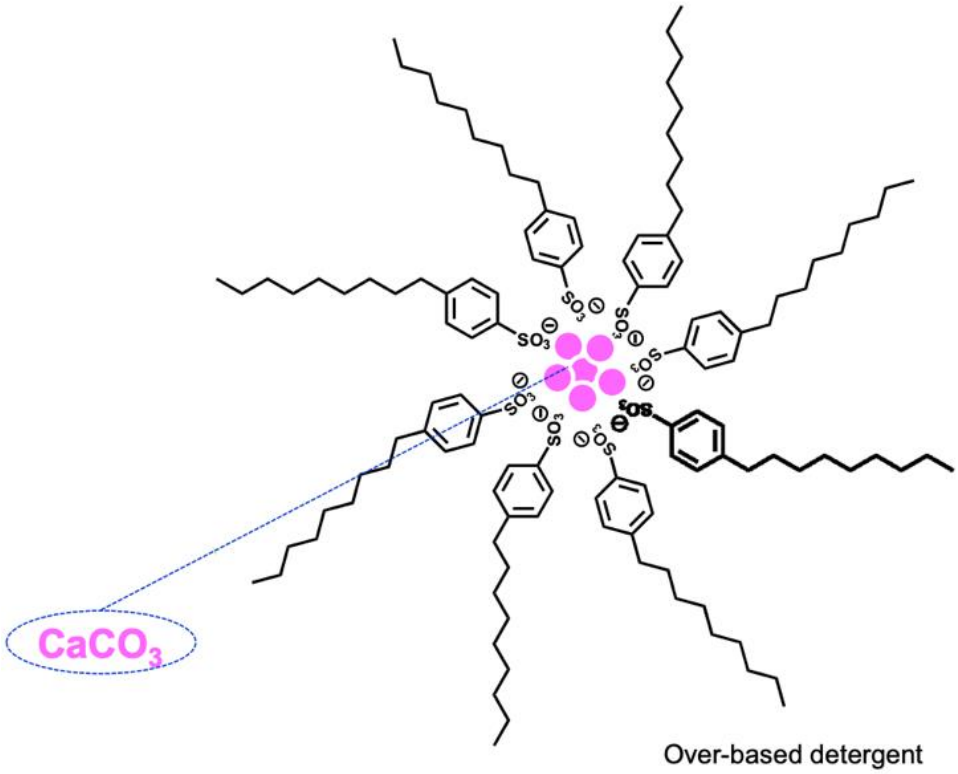



Figure 5: Over-based detergent.

There are four common types of detergent additives: sulfonates, phenates, salicylates, and phosphonates. The most common detergent additives are sulfonates, followed by phenates, salicylates, and phosphonates.[8] Detergents have a wide range of capabilities for preventing engine rust in both low temperature engine operation and when the engine is not in use.[8]

Engine antirust properties are provided by sulfonates, while oxidation inhibition is provided by phenates. Salicylate use is restricted, whereas phosphonate use is minimal.[8]

The additional base added to detergents accomplishes the critical goal of neutralising acids produced by fuel combustion products. Sulfur acid, nitro acid, and oxy acid are the three types of acids produced by fuel combustion. The sulfur compounds in the fuel oxidise to form sulfur oxides during the combustion process.[8] Sulfuric acid is formed when these oxides react with water, which is also a by-product of the combustion process. Sulfuric acid formation is common in diesel engine operation because diesel fuel contains up to 5% sulfur.[8] Nitro acids are produced directly from air, which contains 80% nitrogen, during the combustion process. Oxy acids are produced as a by-product of the oxidation of various lubricant base oils and fuel fragments.[8] The alkaline metal carbonates dispersed in a base oil formulation as colloidal particles must be amorphous as hard-core carbonate-sulfonate or carbonate-phenate reverse micelles.[3] These reverse micelles have previously been referred to as over-based detergents. The extra basicity of detergent additives used in engine oil formulation contains up to 30 times more metals than the corresponding neutral sulfonates detergent.[3]

Internal combustion engines generate by-products such as gases, soot particles, acids, water, and free radical sources.[3] Some of these by-products enter the crankcase via blow-by gases and adsorption in the thin lubricant film.[3] These are partly determined by the degree of additive aggregation in the base oil. In fresh oil, detergent additives take the form of reverse micelles that are in equilibrium with the saturated monomer solution.[3] They are involved in solubilisation, neutralisation, and adsorption depending on their chemistry.

Solubilisation of insoluble oxidation products and soot particles: The formation of reverse micelles prevents the agglomeration and contamination of said products through steric stabilisation (Figure 6) and electrostatic stabilisation mechanisms.[3] The steric stabilisation mechanism acts as a physical barrier to particle agglomeration caused by adsorption on particle surfaces.[3] Adsorbed dispersant acts as a physical barrier to particle attraction. The electrostatic stabilisation mechanism generates a surface charge on the particles via a proton transfer reaction between the surface of the soot particle and the detergent or hydrogen bonding formation complex.[3] The polarity of base oil is critical because solvated molecules in solution attach to insoluble particles via their polar fragment. This results in the formation

of an electrostatic field, which prevents the particles from clumping together.[3] Dispersants form hydrogen bonds with hydroxylic compounds found in used engine oils. This physical effect contributes to engine internal cleanliness by reducing agglomeration and subsequent deposition of sludge particles in the same way that detergents do.[3]

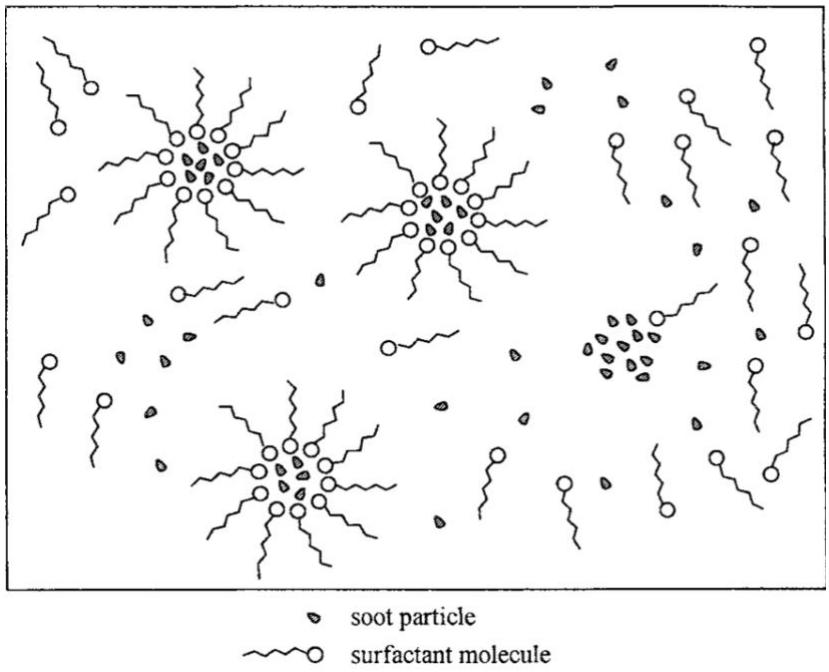



Figure 6: Steric stabilisation mechanism of soot particles by formation of reverse micelles and solubilisation.[3]

**Neutralisation (or deactivation) of acidic products**

Certain fuel materials, such as sulfur, can burn to form strong acids during the combustion process in diesel engines. The presence of highly alkaline materials in the oil aids in the neutralisation of these strong acids as they form.[3] As carbonate-sulfonate and carbonate-phenate contain more basic materials to neutralise mineral acids, the sulfonates and phenates may be neutral or highly alkaline (strong inorganic acids).[3] This neutralisation reduces corrosion and corrosive wear, as well as the acid's proclivity to cause oil degradation.[3] Organic acids can also be formed as a result of the oil's progressive oxidation, and these acids can be deactivated by the formation of hydrogen bonding complexes with detergents and dispersants.[3]

Adsorption on metal surfaces provides protection against pollutant deposition. Surface protection is achieved through physical adsorption, with the polar component of the additive

facing the metal surface.[3] Because the additive's solvation by hydrocarbons is minimal in this case, the hydrocarbon chain must be small enough to ensure additive adhesion. To ensure that the detergent performs optimally, the size of a hydrocarbon chain to which its polar group is bound must be adjusted.[3] The optimum molecular weight of the detergent is between 375 and 700.[3] Detergents compete with other additives through the same mechanism of action because they are physically adsorbed on metal surfaces. This negative synergy is especially noticeable in the case of so-called "friction modifier" additives, which are sometimes used to reduce friction and thus fuel consumption.[3] When detergent additives are present, the effectiveness of the coefficient friction modification is significantly reduced, according to laboratory test results.[3]

The addition of detergent additives has always been critical in the formulation of oils for diesel engines; after all, they are "dirtier" than gasoline engines.[3] The oil temperature in a diesel engine is higher, which promotes oxidation and the formation of insoluble substances. Diesel fuel combustion generates soot and $SO_3$. Diesel engines are also much less sensitive to the accumulation of oil-derived ash in their combustion chambers, allowing for the addition of a much greater amount of metal-based detergents.[3]

## 1.2 Emulsion

Internal combustion engines subject lubricants to significant heating and mechanical shearing during a normal operation. In addition to the primary function of lubrication, oils must contend with a variety of combustion products, primarily acidic gases, moisture, and carbon particles, all of which can harm the engine.[12] As a result, dispersant and detergent additives are included in the lubricant formulation. These surfactants and other additives, such as viscosity index improvers, can help to stabilise foams and emulsions that form under high shear conditions. Emulsions and foams can seriously impair an engine's effective lubrication by starving the lubricant or clogging oil ducts.[12]

The presence of unintentional water in the lubricant will quickly result in the formation of water-in-oil emulsions stabilised by dispersant and detergent surfactants.[12] Dispersants typically have a long hydrocarbon backbone (for example, polyisobutene with a molecular weight greater than 900) and a succinimide head group formed by reaction with a polyamine. Detergents, on the other hand, are made up of a $CaCO_3$ core encased in an alkyl-aryl

sulphonate or a sulfurised alkyl-phenol shell (Figure 5). Clearly, either type of product is capable of forming strongly anchored interfacial layers that provide the emulsions with a high degree of steric stability. Other polar materials, such as soot and oxidation products, tend to collect at interfaces. If the water droplets come into contact with each other, the repulsive interaction of the surfactants' long oleophilic segment keeps them apart.[12]

Water-in-oil (W/O) emulsions are used in a variety of industries, including food, pharmaceutical, petrochemical, and cosmetics. In practise, emulsion is a thermodynamically metastable system, so the main challenge for W/O production is to control the system's stability while also protecting it from destabilisation.[13] The separation of the oil and water phases of an emulsion can be observed during storage and/or as a result of temperature and electrolyte compound addition.[13] In emulsion, the most common destabilisation mechanisms are flocculation, coalescence, sedimentation, and Ostwald ripening.[13] Fluid W/O emulsions are less stable than oil-in-water (O/W) emulsions and can easily coalesce, flocculate, or sediment.[13] Furthermore, unlike O/W emulsions that are stabilised by both steric and electrostatic repulsion, W/O is only expected to be stabilised by steric forces due to the low conductivity of the continuous phase.[13] The addition of surfactant molecules to a particle system, or vice versa, affects their emulsifier efficiency.[14] As a result, the properties of the resulting emulsions are determined by the synergistic interactions between particles and surfactant at the emulsion droplet surface and in the bulk.

Zou êt al. (2013) proposed a synergic stabilisation mechanism for high internal phase W/O emulsions.[15] They demonstrated that neither surfactant nor particles could be used to stabilise emulsions. However, the dual emulsifier system produced satisfactory emulsion preparation results. Big emulsion droplets were preferentially stabilised by particles in the obtained W/O emulsion, while small ones were preferentially stabilised by surfactant molecules.[13] As a result, increasing the particle concentration resulted in a greater number of large emulsion droplets, while increasing the surfactant concentration favoured the formation of fine emulsion droplets.[13] Thus, the wide droplet size distribution was critical for the synergic stabilisation of the W/O emulsion with mixed emulsifier system. Previous research has focused on W/O emulsions stabilised by non-ionic emulsifiers or hydrophobic silica particles.[16] The obtained results demonstrated the difference in the stabilisation mechanisms of two systems. Solid particles efficiently stabilised emulsion droplets by forming a network in the oil phase that acted as a steric barrier to emulsion coalescence.[13] A progressive

destabilisation was observed after the addition of surfactant to a particle stabilised W/O emulsion, which was explained by the destruction of the particle network by surfactant molecules.[13]

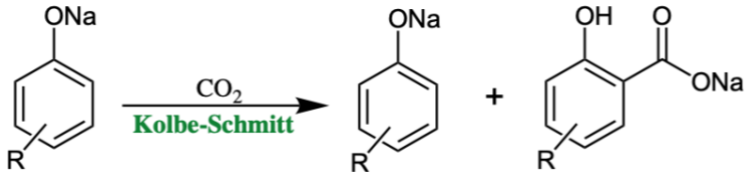
## 1.3 Kolbe-Schmitt Reaction

The quest for eco-efficiency of chemical processes has entered chemistry and chemical engineering, as evidenced by the new terms "Green Chemistry" and "Green Processing." Sustainable development is a global governing objective for a large number of society and industry processes, and it has entered chemistry and chemical engineering with the quest for eco-efficiency of chemical processes.[17] Hence, Lubrizol has invested in the Kolbe-Schmitt reaction as a more effective way of taking a phenolate and converting it to a salicylate to produce lubricants.

Over-based detergent is synthesised in an industrial setting using a four-step procedure. Sodium hydroxide is used to neutralise the alkyl phenol, resulting in sodium phenolate. After the Kolbe-Schmitt reaction, the alkali metal salt is converted to sodium alkyl salicylate. Transmetallation is used to produce calcium phenolate and calcium salicylate from the reaction mixture of sodium phenolate and salicylate salts.

### 1.3.1 Background

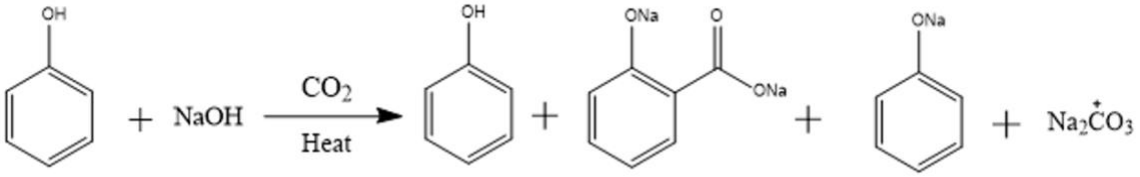
Developed by H. Kolbe in 1860, improved by R. Schmitt in 1885 and simplified by S. Marasse in 1893, the Kolbe-Schmitt reaction is the standard method for the synthesis of aromatic hydroxy carboxylic acids which are used in our daily lives. Kolbe – Schmitt reaction is a carboxylation reaction by heating sodium phenoxide with carbon dioxide under pressure (125 ºC, 4 atm) (Scheme 1).[18]




Scheme 1: Kolbe – Schmitt reaction

Kolbe succeeded in obtaining salicylic acid by heating a mixture of phenol and sodium with carbon dioxide at atmospheric pressure and acidifying the resulting sodium salicylate solution.[18] During his research to improve this variation in yield, Kolbe discovered that the reaction produced not only sodium salicylate and phenol, but also sodium phenoxide and

sodium carbonate (Scheme 2).[18] Despite the reaction's extremely dry conditions, half of the initial amount of phenol was volatilised from the reaction mixture (prior to the Kolbe-Schmitt reaction phenol is neutralised with sodium hydroxide and water is removed).[18] When the side reactions shown in Figure 7 occur, phenol usually distils from the reaction mixture at low $CO_2$ pressure and high temperature. Kolbe discovered that starting the reaction with sodium phenoxide instead resulted in a higher salicylate yield. However, Kolbe's yield was never greater than 50% because half of the starting phenol was lost due to volatilisation.[18]




Scheme 2: Kolbe reaction with phenol and sodium with carbon dioxide

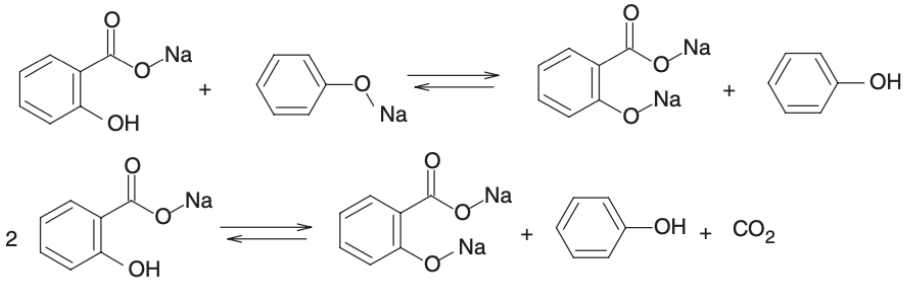



Figure 7: Side reactions [19]

Schmitt proposed a modification to the Kolbe reaction in which carbon dioxide was introduced under pressure, which significantly increased the yield.[18] Baine êt al. , for example, reported a 79 % yield of salicylic acid at 125 ºC and a carbon dioxide pressure of 80-135 atm. Under these conditions, no phenol is lost, and a nearly stoichiometric amount of salicylic acid is obtained.[18] This modification, known as the Kolbe – Schmitt reaction, is still used to make a wide range of hydroxy aromatic acids.

The conditions of the Kolbe – Schmitt reaction vary greatly depending on the starting alkali metal phenoxide, the pressure, temperature, and reaction time used, the use of solvents or suspension media, the degree of dryness, and a few other factors.[20] The difficulty in

achieving anhydrous conditions and maintaining a good dispersion effect for the gas-liquid-solid system is thought to be one of the main challenges in carrying out the Kolbe – Schmitt reaction.[20]

The Kolbe-Schmitt reaction takes place in the gas-solid phase in the modern industrial process for producing salicylic acid.[19] At 5 atm and temperatures up to 100 ºC, dry sodium phenoxide reacts with carbon dioxide. After approximately one mole of carbon dioxide is absorbed, the temperature is raised and maintained at 150 ºC -160 ºC for several hours. Salicylic acid (94-97 %) is the main product of the reaction between sodium phenoxide and carbon dioxide, though p-hydroxybenzoic and 4-hydroxy-isophthalic acids are also identified in the reaction mixture at low yields (2-4 %).

It is ecologically and scientifically important to activate relatively inert carbon dioxide as a building block for organic molecules. One of the few industrially significant $CO_2$ reactions is the Kolbe-Schmitt reaction. However, the Kolbe-Schmitt reaction exhibits insufficient regioselectivity toward ortho-carboxylation and para-carboxylation, and requires harsh reaction conditions such as elevated temperature and $CO_2$ pressure. Metal catalysis, organic promoters, microwave-assisted reactions, ultrasonication, and ionic liquids as solvents have all been tried to address these disadvantages.

### 1.3.2 Applications of Kolbe – Schmitt reaction

Kolbe-Schmitt reaction is used in different areas for different applications. One of the many applications is to produce aspirin (acetylsalicylic acid) as the product is a precursor to synthesising aspirin. Salicylic acid is used as medication to treat skin conditions like warts and dandruff by removing the outer layer of the skin. It is also a popular ingredient in many skincare products for treatments like dermatitis or acne.

Salicylate as previously mentioned is a detergent additive that improves the performance of lubricants in car engines. Salicylate is also a type of drug that relieves pain, anti-flammatory, reduces fever and prevents excessive blood clot.

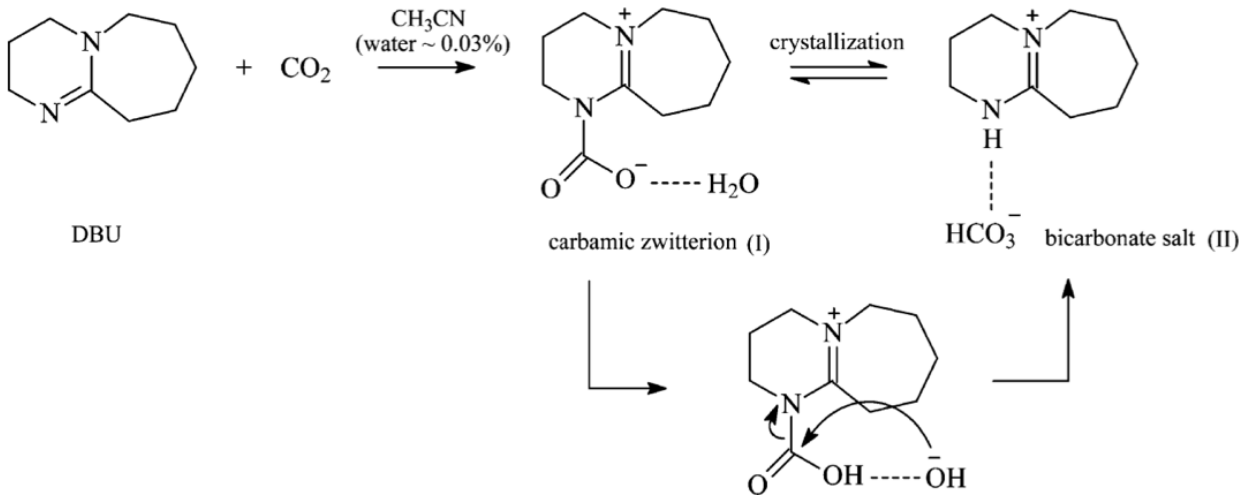
### 1.3.3 Improvements of Kolbe – Schmitt reaction

Since the original report of the Kolbe – Schmitt reaction in the 1900s, great effort has been made for its improvement or modifications; however, harsh reaction conditions such as high temperatures and/or high pressures are still needed for sufficient conversion. Examples of modifications of the reaction that were attempted: i) using promoters like an organic base, hindered phenolate etc, ii) using solvents in the reaction, and iii) using supercritical carbon dioxide.

#### 1.3.3.1 Promoters

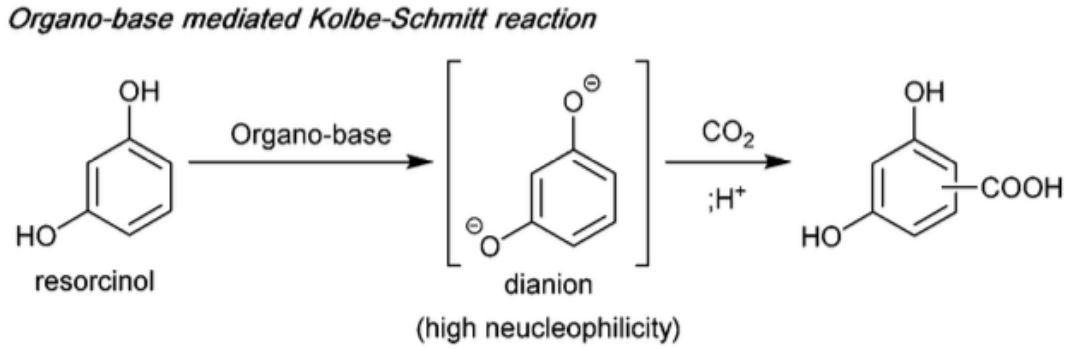
Strong guanidine bases have been known for some time, and it is observed that optically pure bicyclic guanidine bases are effective promoters in a novel catalytic enantioselective Strecker synthesis of chiral α-amino nitriles and α-amino acids.[21] One of the major challenges in developing practical processes to convert man-made $CO_2$ into useful chemicals is the thermodynamic stability of $CO_2$.[22] However, the simple reactions of organic bases with $CO_2$ to produce carbonate and carbamate salts are well-known and have been used in $CO_2$ scrubbing and, more recently, switchable polarity solvents. Understanding '$CO_2$ activation,' especially in the catalytic context, is critical to long-term $CO_2$ capture and utilisation processes.[22]

a) 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) a bicyclic guanidine that are strong nucleophilic bases (pKa = 23.9 in $CH_3CN$ and pKa = 16.8 in THF, nucleophilicity in $CH_3CN$ = 15.3). While the organic base-catalysed carbon dioxide fixation reaction into aromatics has received a lot of attention, there have been few reports on the reaction involving aromatic carbon-carbon bond formation with carbon dioxide.[23] Skydstrup recently reported organic base-catalysed carbon dioxide incorporation into alkynyl indoles via the formation of a $CO_2$ – guanidine complex (Scheme 3). This is an example of organocatalyzed $CO_2$ fixation involving C – C and C – O bond formation, and the reaction proceeds well with a small amount of carbon dioxide under atmospheric pressure, but the reaction still requires a high temperature (100 $^oC$).[23]




Scheme 3: Mechanism of formation of $CO_2$ – guanidine complex[24]

Sadamitsu êt al. (2019) used an organic base for resorcinols and observed a Kolbe – Schmitt type reaction under ambient conditions. When resorcinol (3-hydroxyphenol derivatives) was treated with DBU in a carbon dioxide atmosphere, the corresponding salicylic acid derivatives were produced in high yields via nucleophilic addition to carbon dioxide. They hypothesised that dianion species derived from resorcinol would have a high enough nucleophilicity to efficiently promote the addition reaction to carbon dioxide. Resorcinol has a low pKa, and the corresponding dianion could be easily generated by treating it with a strong organic base.[23]




Scheme 4: Kolbe-Schmitt type reaction of resorcinol using organic base[23]

b) Another organic base that is similar to that of DBU is 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (mTBD) Figure 8: . mTBD (pKa = 25.43 in $CH_3CN$ and pKa = 17.9 in THF, nucleophilicity in $CH_3CN$ = 14.4), like other guanidine bases, have been reported to catalyse reactions involving $CO_2$ and propargylamines. The proposed mechanism involves deprotonation of the substrate by a superbase, ie, the guanidine, rather than the formation of a guanidine-$CO_2$ complex.[22]

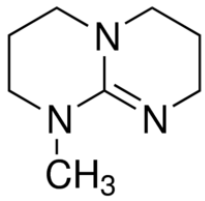
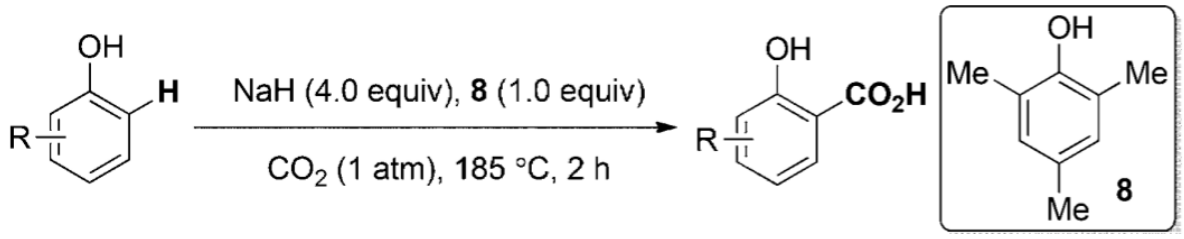



Figure 8: Structure of 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (mTBD)

c) Hindered phenol is another type of promoter that is used (Scheme 5). According to Junfei Luo êt al. (2016), using 2,4,6-trimethylphenol as a recyclable additive proved significant for the Kolbe – Schmitt reaction, as it increases the initial reaction rate while also improving the final carboxylation yield.[25] By avoiding the isolation of phenoxide, this method provides simple access to salicylic acids. Unlike the Kolbe – Schmitt reaction, their method allows for the transformation of a wide range of phenols into the corresponding salicylic acids in high yields under unified conditions.[25]



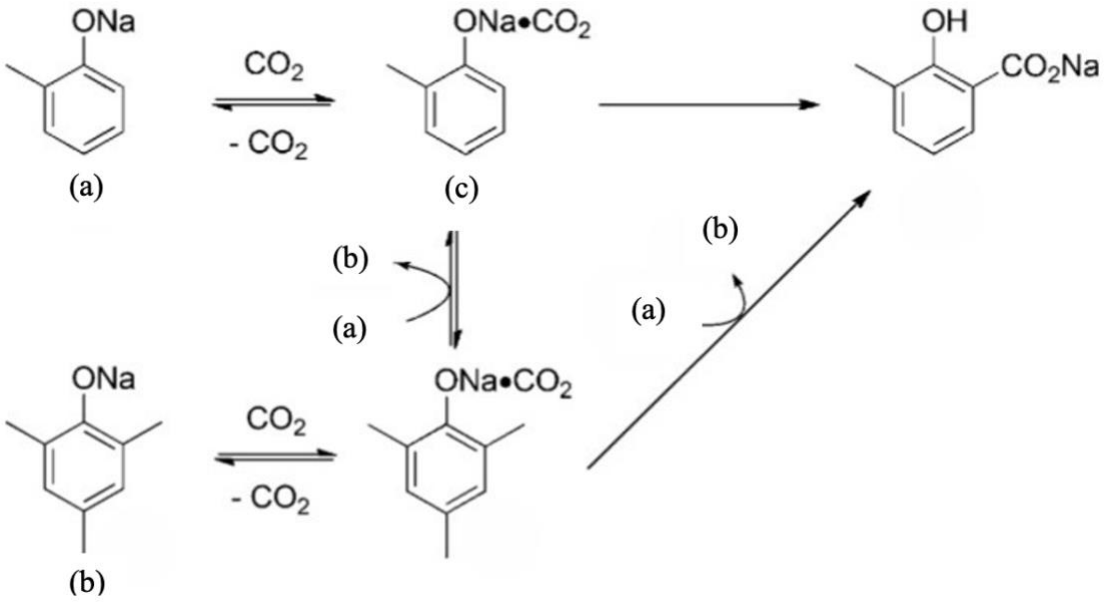

Scheme 5: Carboxylation of phenol with 8 being the hindered phenol used as a promoter.[25]

Junfei Luo êt al. investigated the kinetic profile of carboxylation in the presence and absence of 2,4,6-trimethylphenol to evaluate the effect of this additive. The addition of trimethylphenol significantly increases the initial reaction rate while also improving the final

carboxylation yield. This suggests that trimethylphenol plays an important role in facilitating the carboxylation reaction.[25]

Since the carboxylation reaction is dependent on the rate of mixing between the gas and solid phases, it was hypothesised that trimethylphenol could act as a mixing aid, thereby promoting carboxylation by increasing the surface area of the solid. The hypothesis was rejected since using glass beads instead of trimethylphenol in the carboxylation reaction did not improve the yield. As a result, this finding suggests that trimethylphenol does not serve as a mixing aid, but rather aids in $CO_2$ fixation and delivery to the reactive phenoxide.[25]

$CO_2$ is "fixed" (absorbed or adsorbed) by the solid reagents, and this fixed $CO_2$ is reactive during carboxylation. It has previously been proposed that only fixed $CO_2$ is reactive in the carboxylation step, not gaseous $CO_2$. According to Junfei Luo and colleagues, the primary role of sodium 2,4,6-trimethylphenolate, (b), may be to aid $CO_2$ fixation by increasing the amount of $CO_2$ able to react during the carboxylation step. Because 2,4,6-trimethylphenolate, (b), is ortho- and para-substituted with a methyl group, it cannot be carboxylated with the fixed $CO_2$. As a result, this fixed $CO_2$ can only react with (a), either by exchanging to form (c) and then carboxylating intramolecularly, or by reacting directly with (a) intramolecularly (Scheme 6).[25]




Scheme 6: Proposed mechanism for the role of trimethylphenol.[25]

d) Aluminium bromide

Iijima êt al. used $scCO_2$ to perform a regioselective carboxylation of phenol to salicylic acid in the presence of aluminium bromide.[26] They demonstrated that, in order to avoid the production and purification of alkali metal phenoxides in the two-step manufacturing process, the direct carboxylation of phenols and carbon dioxide is the most desirable route for the synthesis of aromatic hydroxycarboxylic acids. In previous studies, they used a variety of basic metal oxides, and the most effective base catalyst tested was potassium carbonate, which was 99% carboxylation selective for salicylic acid.[27] The reaction, on the other hand, took 10 hours to complete.

In this study, Iijima êt al demonstrated that the direct synthesis of salicylic acid in $scCO_2$ with the aid of a Lewis acid catalyst at moderate temperatures can be performed. This method yielded 56 % after the study and shows a high regioselectivity in the substitution of a carboxyl group in an ortho position.[26]

e) Potassium carbonate

The application of potassium carbonate as a promoter in Kolbe-Schmitt reaction is not uncommon. However, the catalytic mechanism of $K_2CO_3$ remains unknown. One group noticed that $K_2CO_3$ has a hybrid catalytic effect on the synthesis of salicylic acid from carboxylation of phenol with $CO_2$.[28]

They compared reaction of 3,6-dichlorosalicylic acid (3,6-DCSA) from 2,5-dichloro phenoxide and $CO_2$ to the same reaction with the addition of $K_2CO_3$. The first has a lower yield and slower rate compared to the latter. However, the yield of 3,6-DCSA is only minorly affected (deviation of 5%).[28] The results indicated that the Kolbe-Schmitt reaction between phenoxide and $CO_2$ can proceed without catalyst, but both the yield and the reaction rate are much lower than those using $K_2CO_3$. The reaction exhibits a better yield at higher temperatures, and doesn't occur below 80C, which proves that a higher temperature is favourable to form 3,6-DCSA.[28]

They performed an in depth DFT study on the structural $K_2CO_3$ and how it activates the $CO_2$ and behaves as a co-reactant. According to their results, $K_2CO_3$ may on one hand act as a

catalyst for the activation of $CO_2$ so that the reaction can be accelerated, while on the other hand, it also acts as a co-reactant in deprotonating the phenol formed by the side reaction to phenoxide, which is further converted to salicylate.[28]

Other studies that involve $K_2CO_3$ like the carboxylation of phenol with $CO_2$ under supercritical conditions, the hydroxyl group of phenol bonds to the basic $O^{2-}$ site on the surface of $K_2CO_3$, forming a phenoxyl anion that then releases a hydrogen atom to react with $CO_2$ to form salicylate anion.[27] [28] Yamaguchi êt al. proposed a catalytic mechanism for $K_2CO_3$ as a base catalyst based on their studies of new solid bases derived from supported metal nitrates or carbonates.[29] [28] They believe that $K_2CO_3$ supported on metal-oxide would decompose at moderate temperatures to form $(K^+)_2$-$CO_3^{2-}$, which acts as a basic active centre for carboxylation while simultaneously releasing one $CO_2$ molecule. Additionally, Cai êt al. employed an isotope tracer technique to investigate the direct synthesis of dimethyl carbonate (DMC) stimulated by $K_2CO_3$ and discovered that the carbonate group of DMC is partially generated from $K_2CO_3$,[30] [28] showing that $K_2CO_3$ is a precursor of the carboxyl group. Their conclusion appears to be consistent with Yamaguchi et al hypothesis of the $K_2CO_3$ decomposition process.[28]

f) Enzymes

One of the more intriguing approaches to the Kolbe-Schmitt reaction is the use of enzymes. Enzymatic carbon fixation has been known for being an interesting approach for $CO_2$ sequestration. Numerous decarboxylases can catalyse the reversible decarboxylation reaction in vivo, while also strengthening the carboxylation reaction in vitro.[31] In an alkaline environment, the Bio-Kolbe-Schmitt reaction is the mild carboxylation of phenols and $CO_2$ by hydroxybenzoic acid decarboxylases to create hydroxybenzoic acids.[31] Due to its high catalytic efficiency, selectivity, and environmental friendliness, bio-catalytic $CO_2$ fixation has surpassed chemical $CO_2$ fixation as the most important method of $CO_2$ conversion.

In the presence of bicarbonate as a $CO_2$-source, some enzymes catalyse the decarboxylation of benzoic acid derivatives and the reverse carboxylation of phenols to the corresponding salicylic acid derivatives.[32] Enzymatic carboxylation reactions not only avoided severe reaction conditions, but also exhibited exclusive ortho-position regioselectivity and a large substrate spectrum. These enzymatic reactions, however, are reversible.[32] The enzyme

kinetics and thermodynamics of the reaction suggested that the reaction equilibrium was unfavourable for carboxylation but more favourable for decarboxylation. As a result, the reported carboxylation conversions for the majority of decarboxylases and phenols were limited to 40%.[32] Thus, new strategies are formed in order to drive the equilibrium of enzyme-catalysed reaction toward the formation of carboxylation products like adding quaternary ammonium salts into the reaction as a reactant.[32]

#### 1.3.3.2 Effects of solvents on Kolbe – Schmitt reaction

Stanescu êt al. (2006) conducted a theoretical DFT study to confirm the Kolbe-Schmitt reaction mechanism and investigate the effects of solvents on the reaction.[19] The use of a solvent in the Kolbe – Schmitt reaction is desirable in order to achieve a homogeneous reaction mixture and possibly improve the reaction rate. Computer aided molecular design (CAMD) was used to create the candidate solvents, which were then tested using DFT solvation calculations.[19] The quantum mechanical calculations' results were then used to calculate the rate constants for each elementary step, the overall reaction yields, and the corresponding residence time. The methodology was tested on the reaction without a solvent, with solvents from the literature, and with the solvents designed. The study discovered that when high dielectric constant solvents are present, the reaction becomes reversible, resulting in low product yields.[19]

The Kolbe – Schmitt reaction has been reported to use a wide range of organic compounds as solvents or suspension media. Because alkali metal aryloxides are soluble in water, water would have been the obvious choice. Water, on the other hand, inhibits the carbonation of monohydric phenols and should thus be removed from the reactants prior to the reaction.[19] This could be due to strong chelation of water molecules with alkali metal aryloxides, which prevents carbon dioxide from being added at first.[19] Another reason could be the hydrolysis of the alkali salt to phenol and sodium hydroxide, which when combined with carbon dioxide results in the formation of sodium bicarbonate while the phenol remains unreacted.[19]

The design of solvents to be used in the Kolbe – Schmitt reaction includes several criteria:[19]

a) the solvents are inert toward the reactants and products. By reason of the potential reactivity of toward the alkali metal aryloxides, acids and halogens are excluded. Amines are also excluded due to their potential toxicity, which is not desired in the

pharmaceutical process. The types of compounds that are acceptable as solvents: acyclic, aromatic, and cyclic alcohols, phenols, aldehydes, ketones, ethers, and esters, compounds with double and triple bonds.

b) solvents must be able to solubilise and stabilise the product and is liquid under the reaction conditions

c) melting point: $T_m$ < 147 ºC, boiling point: $T_b$ > 152 ºC.

d) solvent with high solubility for the final product, ie, sodium salicylate, will stabilise it within the reaction mixture, thus improve the yield.

e) Solvents with low dielectric constants.

The kinetic analysis of the reaction in the presence of the designed solvents revealed that, while the solvents can dissolve the product and improve the rate constants of the reaction, there was no improvement in product yield.[19] This could be due to the reaction's reversibility. The findings of this study pointed to the final step's reversibility as the key to Kolbe – Schmitt reaction product yield. The final step of the reaction mechanism is irreversible in the classic solvent free reaction procedure. However, the presence of solvent, which keeps the product in the reactive phase, allows for a reverse reaction that shifts the equilibrium towards the reactants.[19]

According to the group's findings, solvents with high dielectric constants and high solubility are unfavourable for the Kolbe – Schmitt reaction.[19] Although the solvent's high dielectric constant can increase reaction rates, it can also allow reversibility to the point where no product is obtained. Solvents with a low dielectric constant, on the other hand, still favour reversibility of the final step of the reaction but have higher product yields.[19]

#### 1.3.3.3 Ultrasonication of Kolbe-Schmitt reaction

Shanthi êt al. carried out a variant of the Kolbe – Schmitt reaction that employs an ultrasonic environment to achieve milder conditions rather than employing energy-intensive high pressure and high temperature.[33] They discovered that using ultrasound to the Kolbe – Schmitt reaction saves more than 95 % and 38.6 % energy, respectively, and that the maximum yield of resorcylic acid is 30 % and 65 % in bath type and horn type sonicators.[33]

The use of ultrasound in organic synthesis has proven to be a valuable tool for increasing reaction rates and yields. It promotes the reaction in milder conditions where harsh conditions are normally required.[33] Ultrasound is capable of breaking the extremely stable bonds in $CO_2$. It has been used to speed up the rates of many chemical reactions; intense ultrasonic waves travelling through liquids create small cavities that enlarge and implode, producing enormous heat.[33]

### 1.3.4 Mechanism of Kolbe – Schmitt reaction

Despite extensive research and numerous theories proposed to explain the Kolbe-Schmitt reaction mechanism, this topic remains unresolved. Early research suggested that the reaction takes place via an intermediate complex called "sodium phenyl carbonate" (PhO – $CO_2$Na) that forms at room temperature.[19] However, Tijmstra asserted that the complex formed between $CO_2$ and PhONa is not "phenyl sodium carbonate," because this species readily loses carbon dioxide at 120 ºC.[34] Tijmstra hypothesised that a simple addition of carbon dioxide to sodium phenoxide results in the formation of a "phenyl sodium—carbonic acid" (Ph(ONa) – COOH). In the synthesis of ortho substituted products, Johnson and Luttringhaus demonstrated that the initial chelate rearranges with the formation of a cyclic intermediate, followed by hydrogen atom migration.[35] [19] A different mechanism involving phenyl sodium carbonate and metalated compounds was proposed by Gilma êt al.

Using infrared absorption spectra, Hales êt al. discovered evidence of the formation of a weak chelate complex between PhONa and $CO_2$ (PhONa – $CO_2$).[36] When the temperature is raised to 80 ºC the complex dissociates into the original reactants at low pressure (atmospheric or sub-atmospheric pressure). When pressure exceeds 4 atm, it does not dissociate under the Kolbe – Schmitt reaction conditions at 120 ºC -160 ºC. This research shows that when thermally activated, the chelate complex undergoes an intramolecular rearrangement, followed by electrophilic displacement of the ortho hydrogen. The absence of disodium salicylates products explained why Hales êt al. excluded ortho metallated aryloxides and dimetallated intermediates from the reaction mechanism.[36] [19]

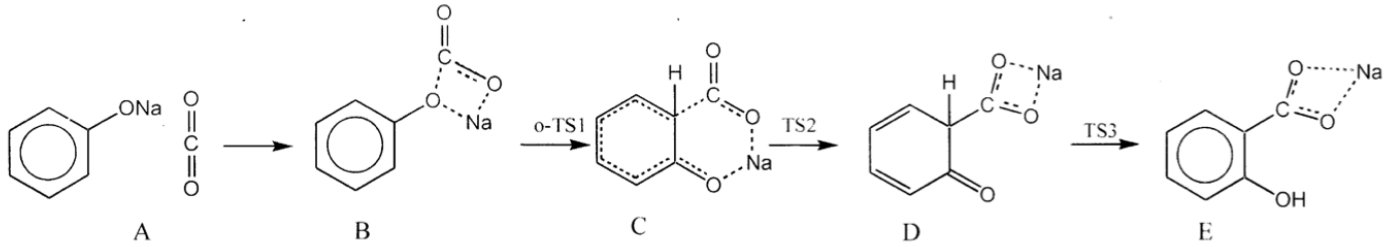
According to Ayres, the chelate complex undergoes further rearrangement into a complex with C – alkylation in the ortho position, followed by proton transfer to the phenolic oxygen.[37] Ayres also demonstrated that when solvents are added to the chelate, it

decomposes into $CO_2$ and PhONa (such as acetone, known to form complexes with phenoxides).[37] [19] Kunert êt al. used FT-IR and DTA to investigate the structure of solvent-free sodium phenoxide, revealing the presence of the PhONa – $CO_2$ complex as well as a further intermediate.[38] They came to the conclusion that direct carboxylation could be ruled out of the Kolbe – Schmitt reaction mechanism.

According to Kosugu êt al., the reaction proceeded via direct carboxylation of the aromatic ring, and the PhONa – $CO_2$ complex was not an intermediate in this process.[39] Thus, the formation of chelates competes with the formation of salicylic or p-hydroxybenzoic acid. However, their research was primarily focused on the carbonation of potassium phenoxide, and no precise mechanism based on their hypothesis has been presented.

Markovic êt al. employed quantum mechanical using Gaussian 98 software package and proposed a complete mechanism including three intermediates and three transition states:[40]

PhONa + $CO_2$ → B → TS1 (o-TS1, p-TS1) → C → TS2 → D → TS3 → Sodium salicylate (E).




Scheme 7: Mechanism for the Kolbe – Schmitt reaction. A: reactants, B, C and D: intermediates, o-TS1, TS2 and TS3: transition states, E: products. [40]

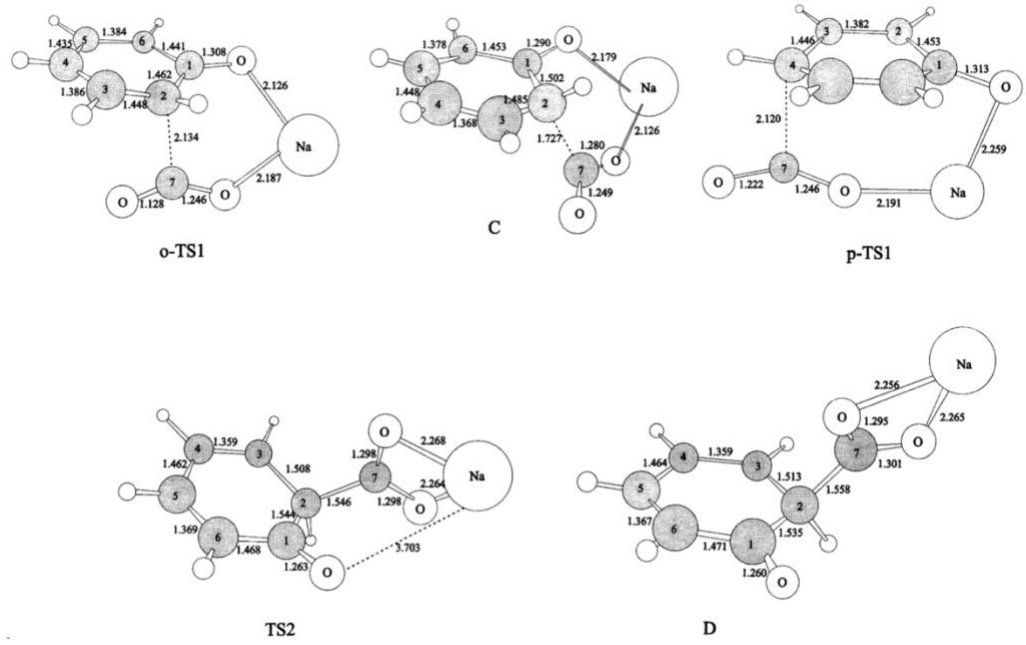



Figure 9: The optimised geometries of the transition states o-TS1, p-TS1 and TS2; and the intermediates C and D. [40]

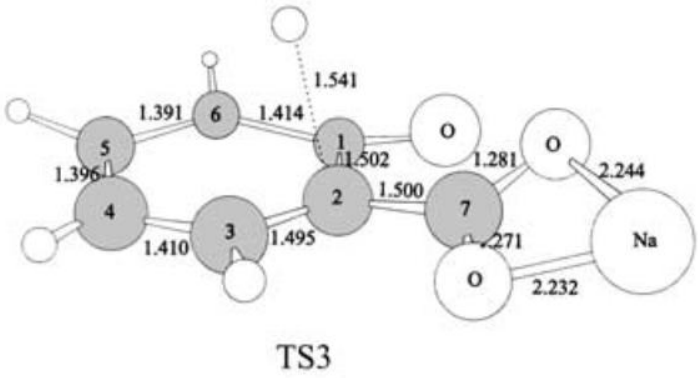



Figure 10: The optimised geometry of the transition state TS3. [40]

They identified the first intermediate as PhONa – $CO_2$ chelate, illustrating that carbon dioxide can only attack at the – O – Na site. The chelate undergoes intramolecular rearrangement, followed by electrophilic attack with ortho hydrogen atom displacement. Intermediate C has a structure similar to the chelate complex proposed by Hales êt al (1954). Markovic's research also explains quantitatively the low yields of p-hydroxybenzoic acid by-products and the equilibrium behaviour of the Kolbe – Schmitt reaction.

A mechanism (Scheme 7) based on the initial association of sodium phenoxide with carbon dioxide to form a complex, involving an intramolecular reaction with electrophilic displacement of the ortho – hydrogen.[40] The absence of disodium salicylate in the carboxylation products supports the mechanism. An intermediate complex structure in which the - electrons of sodium phenoxide are attracted by carbon dioxide, resulting in the formation of a weak Na-O bond. When exposed to higher temperatures, the NaOPh-$CO_2$ complex underwent an irreversible phase transition; the asymmetric stretching vibration at 1685 $cm^{-1}$ was divided into two bands at 1680 $cm^{-1}$ and 1651 $cm^{-1}$,[40] indicating the formation of a further intermediate of the Kolbe – Schmitt reaction. Sodium phenoxide has a melting point of 61 ºC - 64 ºC, implying that the crystal structure of sodium phenoxide must be destroyed under the conditions of the Kolbe – Schmitt reaction.[40]

Carbon dioxide can attack two positions in a sodium phenoxide molecule: the benzene ring and the polarised O-Na bond.[40] These two site attacks are regarded as the first step in the Kolbe – Schmitt reaction. Because carbon dioxide is a weak electrophile, a direct attack on the benzene ring (ortho, meta, para) yields no possible reaction path. As a result, carbon dioxide can only attack the O-Na bond, causing the system to stabilise and form the intermediate NaPh-$CO_2$ complex. This is due to the polarity of the O-Na bonds in sodium phenoxide and the C-O bonds in $CO_2$. According to the HOMO – LUMO analysis, the LUMO orbital of sodium phenoxide is practically only on the sodium atom, whereas the HOMO orbital of carbon dioxide is on the oxygen atoms.[40] The HOMO orbital of sodium phenoxide extends across both the benzene ring and the oxygen atom, whereas the LUMO orbital of carbon dioxide is primarily located on the $CO_2$. As a result, in the first step of the reaction, the reactive site is the O-Na bond; this step of the reaction proceeds without any activation barrier.[40]

The electrophilic carbon atom of carbon dioxide then attacks the ring at the ortho, meta, or para position. The activation energies of the ortho and para positions are 5.44 kcal/mol and 10.37 kcal/mol, respectively, but the activation energy of the meta position is unknown due to a lack of studies (Figure 11).[40] The difference in free energies of the two transition states determines the product distribution. The 4.9 kcal/mol difference in free energy between the ortho and para products results in a product concentration ratio of about 3300:1. With this information, the para substituted product is expected to have a very low yield.

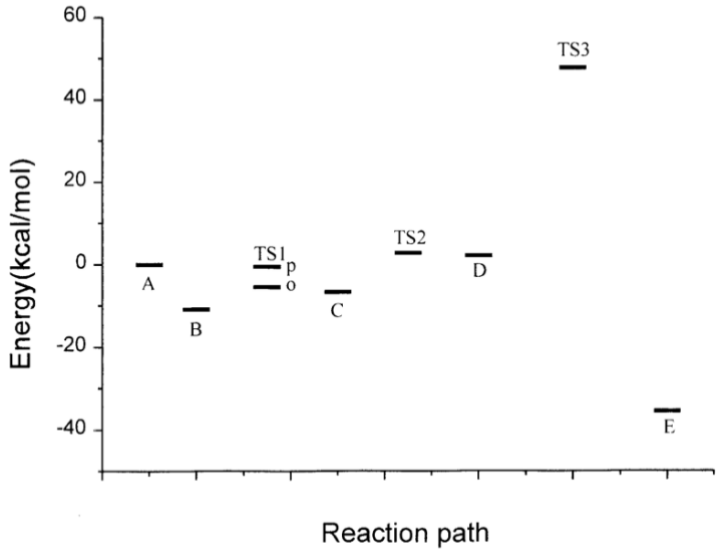



Figure 11: Energy diagram for the Kolbe – Schmitt reaction [40]

As a result, the electrophilic carbon atom primarily attacks the benzene ring in the ortho position. The reaction proceeds through the transition states o-TS1 and TS2 (Figure 9), producing the intermediates C and D. (Figure 9).[40] The intermediate D is converted to the final product, sodium salicylate, in the final step of the reaction by a 1,3-proton shift from C to O atom. This reaction path requires a high activation energy because it involves deprotonation of the C atom followed by protonation of the O atom via the transition state TS3 (Figure 10).[40] Because of their low activation energies, the intermediates C and D can easily undergo a reverse reaction, indicating that by performing the reaction under increased carbon dioxide pressure, the equilibrium is shifted to the final products of the reaction.[40]

It is worth noting that the distribution of the products in the Kolbe – Schmitt reaction is highly dependent on the metal cation, implying that the metal cation plays an important role in the reaction mechanism.

## 1.4 Supercritical Fluids

Global environmental awareness has resulted in the chemical industry exerting ever-increasing control over the use and disposal of hazardous materials. As a result, the chemical industry is constantly looking for new ‘cleaner' alternatives to its existing processes. The solvent is an obvious target area. Supercritical fluids (particularly $CO_2$), ionic liquids, perfluorinated hydrocarbons, and water are suitable candidates for replacing conventional organic solvents, or reactions can be carried out neat in the absence of a solvent.[41] Most chemical processes are performed in dilute solution to homogenise reactants, increase reaction control, and allow for simple product isolation.[41] This does, however, imply that massive amounts of waste solvents are produced in the production of relatively small quantities of products, particularly in the fine chemical and pharmaceutical industries.

Supercritical fluids (SCFs) have already proven to be effective solvents in extraction, chromatography, and a few specialised reactions.[41] SCFs are used on an industrial scale to extract hops, spices, flavours, perfumes, and to decaffeinate coffee. They have also been used in the extraction of natural product pharmaceuticals such as Taxol on a laboratory preparative scale.[41] The use of SCFs as reaction media has gained acceptance in the polymer industry, with polyethylene produced at levels exceeding 500 million lb/yr globally.[41] Recently, the use of supercritical carbon dioxide ($scCO_2$) as a polymerisation solvent has been used in the production of polymethylmethacrylate and polystyrene (Xerox, Toronto, Canada) and DuPont (USA) are reported to be investigating in a pilot plant for the production of fluoropolymers.[41] Other significant large-scale applications for $scCO_2$ are emerging, such as dry cleaning and spray painting, which will play an important role in the adaptation and acceptability of such technologies.[41]

A SCF is substances entering the SCF phase above their critical pressures (Pc) and temperatures (Tc) (Figure 12).[42] Some substances have readily accessible critical points, for example Tc for carbon dioxide is 31 ºC and Pc is 72.8 atm, whereas other substances need more extreme conditions. For example, Tc for water is 374 ºC and Pc is 218 atm.[42] The most useful SCFs to green chemists are water and carbon dioxide, which are renewable and non-flammable. In addition to reactions in the supercritical phase, water has interesting properties in the near-critical region and carbon dioxide can also be a useful solvent in the liquid phase.

Collectively, carbon dioxide under pressurised conditions (liquid or supercritical) is sometimes referred to as dense phase carbon dioxide. [42]

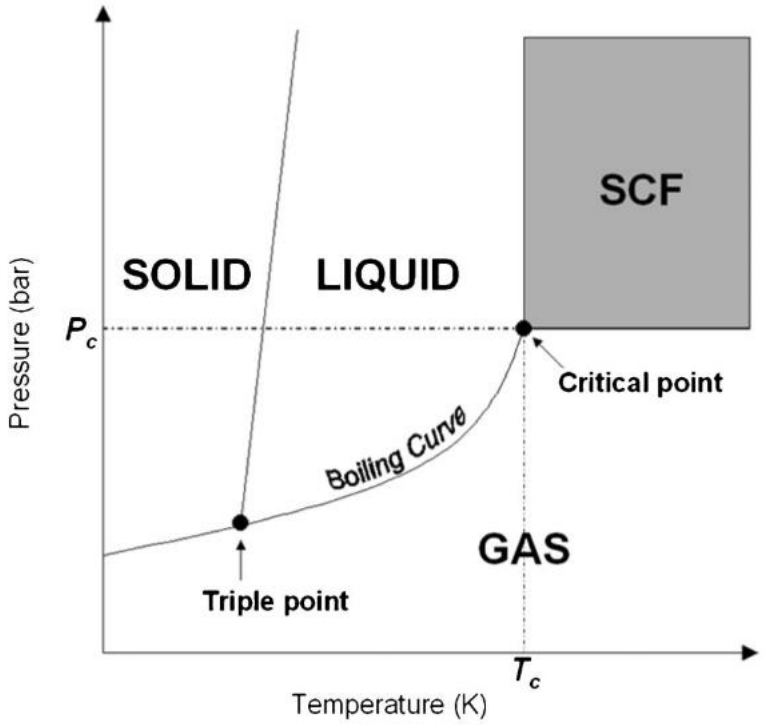



Figure 12: single-component phase diagram highlighting the supercritical fluid (SCF) region and the critical point. [42]

The critical point of a SCF is the highest temperature and pressure at which the substance can exist in equilibrium as a vapour and liquid.[42] The solid, liquid, and gas phases coexist at the triple point. The boiling curve denotes the gas-liquid coexistence curve. As the temperature and pressure rise along the boiling curve, the liquid becomes less dense due to thermal expansion, while the gas becomes denser as the pressure rises.[42] The densities of the two phases eventually converge and become identical, the distinction between gas and liquid vanishes, and the boiling curve terminates at the critical point.[42] A high-pressure view cell can be used to observe this transition. It is important to remember that the homogeneity of a reaction mixture can change during the course of the reaction.[42] It should also be noted that when reagents or cosolvents are added to a SCF, its properties can change dramatically, and the phase diagram for the reaction mixture can differ significantly from that of the pure substance. [42]

One of the primary distinctions between SCFs and traditional solvents is their compressibility. [42] Above the critical point, no distinct gas or liquid phase can exist, and the SCF phase has a unique combination of properties from both gas and liquid states. SCFs have low viscosity and high diffusion rates at liquid-like densities, just like a gas. Conventional solvents require very large pressure changes to change density, whereas the density of a SCF changes significantly as pressure increases. [42] Because solubility in a SCF is proportional to density, this medium has the added benefit of being tuneable, allowing species solubility to be directly controlled. Purification or reaction quenching can thus be accomplished by lowering the density of the solvent and precipitating the product. [42] The selectivity and outcome of some chemical reactions can be affected by varying the density. Gases at pressures lower than supercritical can be used to expand organic solvents, resulting in the formation of a gas-expanded liquid (GXL) phase. [42]

The widespread interest in SCFs is due, in part, to the additional benefits that SCFs provide aside from being environmentally friendly. Many of these are the result of SCFs having physical properties that are intermediate between those of gases and liquids. [42] It should be noted that reactions or other processes in SCF media are not novel on an industrial scale. Many industrial reactions developed in the early twentieth century, such as ammonia synthesis (BASF, 1913), methanol synthesis (BASF, 1923), and ethylene polymerisation, are carried out under supercritical conditions of either their product or reagent (ICI, 1937). [42]

### 1.4.1 Supercritical and liquid carbon dioxide

Carbon dioxide is widely regarded as the most viable supercritical solvent in many cases. It is relatively cheap and can be obtained as a by-product of fermentation and combustion. It is nontoxic and free of VOCs. [42] When compared to other alternatives, it is non-flammable and relatively inert. It can react with nucleophiles (for example, carbamic acid formation from amines), but this is reversible and can be used synthetically. [42] Carbon dioxide also has many chemical advantages that help it to be more environmentally friendly by reducing waste. For example, it cannot be oxidised, so oxidation reactions involving air or oxygen as the oxidant have been extensively studied. In addition, unlike many conventional solvents, it is inert to free-radical chemistry. [42] This has resulted in a great deal of research into free-radical-initiated polymerisations. There are also a number of practical advantages to using $scCO_2$ as a solvent. Simple evaporation is used to isolate the product to total dryness, which could be

useful in the final stages of pharmaceutical synthesis where even trace amounts of solvent residues are considered problematic. [42] Given the critical point of carbon dioxide, the majority of processes reported to date have been carried out at pressures ranging from 100 to 200 bar. The potential danger of such conditions should never be ignored, and safety precautions should be taken for all experiments.

The disappearance of the distinction between liquid and gas phases can be seen visually in an autoclave with a window, where the meniscus between liquid and gas disappears as the critical point is reached (Figure 13).

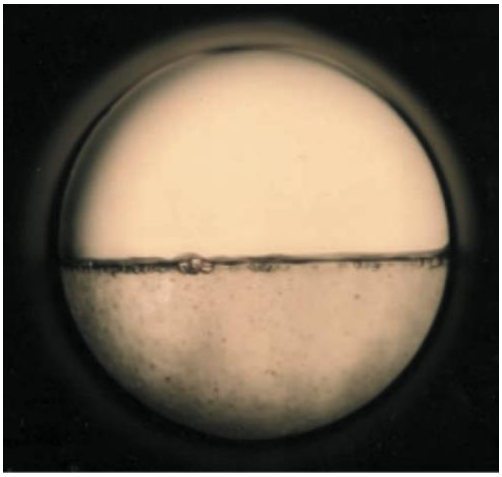
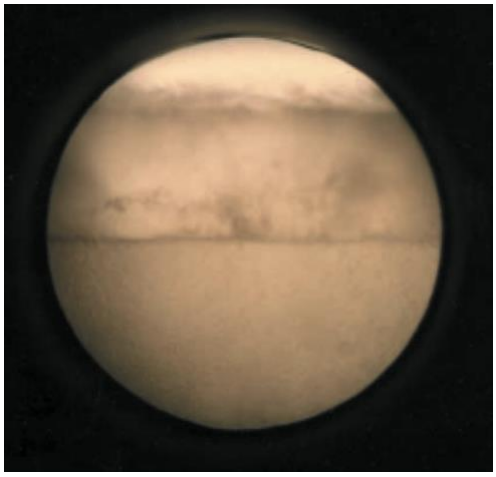
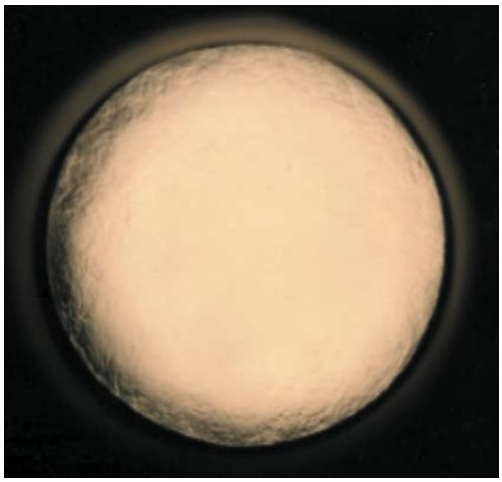


Figure 13: (a) Two-phase system - depicts a two-phase liquid-gas system with a distinct meniscus. The meniscus becomes less defined as the system's temperature and pressure rise.



(b) Less defined meniscus - This is due to a decrease in the difference in densities between the two phases.



(c) Homogenous system - there is no meniscus, and the system is now a single homogeneous SCF. [41]

It should be noted that adding reagents or co-solvents to a SCF can cause significant changes in its properties. [42] Although $CO_2$ is described as supercritical in many examples in the literature, this may not be the case for solutions containing significant concentrations of additional reagents, so the term should be used with caution. The term ‘dense phase $CO_2$' is frequently used, especially when the actual phase of a mixture is unknown. [42]

A SCF has physical properties that are intermediate between those of a gas and those of a liquid. In reality, this definition is oversimplified because the properties of a substance can vary dramatically within the SCF phase boundaries as temperature and pressure are changed. [41] Carbon dioxide has a density of approximately 0.41 gml-1 near the critical point. [41] However, as the pressure is increased, the density of the fluid increases dramatically, to the point where the SCF has a density comparable to that of liquid carbon dioxide at approximately twice the critical pressure (Figure 14). [41]

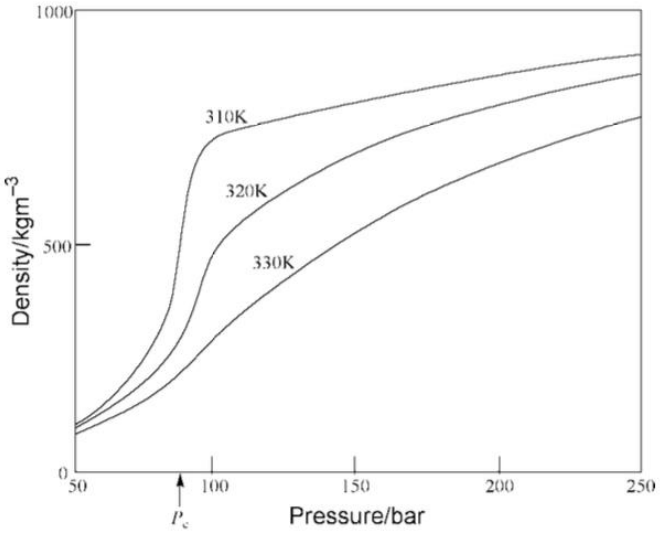



Figure 14: Variation of density with pressure for pure carbon dioxide above the critical temperature. [41]

Modification of the density (and hence solvent power) of this reaction medium may exhibit some control over reaction pathways. A number of reactions have been reported in which product selectivity is controlled by variation in SCF density, in some cases, with results far superior to anything possible using conventional solvents. [41]

Table 1 compares typical values for physical properties of a pure substance in various phases, including that of a SCF, which is approximately two orders of magnitude higher than that of a gas but less than half that of a conventional liquid phase. [41] The viscosity and diffusivity (which is strongly related to viscosity) are also temperature and pressure dependent and are generally at least an order of magnitude lower and higher than in the liquid phase. [41] If a chemical reaction is particularly fast, diffusion may be rate limiting, and an increase in diffusivity may result in an increase in reaction rate. [41] This principle is especially relevant to unimolecular fission reactions (where increased diffusion allows for an increase in radical

separation rather than recombination) and highly efficient bimolecular processes such as free radical or enzymatic reactions. [41]

Table 1: comparison of the physical properties of gases, liquids and SCFs [41]

| Property | Gas | SCF | Liquid |
|---|---|---|---|
| Density/ g $ml^{-1}$ | $10^{-3}$ | 0.4 | 1 |
| Viscosity / Pa s | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ |
| Diffusivity / $cm^2$ $s^{-1}$ | 0.1 | $10^{-3}$ | $10^{-5}$-$10^{-6}$ |

### 1.4.2 Solubility in $scCO_2$

All gases are miscible with SCFs. This is especially important for catalysis in SCFs, specifically $scCO_2$. [42] The concentration of hydrogen in a supercritical mixture of hydrogen (85 bar) and carbon dioxide (120 bar) at 50 ºC, for example, is 3.2 M, whereas the concentration of hydrogen in THF at the same pressure is only 0.4 M. [42] As a result, where gaseous reagents have traditionally been used in the solution phase, there is the potential for significantly improved chemical processes. [42] Solute-solvent clustering is another feature of SCFs that improves solubility at moderate densities (near the critical point) (Figure 15).

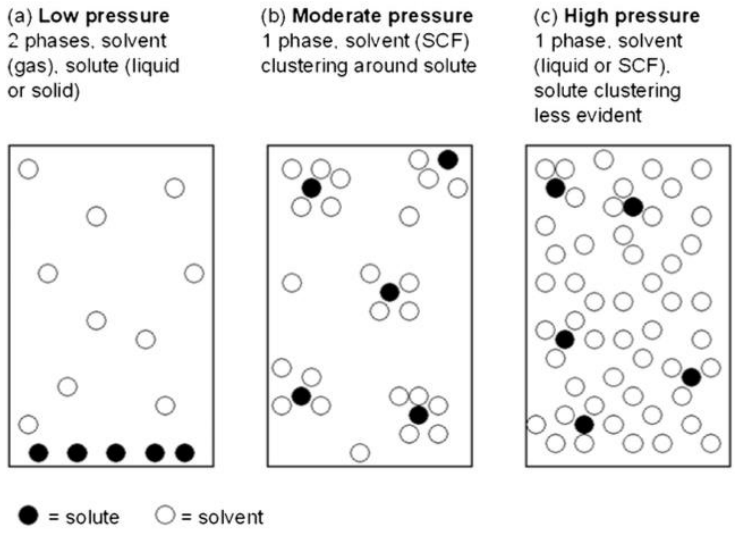



Figure 15: Schematic representation of solute–solvent clustering in an SCF, compared with liquid-phase solvation and lack of solvation in the gas phase [42]

Other reagents, in addition to gases, have good miscibility or solubility in SCFs, such as low molecular weight organic compounds such as cyclohexene and caffeine. [42] It is critical to evaluate the solubility and phase behaviour of reactants because the reaction could be occurring as a ‘solvent-free' process in a carbon dioxide atmosphere and not reaping the full benefits of using $scCO_2$. [42] It should be noted, however, that performing biomass transformation under carbon dioxide can have a beneficial effect on reaction outcomes even when the reaction is not in $scCO_2$. Cloud-point data is the traditional method for obtaining solubility data for substances in SCFs. [42] Temperature and pressure are varied in a solvent-solute system, and a graph is obtained to show when the substance falls out of solution and forms 'clouds.' [42]

There are a number of methods that can be used to overcome the limited solvating power of supercritical carbon dioxide: [42]

- Increasing the bulk density of the SCF. This is simple but not always desired, as higher pressures mean higher costs. Addition of a cosolvent.
- Modifiers (e.g. MeOH) can be added to increase or decrease polarity. However, the more modifier that is added, the further $scCO_2$ moves away from being the ideal green solvent. Reagents themselves may also in effect act as cosolvents.
- Biphasic syntheses.
- Carbon dioxide is finding increasing use in combination with other green solvents, including ionic liquids and water.
- Modification of the solute
- Organic fluorocarbons, siloxanes, and related compounds are more soluble in $scCO_2$ than corresponding hydrocarbons. These compounds are referred to as '$CO_2$-philes' as a group. The effect of increased fluorocarbon species solubility has been used in the design of surfactants, chelating agents, and ligands to improve the solubility of polymers, metals, and catalysts, respectively.

### 1.4.3 Extraction

Supercritical carbon dioxide is frequently used in Supercritical Fluid Extraction (SFE) and Supercritical Fluid Chromatography (SFC) (SFC). [42] Because it is chemically pure, nontoxic, non-flammable, nonpolar, stable, colourless, odourless, and tasteless, it is an excellent extraction solvent. Most importantly, it is simple to remove and highly selective. Further processing is possible after extraction; for example, the scent can be impregnated into a material for slow release. [42] Carbon dioxide has been used in the beverage, food, flavouring, and cosmetics industries. This is attributable in terms of the fact that products that are processed using carbon dioxide can be labelled as natural and environmentally friendly. [42] Some of the benefits and drawbacks of SFE in comparison to other extraction techniques are discussed in Table 2. [42]

Table 2: Comparison of SFE with some other commonly used extraction techniques. [42]

| | Advantages |
|---|---|
| SFE | – low-temperature extraction results in minimal degradation of volatile compounds<br><br>– higher product yields than with steam distillation<br><br>– spent material undamaged unlike steam distil/solvent extraction |
| Steam Distillation | – low capital running costs<br><br>– applicable to most essential oils, fragrances and flavour compounds<br><br>– designs available to suit all volumes |
| Solvent Extraction | – nonselective; wide spectrum of compounds extracted simultaneously that can be a disadvantage too.<br><br>– extraction carried out at various temperatures and pressures<br><br>– solvents can be readily removed at atmospheric or reduced pressure |

Disadvantages:

– very high capital installation costs

– high running costs

– requires technically skilled operators

– not suitable for wet raw materials

– lower product yield than solvent extraction

– unpredictable degradation of some groups of compounds

– cleaning between products can be difficult

– extraction of further products from residue can be difficult due to high moisture level

– most solvent residues must be monitored and tightly controlled

– most used solvents are highly flammable and possibly toxic

– waste has little or no value

**Carbon dioxide as a replacement solvent**

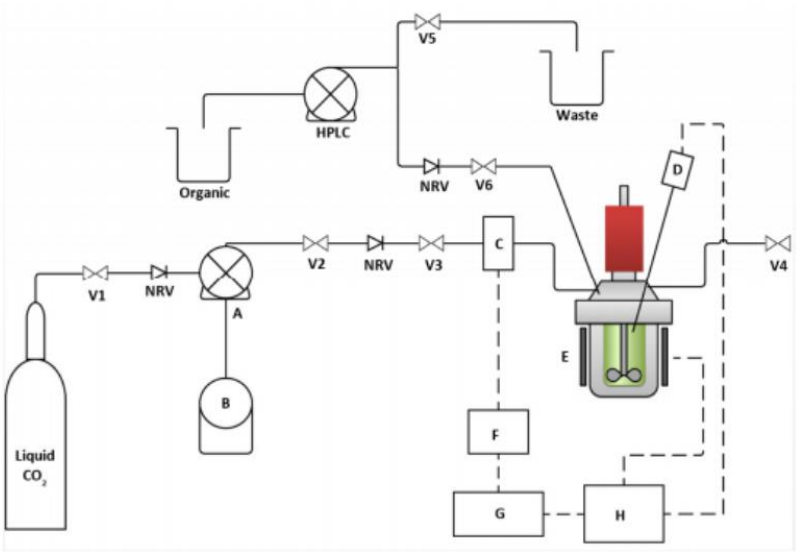
Supercritical $CO_2$ has the potential to be the ideal green solvent. It is non-toxic to the environment and personnel, but it is an asphyxiant, and a large accidental release could be hazardous. Because carbon dioxide is gaseous at atmospheric pressure, simple depressurisation will result in no hazardous solvent effluent requiring complex and/or expensive waste treatment. Carbon dioxide is a greenhouse gas, but it is abundant as a by-product of fermentation, combustion, and ammonia synthesis. It is relatively inexpensive and readily available on an industrial scale in extremely pure form (>99.9% purity). On a laboratory scale, high grade carbon dioxide is available in >99.995% purity, at a cost of approximately £70 per 25kg. [41]

There are also a number of practical advantages to using $scCO_2$ as a solvent. Simple evaporation is used to isolate the product to total dryness. This could be especially helpful in the final stages of pharmaceutical synthesis, where even trace amounts of solvent residues are considered problematic. [41] Rapid expansion of supercritical solutions (RESS) and supercritical anti-solvent precipitation are two complementary routes to particle formation with SCFs and $scCO_2$ (SASP). [41] These techniques, when combined, enable the processing of a wide range of solid materials with high morphology control. In terms of the chemistry that can be achieved, there are a number of potentially interesting and useful properties of $scCO_2$ media. [41] Most conditions render carbon dioxide chemically inert. It is non-flammable, non-protic, not strongly lewis acidic or basic, and is inert to radical and oxidising conditions. It can react with nucleophiles (for example, carbamic acid formation from amines), but this reaction is reversible and can be used synthetically. This general lack of reactivity is critical to $scCO_2$'s success as a common replacement for more traditional solvents.

# 2. Experimental

## 2.1 High pressure equipment and setup

A 60 mL base autoclave was used throughout the project. The reaction vessel was designed and built at the University of Nottingham. The autoclave is pressurised through a Pickel's pump NWA PM101 and is then vented through an outlet tap. Figure 16 illustrates the key parts and safety features of the autoclave.




| | | | |
|---|---|---|---|
| V1-6 | HiP needle valves | D | K-type thermocouple |
| NRV | Non-return valve | E | Heating jacket |
| HPLC | HPLC pump | F | Pressure monitor |
| A | PM-101 SFE pump | G | Trip-fuse box |
| B | Compressor | H | Heater control box |
| C | Pressure transducer | | |

Figure 16: Schematic diagram of a high-pressure autoclave setup [43]

The carbon dioxide is supplied from a liquid carbon dioxide ($CO_2$) cylinder with a dip tube, which travels through the V1 needle valve and then through the non-return valve. The non-return valve prevents materials from the autoclave flowing back into the carbon dioxide cylinder. $CO_2$ is pumped with the aid of a pump (A) and a compressor (B) and monitored with the pressure transducer (C). This is a piezoelectric transducer which is connected to the inlet pipe leading to the autoclave. The applied pressure deforms the piezoelectric material in the transducer, which produces a measurable current. The pressure transducer is placed outside the autoclave to prevent interference from the reagents inside the autoclave. The transducer (C) is connected to a pressure monitor (F), which is connected to the heating

control box (H) that controls the temperature of the heating jacket (E). The temperature inside the autoclave is determined by the thermocouple (D), which sends a signal to the heating control box to display the temperature. One of the safety features of the autoclave is that the trip-fuse box (G) is connected to the pressure monitor and the heating control box. The trip-fuse is set to a certain safe pressure (<30 MPa). If this pressure is exceeded, the heating is turned off in order to lower the pressure. The autoclave is also connected to a high-performance liquid chromatography (HPLC) pump, which is used to pump reagents into the autoclave while at high pressure.

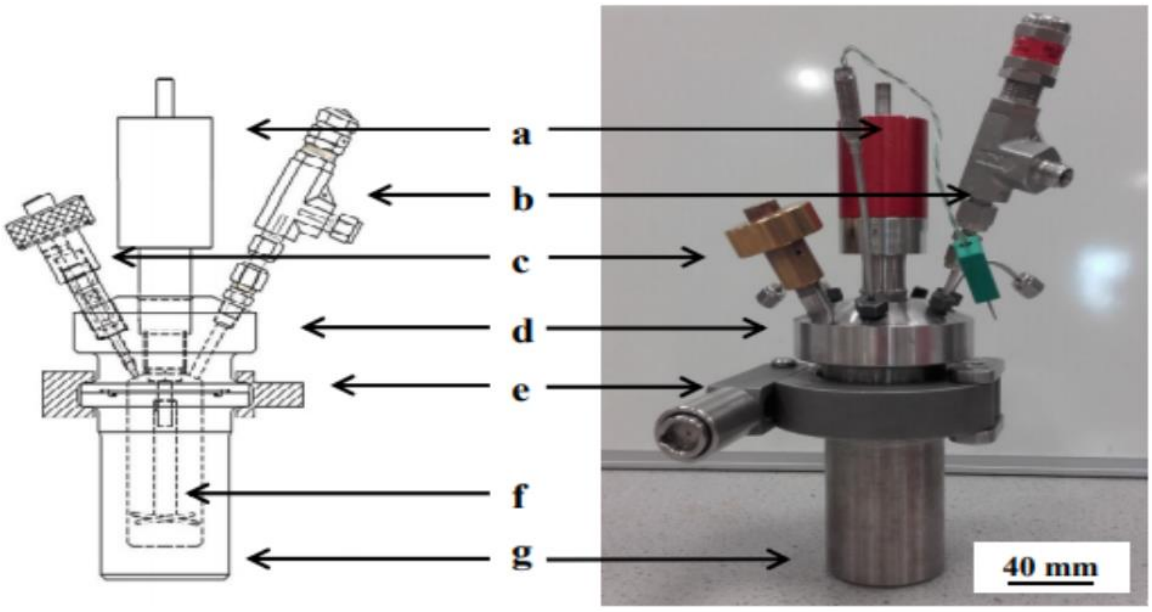



Figure 17: Schematic diagram of key autoclave features: A – magnetically coupled stirrer, B – burst disk, C – clamp key and safety needle, D – autoclave head, E – clamp, F – Stirrer, G – autoclave base.[43]

The key parts of the autoclave are shown in Figure 17. The sample is transferred into the autoclave base (g) and the autoclave is held together by the clamp (e), which can only be locked and opened with its unique clamp key. An EPDM O-ring is inserted between both the head and the base to act as a seal between the interfaces. The stirrer (f) is connected to a magnetically couple stirrer (a), and it is powered by an overhead stirrer, which is connected by plastic tubing. The autoclave head has several openings: one for the thermocouple, one for the clamp key, one for the outlet tap, one for the HPLC inlet tap, and one for a burst disc (b). This is another safety feature as the burst disc is set to rupture at 34 MPa thereby safely

venting the excess pressure. Reactions at higher temperature (>120 °C), a different burst disc is used.

The autoclave used is made of 316 stainless steel and can be safely used up to 34.5 MPa and 300°C. Although the autoclaves can reach these conditions safely, the O-rings which are used in the autoclave cannot. The O-rings are composed of an ethylene propylene diene polymer (EPDM) rubber and can withstand temperatures from -55 °C to 150 °C. Therefore, for reactions above 120 °C, a Teflon O-ring with silicone core must be used instead as it withstands temperatures from -100 °C to 250 °C.

**Set-up variations for high temperature reactions**

**O – Rings**

Two different types of O – rings were used in the reactions (Figure 16). Rubber O - rings, or ethylene propylene (EPDM) O - rings, are a family of synthetic elastomers with lower cost steam and chemical resistance, particularly for applications involving solvents, acids, and other mild chemicals. These O – rings can withstand temperatures from -55 ºC to 150 ºC. The other O – ring is the FEP encapsulated O-ring, which is comprised of an elastomer core which has been seamlessly encapsulated in a jacket of Teflon fluoropolymer. The core is either Viton, Silicone or EPDM. The jacket is FEP or PFA and it can withstand temperatures from -100 °C to 250 °C.



Figure 18: Left – (EPDM) rubber O – ring, Right – Teflon O – ring

**Burst disc**

Burst discs (Figure 19) are used in autoclave safety heads assemblies as an economical replaceable relief device to guard against system over-pressure. There are two different burst discs used during the reactions, a regular burst disc that withstands up to 4000 psi / 276 bars of pressure at maximum temperature of 120 ºC. The second kind is a high pressure burst disc that could withstand up to 4000 psi / 276 bars or more of pressure at temperatures up to 200 ºC.

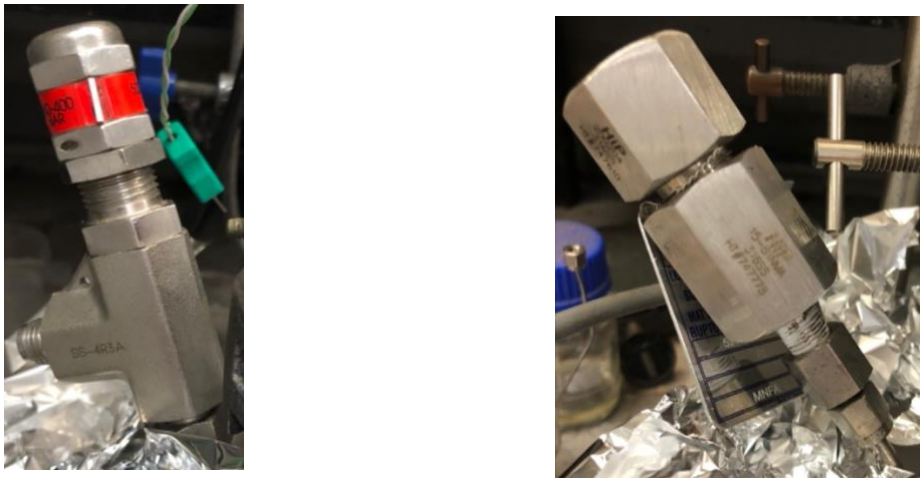


Figure 19: Left – regular burst disc, Right – high pressure burst disc

## 2.2 Materials

Sodium alkyl phenolate (OS 432459), calcium alkyl phenolate (OS 435989), alkylphenol (OS 390095), calcium alkyl sulfonate (OS 104413CJ), diluent oil (OS 79419BC) were supplied by Lubrizol. Potassium hydroxide, magnesium sulfate, hydrochloric acid, sodium chloride, calcium carbonate, calcium chloride purchased from Fisher Chemical. t-Butyl methyl ether, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 2,4,6 – trimethylphenol were purchased from Sigma Aldrich. $CO_2$ was purchased from Air Products.

Sodium alkyl phenolate, calcium alkyl phenolate, calcium alkyl sulfonate were weighed accordingly beforehand and left in vacuum overnight to ensure there were no water/moisture before using as any water present would inhibit the reaction. The rest of the materials were used as received.

## 2.3 Superbase surfactant Characterisation

### 2.3.1 $^{1}$H and $^{13}$C Nuclear Magnetic Resonance (NMR) spectroscopy

$^{1}$H and $^{13}$C NMR spectra were recorded using a Bruker AV-III 400 MHz spectrometer that is two channel with broad-band tuneable liquid-nitrogen cooled cryoprobe. Chemical shifts were recorded in $\delta_H$ (ppm). Samples were dissolved in deuterated chloroform to which chemical shifts are referenced. MestreNova software was used for analysis of spectra.

**Quantitative $^{13}$C Nuclear Magnetic Resonance (NMR) spectroscopy**

The quantitative carbon NMR was recorded using a Bruker 500 MHz spectrometer that is two channel equipped with a dual $^{1}$H/$^{13}$C helium-cooled cryoprobe using deuterated chloroform ($CDCl_3$ – d) as solvent. $^{13}$C NMR Inverse Gated Decoupling method using a Udeft method with 60 scans and 4 seconds' delay.

**NMR sample preparation**

100 mg of sample in dissolved in 0.6 mL deuterated chloroform and poured into NMR tube.

### 2.3.2 Attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR)

IR spectra were recorded on a Bruker ALPHA FTIR Spectrometer, using a diamond ATR accessory. The spectra were recorded in transmission mode in the spectral region from 4000 to 400 $cm^{-1}$ with a resolution of 4 $cm^{-1}$, and an average of 24 scans.

## 2.4 Experimental procedure

### Synthesis of sodium alkyl salicylate in $scCO_2$ at high pressure

Sodium alkyl phenolate (5 g, 16.9 mmol) was weighed and added into the autoclave and the key was used to safely close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to the desired temperature and at 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After reaching stable T and P, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product was 98% as some were lost during collection. The reaction conditions used are summarised in Table 3.

Table 3. Reaction conditions for the Kolbe-Schmitt reaction of sodium alkyl phenolate at 4000 psi

| Sample | Temperature (°C) |
|---|---|
| MY 51 | 100 |
| MY 11 | 120 |
| MY 28 | 150 |
| MY 29 | 180 |

### Synthesis of sodium alkyl salicylate in $scCO_2$ at low pressure

Sodium alkyl phenolate (5 g, 16.9 mmol) was added into the autoclave and the key was used to close the autoclave. The temperature was then slowly increased to the desired temperature. After temperature stabilisation, the pressure was increased up to 73 psi / 5 bars by saturating the vessel with $CO_2$. The autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage

yield of the product is 98% as some were lost during collection. The reaction conditions used are summarised in Table 4.

Table 4. Reaction conditions for the Kolbe-Schmitt reaction of sodium alkyl phenolate at 73 psi

| Sample | Temperature (°C) |
|---|---|
| MY 22 | 100 |
| MY 12 | 120 |
| MY 34 | 150 |

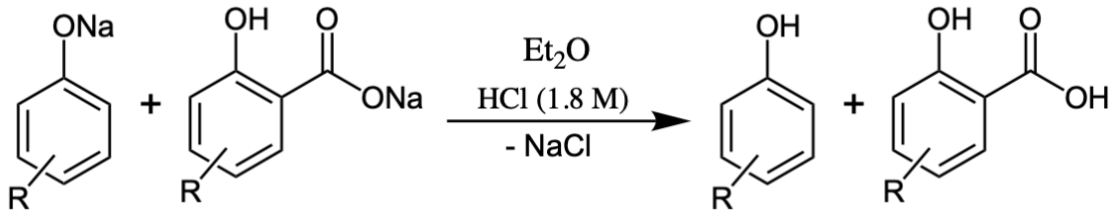
## Analysis

The starting material, sodium alkyl phenolate is a mixture of ortho and para isomers (40:60) and constitutes of 71.5% sodium salt and 28.5% diluent oil. The alkane chain length is a mixture between 16 to 18 carbon and a combination of linear and branched isomers. Due to the complexity of the sample, the successful synthesis of sodium alkyl salicylate was qualitatively confirmed by the combination of FTIR and $^{1}H$ NMR spectroscopies and quantified by $^{13}C$ NMR Inverse Gated Decoupling method. However, regardless from the starting materials and from the reaction conditions, the material after deashing was a similar mixture of salicylic acids. For this reason, the general analysis steps have been reported, before any discussion, for an easier fruition of the thesis for readers.

Figure 20 shows the FTIR spectra of the starting material, sodium alkyl phenolate before and after deashing. By comparing both spectra, it shows that by deashing the material, the peaks are more defined as the metal cation is removed.

Figure 21 and 22 shows the $^{1}H$ and $^{13}C$ NMR spectra of metal salicylate before and after deashing (Figure 20). The characteristic COOH and C-OH peaks were not observed in both spectra of the metal salicylate. Following the deashing procedure, the sodium cations and calcium cations were removed, and the carboxylate group was protonated (Scheme 8). The resulting $^{1}H$ NMR spectrum showed a peak at 10.3 ppm corresponding to -COOH and a singlet around 10.8 ppm corresponds to the proton of phenol and the singlet next to it is attributed to the phenol in the starting material. The resulting $^{13}C$ NMR spectrum showed a singlet at 175 and 160 ppm, corresponding to $C_{ar}$-COOH and $C_{ar}$-OH, respectively. In general, the data from

all the analytical experiments performed for all samples are similar, and thus only deashed sodium alkyl salicylate is involved in the following results and discussion.




Scheme 8: Reaction scheme for the deashing of sodium alkyl salicylate.[43]

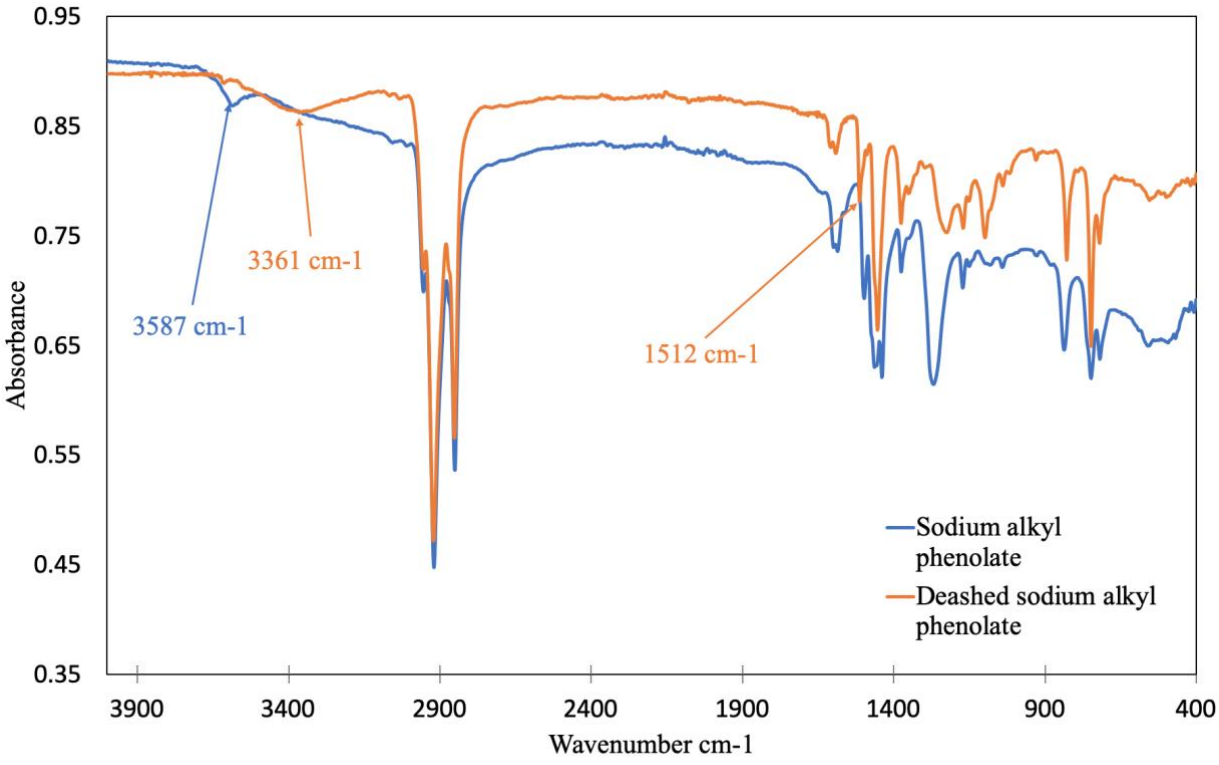



Figure 20: FTIR spectra of starting material, before (blue) and after (orange) deashing. It is well-known that in this process, when there is ortho substitution, the C-H bending mode at 1512 $cm^{-1}$ disappears and it has been used as a measure of how successful the reaction is.

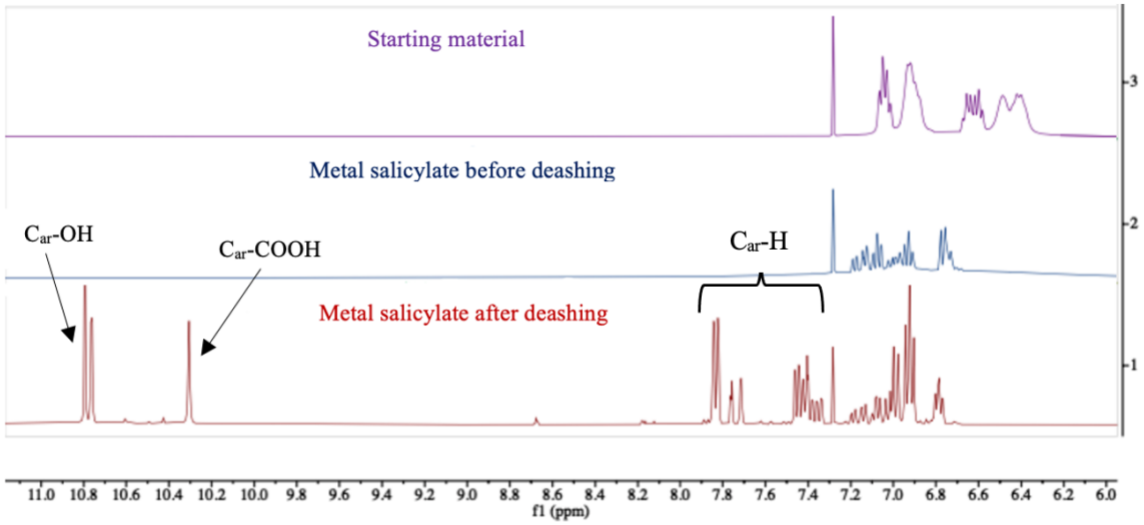



Figure 21: $^{1}$H NMR spectra of starting material, metal salicylate before and after deashing.

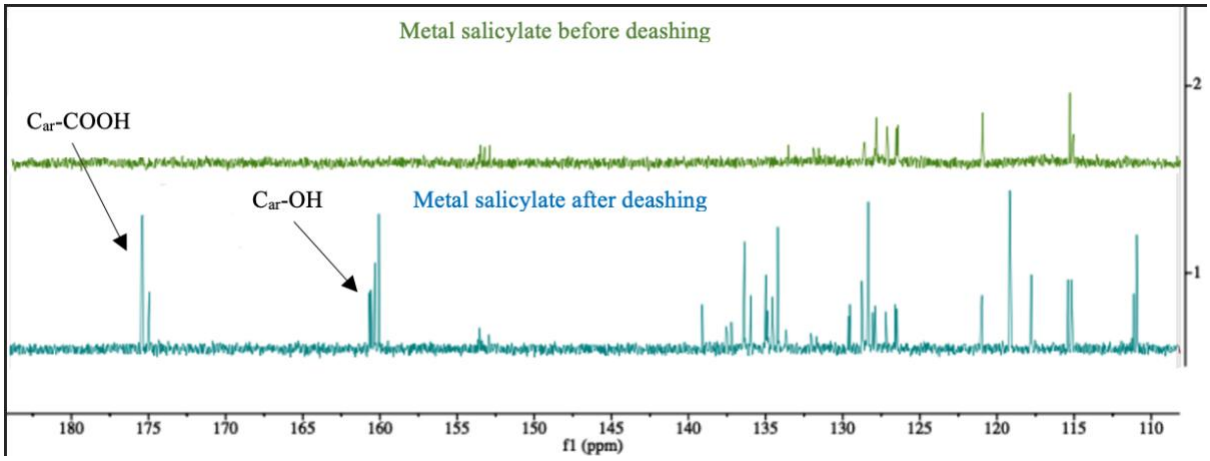



Figure 22: $^{13}$C NMR of spectra of metal salicylate before and after deashing.

However, FTIR, $^{1}$H NMR and $^{13}$C NMR spectroscopy are qualitative analysis, and the conversion of sodium alkyl salicylate from sodium alkyl phenolate cannot be calculated. Thus, $^{13}$C quantitative NMR spectroscopy is used and the spectra are integrated to obtain conversion percentage.

## Results and Discussion

### ATR – FTIR spectra

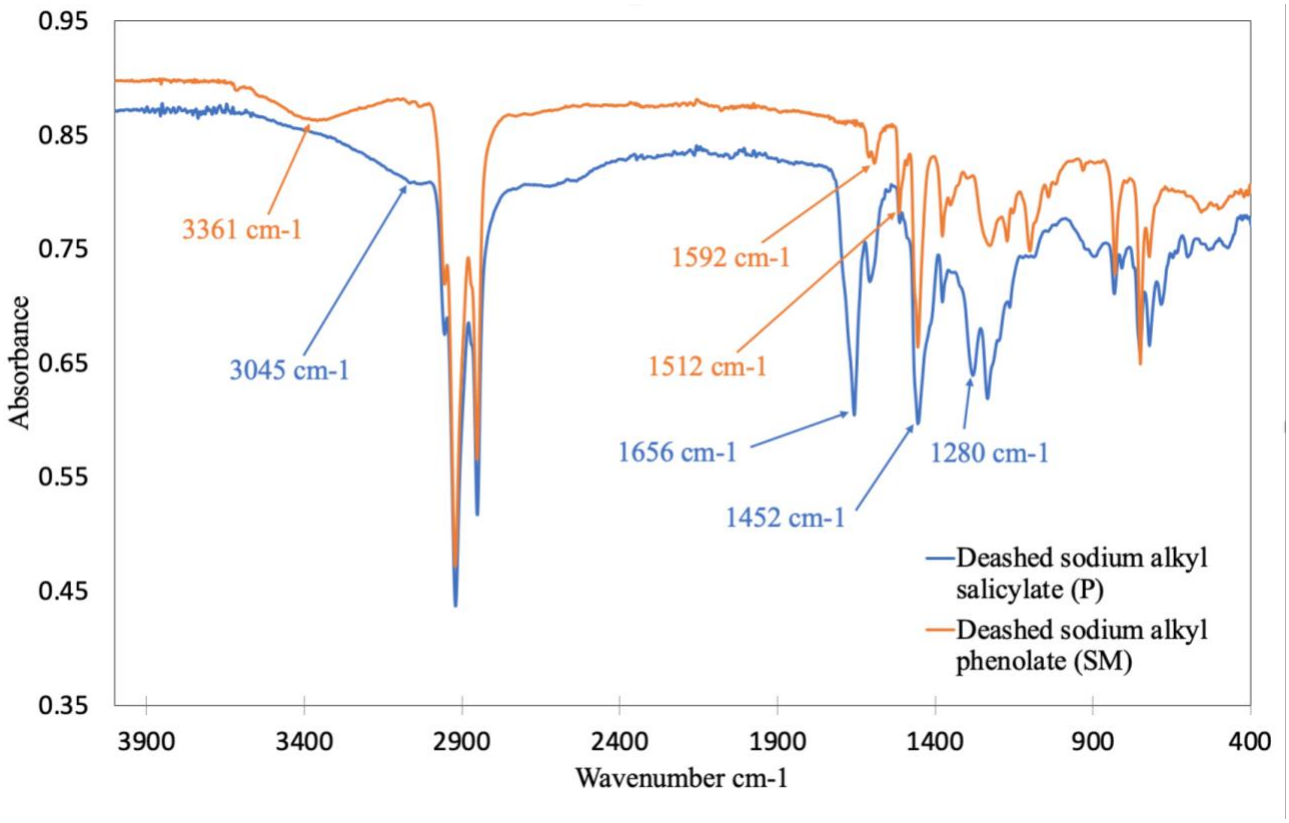



Figure 23: FTIR spectrum of deashed sodium alkyl phenolate (starting material, orange) and deashed metal alkyl salicylate (product, blue)

The FTIR spectrum of sodium alkyl phenolate (starting material) is compared to sodium alkyl salicylate, the product (Figure 23). Both samples were deashed to remove the metal ion and to protonate the samples for clearer FTIR spectra results. The spectrum focusses in the 2000 – 500 $cm^{-1}$ regions, excluding the aliphatic region to assign peaks from the carboxylate and phenol functional groups. The peaks around the regions between 1600 and 1400 $cm^{-1}$ belong to the C=C stretching vibration of the aromatic ring. Significant changes in peak shape between the regions 1450 and 1600 $cm^{-1}$ are observed. The peak at 1512 $cm^{-1}$ is absent in the metal salicylate and the peaks in metal salicylate are much broader and are stronger in intensity. This indicates that the ortho substitution of the phenolate took place, which causes the change of symmetry in the molecule, and thus having different vibrational frequencies compared to the starting material. The C=O of carboxylic acid group is the sharp peak at 1656 $cm^{-1}$, O-H peak for the starting material is the small broad peak at 3361$cm^{-1}$. The new

peak at 1276 $cm^{-1}$ in salicylate can be assigned to the symmetric stretching vibration of acyl group ($\upsilon_s$(C-O)). The reported $\upsilon_s$(C-O) are typically within the range of 1210 – 1320 $cm^{-1}$.

Thus, the changes in C=C stretching vibration of the aromatic ring, the absent peak at 1512 $cm^{-1}$, and the peak at υC-O suggest that the carboxylation reaction took place in $scCO_2$.

$^1$H NMR spectra

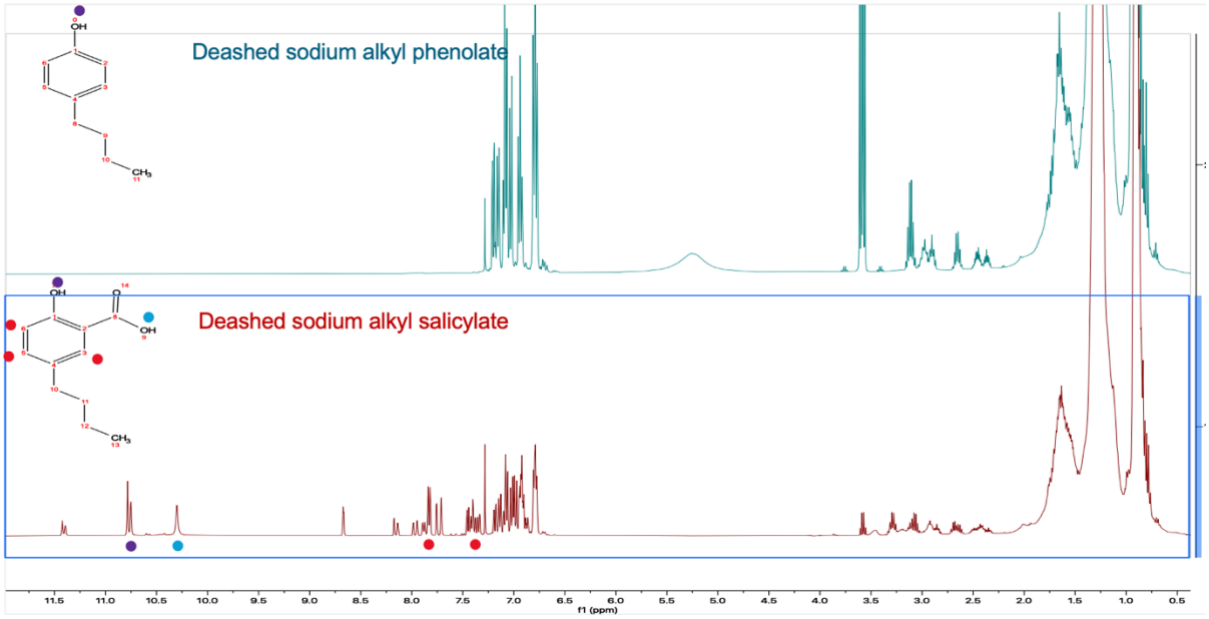



Figure 24: $^1$H NMR spectra of deashed sodium alkyl phenolate (starting material, green) and deashed sodium alkyl salicylate (product, red)

$^1$H NMR spectroscopy was done in order to confirm if the aromatic splitting pattern had changed from that of salicylic acid to that of a substituted salicylic acid. The splitting pattern for an ortho-sodium alkyl phenolate would be two doublets and two triplets, whereas for that of a para-sodium alkyl phenolate would be two doublets. Carboxylation at the ortho or para position of sodium alkyl phenolate would yield 5- alkyl-2-hydroxybenzoic acid and 4-hydroxy-3-alkylbenzoic acid respectively. The protons in the carboxylated products would exhibit different chemical shifts and splitting patterns in comparison to the starting materials.

Figure 24 shows the $C_{ar}$-OH peak is not present in the spectrum for the starting material (deashed sodium alkyl phenolate) because it could undergo labile proton exchange. Protonation of the sodium salicylate product gave alkyl salicylic acid. The peak reported for

$C_{ar}$-COOH in 4-methylsalicylic acid typically falls in the range of 10.3 to 10.7 ppm. Thus, the peak at 10.3 ppm in spectrum is assigned to the proton of carboxylic acid. The singlet at around 10.7 ppm is attributed to the proton of phenol, and the singlet next to it is assigned to the phenol in the starting material. The peaks around 7.5-8 ppm suggest the protons of the aromatic ring as there would a shift after the ortho-substitution. The substitution pattern (eg, ortho, meta, para) can be derived from examination of an aromatic species and can be determined by measuring the coupling constant of the aromatic region. Since the alkyl salicylic acid is ortho substituted, the typical J-coupling of ortho-substituted molecules is ~7-9 Hz (7.84x400 - 7.82x400 = 8 Hz) (Figure 25). This corroborates with the disappearance of IR peak at 1512 $cm^{-1}$.

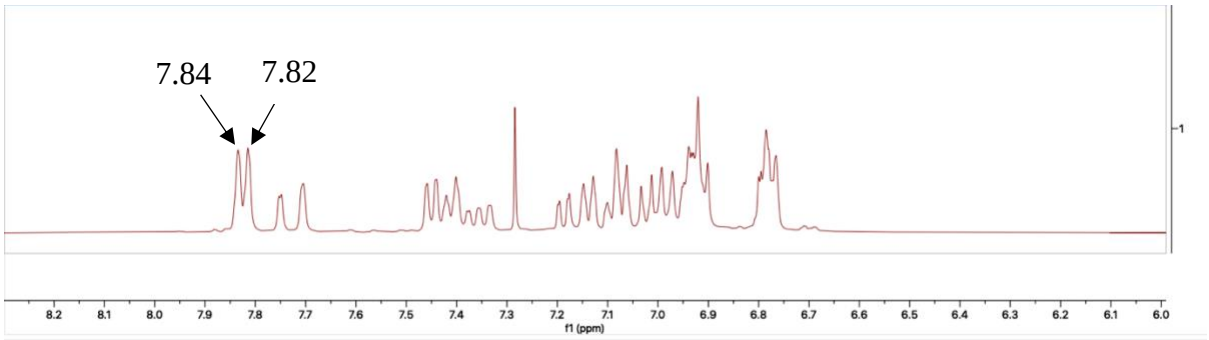



Figure 25: $^{1}H$ Proton NMR of deashed metal alkyl salicylate.

Further investigation is needed to confirm the theory. Normally, peaks of labile proton such as -OH and -COOH are absent in proton NMR spectrum. However, the presence of intermolecular hydrogen bonding in salicylic acid could have affected the resulting spectrum.

Relative change in these peaks compared to the new aromatic proton signals has also been used to quantify conversion to corroborate the data from $^{13}C$ NMR.

An attempt to calculate the conversion of sodium alkyl phenate to sodium alkyl salicylate through integrating the $^{1}H$ NMR spectra was carried out. The $C_{ar}$-OH, $C_{ar}$-COOH, and the aromatic region of the samples yielded after deashing were integrated. An example of the integrated region of interest is depicted in Figure 29. The integration values of the two phenol peaks at around 10.8 ppm were normalised to 1.00 and the corresponding integration values for the aromatic region, carboxylic acid, and phenol were obtained. The ratio between the

integration values of carboxylic acid and phenolic proton arising from alkyl salicylic acid should give insight into the conversion of phenate to salicylate in $scCO_2$.

A 1:1 ratio of -OH (P) to - COOH is observed in the salicylic acid product. However, the integration values observed for the aromatic region are between 7 to 9. This value does not reflect the true proportion of aromatic protons. After discussion with Lubrizol (sponsor company), the use of $^{1}H$ NMR spectroscopy to calculate the conversion might be unreliable. Thus, they have suggested to use quantitative $^{13}C$ NMR to accurately quantify and calculate the conversion.

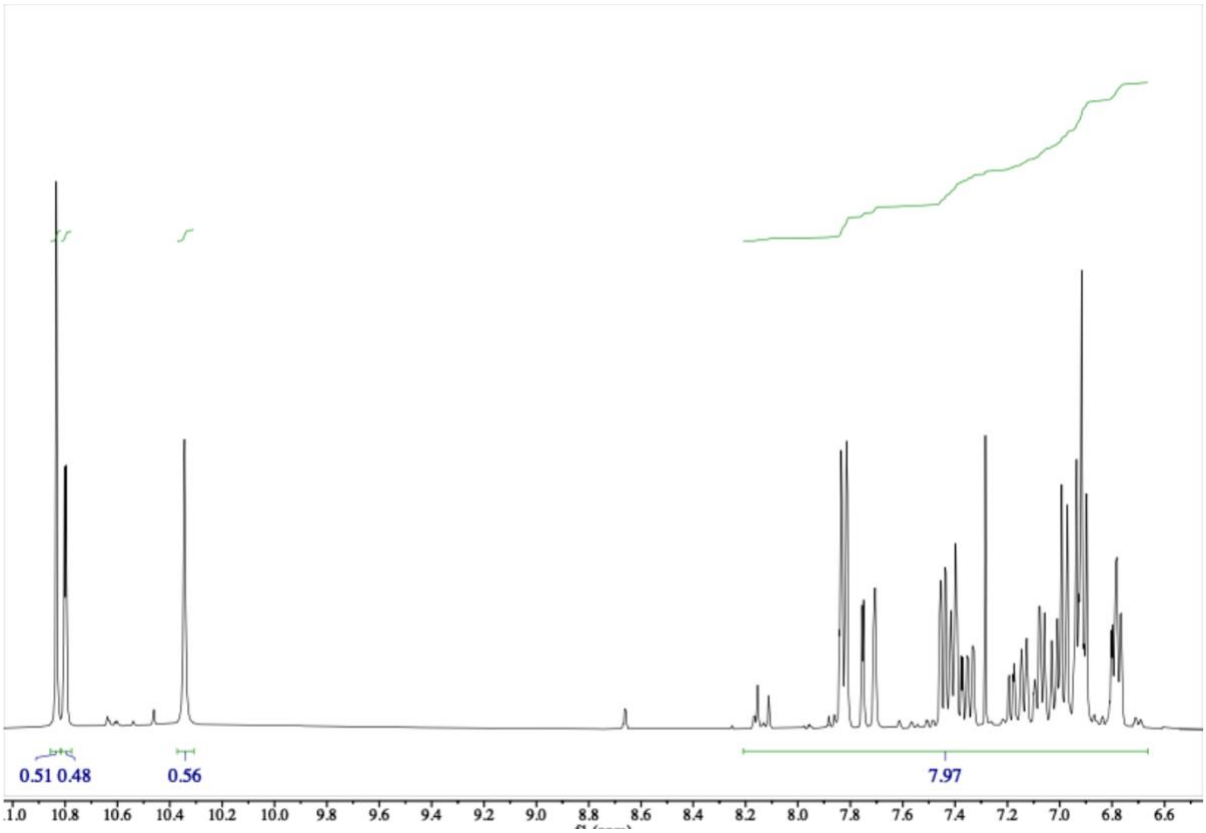



Figure 26: Integration of $^{1}H$ NMR of deashed metal alkyl salicylate.

### $^{13}$C Quantitative NMR

The conversion of sodium alkyl phenolate to sodium alkyl salicylate was calculated by integrating the quantitative carbon NMR. The peaks of $C_{ar}$-OH (P), $C_{ar}$-OH (SM), and $C_{ar}$-COOH of the samples obtained after deashing were integrated, and the conversion was calculated with the equation below:

$$\text{Conversion} = \frac{\text{COOH}}{\text{OH(P)} + \text{OH (SM)}} \times 100\% \qquad (1)$$

An example of the integration of peaks is shown in Figure 27.

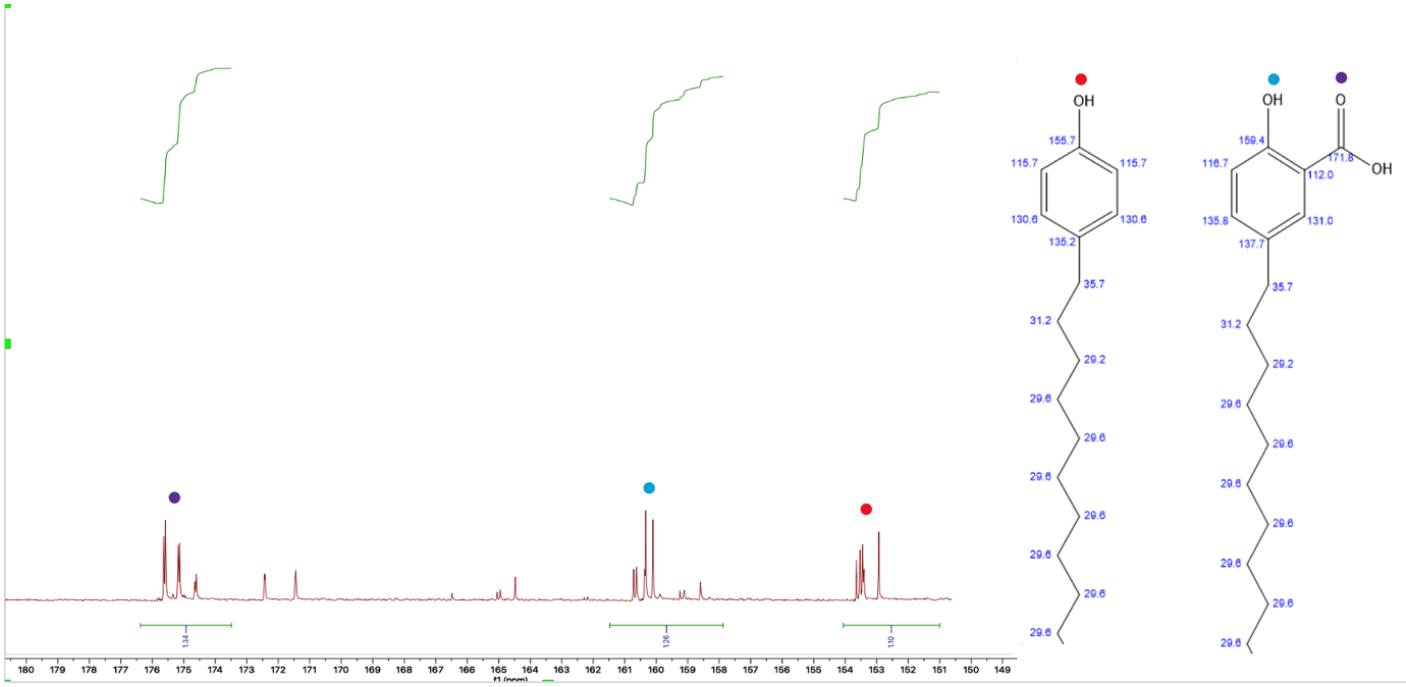



Figure 27: Quantitative Carbon NMR of metal salicylate.

The integration values of two phenol peaks at around 153 ppm and 160 ppm gave 1.10 and 1.26 respectively, and the integration values of the carboxylic acid at around 175 ppm gave 1.24. The conversion was then calculated with these values using equation (1). Table 10 shows the conversion percentage of all the samples mentioned in the experimental section in the appendix.

**$^{13}$C NMR spectra**

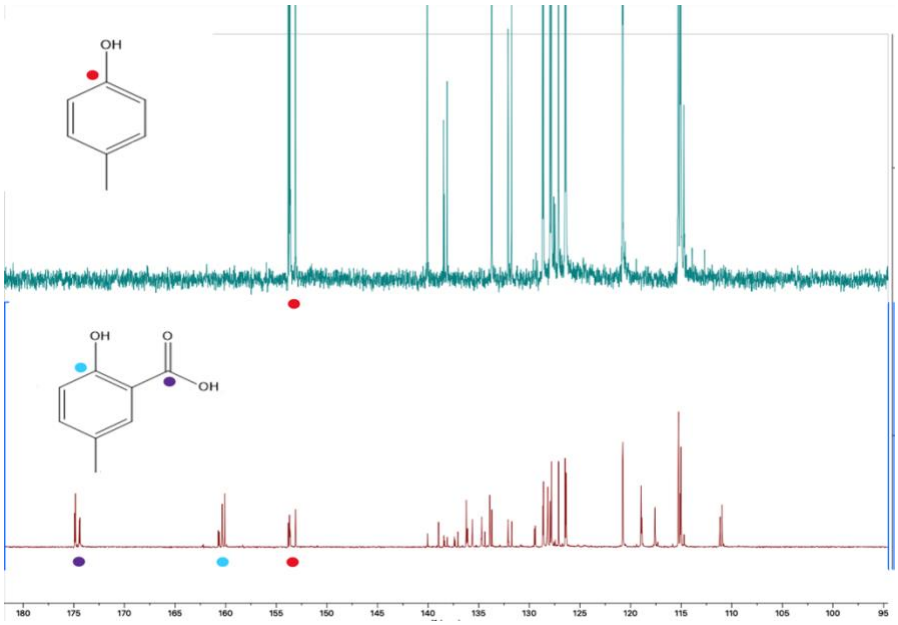



Figure 28: $^{13}$C NMR spectra of deashed sodium alkyl phenolate (SM) (top) and deashed sodium alkyl salicylate (P) (bottom).

The synthesis of sodium alkyl salicylate was further confirmed by carbon NMR spectroscopy (Figure 28). The characteristic $C_{ar}$-OH and $C_{ar}$-COOH peaks were not observed in the spectrum. After deashing the samples, the sodium cations were removed, and the carboxylate group was protonated (Scheme 8). The spectrum after deashing shows a singlet at 160 ppm and 175 ppm, which corresponds to $C_{ar}$-OH and $C_{ar}$-COOH respectively. The peak at around 154-155ppm in both spectra is the $C_{ar}$-OH of the starting material as they are still starting material remaining in the product mixture.

### 2.4.1 The effect of temperature on the Kolbe-Schmitt reaction of sodium alkyl phenolate at high pressure.

Different reaction temperatures at 100 °C, 120 °C, 150 °C, and 180 °C were studied under supercritical $CO_2$ conditions to find the optimal reaction temperature for Kolbe-Schmitt reaction. As the temperature increases, particles collide more often due to the increase in kinetic energy, which increases the rate of reaction. This was observed up to 120 °C, however, the

conversion of metal salicylate from phenolate decreased at higher temperatures (150 °C and 180 °C).

This may be due to the decreasing density of carbon dioxide in reaction. The density of carbon dioxide decreases with increase in temperature because of the increase in kinetic energy, causing the particles to collide more often, thus less carbon dioxide surrounding the reactants. In other words, the carbon dioxide behaves more as a gas than a liquid. (Figure 29)

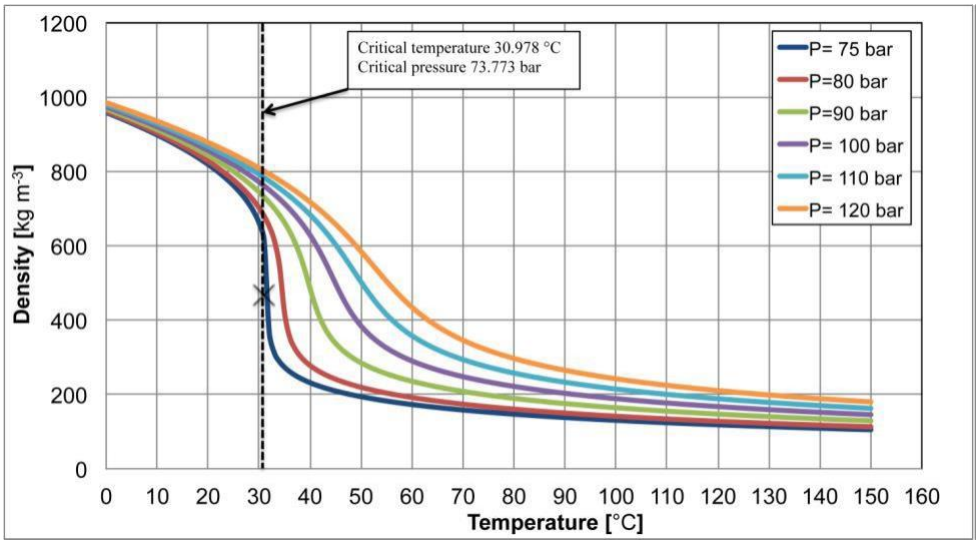



Figure 29: Supercritical carbon dioxide density as a function of the pressure and temperature. The dotted line indicates the critical temperature.

Figure 30 shows the successful synthesis of sodium alkyl salicylate under all temperatures studied. However, the $^{1}H$ NMR spectra fails to show how much salicylate is produced as $^{1}H$ NMR, as well as FTIR and $^{13}C$ NMR are qualitative analysis. Hence, the conversion of salicylate from phenolate is calculated by using quantitative carbon NMR and the results are plotted in graphs (Figure 31).

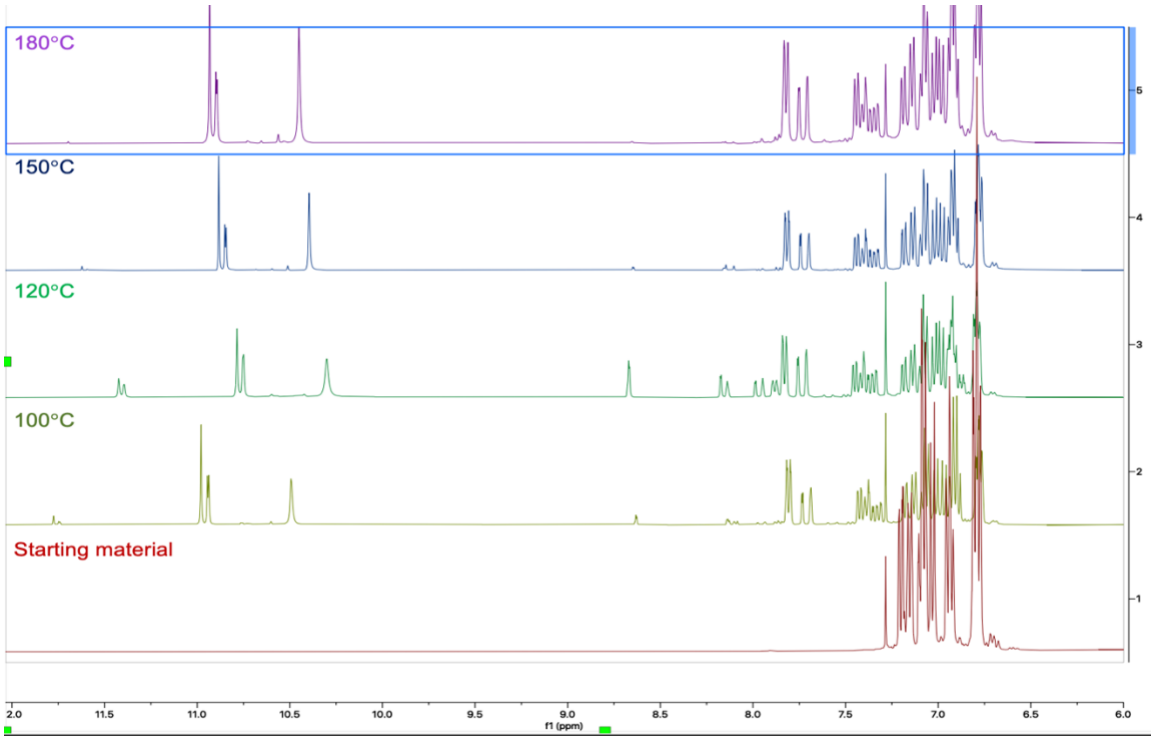



Figure 30: $^{1}H$ NMR spectra of sodium alkyl salicylate at different temperatures. In discussion with Lubrizol, they also confirmed that they have observed the unusual shifts in the NMR peak. Thus, this should be investigated in the future work.

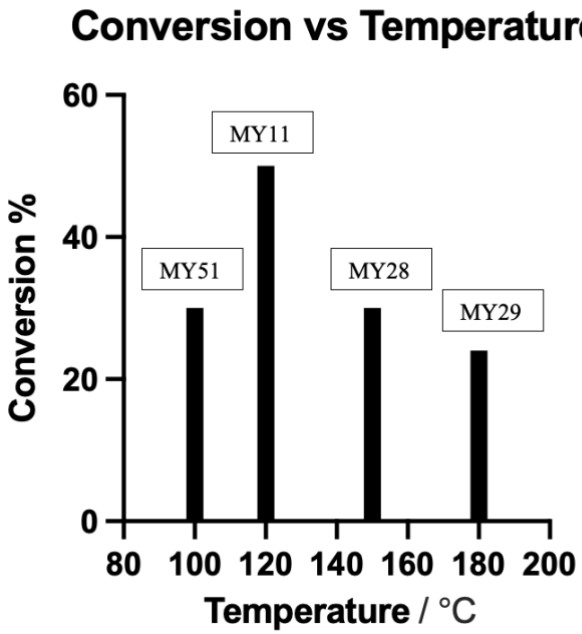



Figure 31: Graph of conversion of sodium alkyl salicylate with temperature.

### 2.4.2 The effect of pressure on the Kolbe-Schmitt reaction of sodium alkyl phenolate

Two different $CO_2$ conditions (supercritical $CO_2$ and gaseous $CO_2$) were studied at fixed temperatures. Iijima êt al claimed that there was a significant increase in product yield under supercritical $CO_2$ compared to reactions in gaseous $CO_2$ (Figure 30). This observation was attributed to the increase in local concentration of carbon dioxide around the reactants as supercritical $CO_2$ is denser than gaseous $CO_2$. However, it is observed that at higher temperatures, the product yield under gaseous conditions is greater than in supercritical conditions.

Density of carbon dioxide decreases with increase in temperature and not with pressure. For example, the density at 120 °C and 4000psi / 276 bars is greater than the density at 150 °C and 4000 psi / 276 bars. Whereas, when the temperature is the same, the density will increase with increase of pressure. Moreover, when the temperature increases, the pressure also increases but the density remains the same. Table 11 shows a rough estimate of the density of supercritical $CO_2$ under certain conditions.

Table 11: Density of $scCO_2$ under certain conditions.

| Conditions | Density of $scCO_2$ / $gcm^{-3}$ |
|---|---|
| 120 °C and 4000psi / 276 bars | 0.549 |
| 150 °C and 4000psi / 276 bars | 0.456 |
| 180 °C and 4000psi / 276 bars | 0.392 |
| 120 °C and 1500psi / 103 bars | 0.174 |
| 150 °C and 1500psi / 103 bars | 0.151 |
| 180 °C and 1500psi / 103 bars | 0.135 |

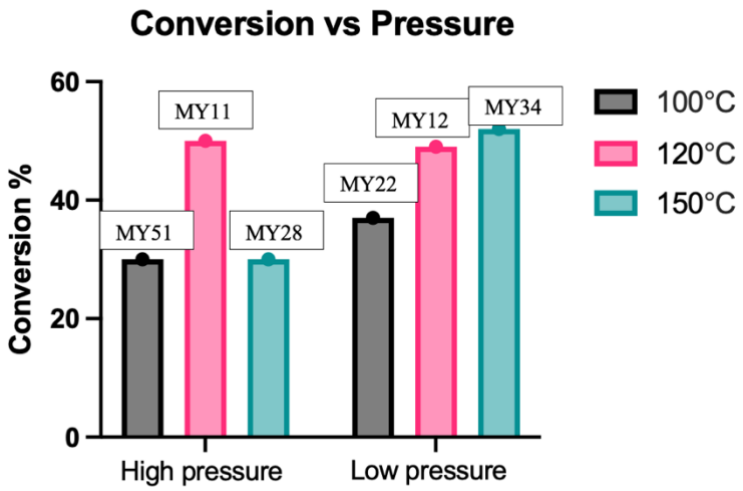



Figure 32: Graph comparison of conversion of temperatures at high and low pressures.

This phenomenon demonstrate that supercritical reactions do not always show advantages, especially for gas-liquid-solid reaction. A possible explanation is that a gas-liquid system tends to be homogenous, which is more like a gas phase, with a worse dispersion property compared to the liquid solution.

### 2.4.3 Synthesis of sodium alkyl salicylate in $scCO_2$ with promoters at low pressure

**DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene)**

Sodium alkyl phenolate (5 g, 16.9 mmol) and DBU (2.6 g, 16.9 mmol, 1eqv.) were added into the autoclave and the key was used to close the autoclave. The temperature was then slowly increased to 120 °C. After temperature stabilisation, the pressure was increased up to 73 psi / 5 bars by saturating the vessel with $CO_2$. The autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection.

**mTBD (7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene)**

Sodium alkyl phenolate (5 g, 16.9 mmol) and mTBD (2.5 mL, 16.9 mmol, 1eqv.) were added into the autoclave and the key was used to close the autoclave. The temperature was then slowly increased to 120 °C. After temperature stabilisation, the pressure was increased up to 73 psi / 5 bars by saturating the vessel with $CO_2$. The autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection.

**Hindered Phenolate**

Sodium alkyl phenolate (5 g, 16.9 mmol) and hindered phenolate (2.6 g, 16.9 mmol, 1eqv.) were added into the autoclave and the key was used to close the autoclave. The temperature was then slowly increased to 120 °C. After temperature stabilisation, the pressure was increased up to 73 psi / 5 bars by saturating the vessel with $CO_2$. The autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection. The promoters used are summarised in Table 5, structures in Figure 33.

Table 5. Promoters for the Kolbe-Schmitt reaction of sodium alkyl phenolate at 73 psi

| Sample | Promoters |
|---|---|
| MY 14 | DBU |

| | |
|---|---|
| MY 23 | mTBD |
| MY 26 | Hindered phenolate |

**Synthesis of sodium alkyl salicylate in scCO$_2$ with promoters at high pressure**

**DBU(1,8-Diazabicyclo[5.4.0]undec-7-ene)**

Sodium alkyl phenolate (5 g, 16.9 mmol) and DBU (2.6 g, 16.9 mmol, 1eqv.) were added into the autoclave and the key was used to safely close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to 120 °C and at 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After reaching stable T and P, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection.

**Hindered Phenolate**

Sodium alkyl phenolate (5 g, 16.9 mmol) and DBU (2.6 g, 16.9 mmol, 1eqv.) were added into the autoclave and the key was used to safely close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to 120 °C and at 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After reaching stable T and P, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection. The promoters used are summarised in Table 6.

Table 6. Promoters for the Kolbe-Schmitt reaction of sodium alkyl phenolate at 4000 psi

| Sample | Promoters |
|---|---|

| | |
|---|---|
| MY 13 | DBU |
| MY 27 | Hindered phenolate |

## Results and Discussion of synthesis of sodium alkyl salicylate in the presence of promoters

The effect of promoters in the Kolbe-Schmitt reaction were studied. There were several promoters used in this study: 1,8-Diazabicyclo[5.4.0]undec-7-ene(DBU), 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (mTBD), hindered phenolate (Figure 33)

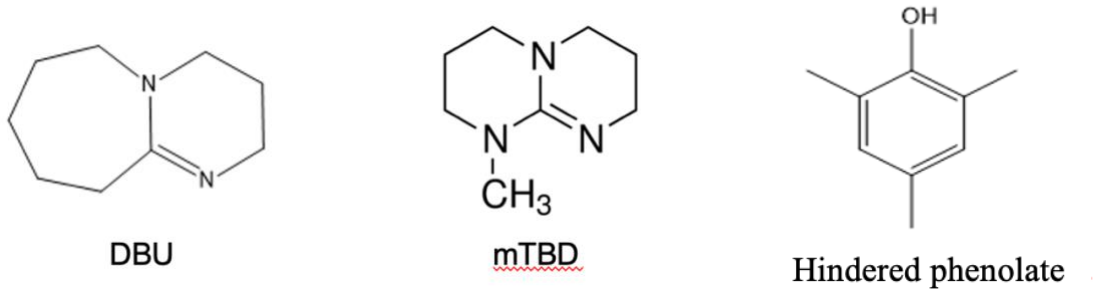



Figure 33: Promoters used in synthesis of sodium alkyl salicylate.

### DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene)

Sodium alkyl phenolate was reacted with DBU under a carbon dioxide atmosphere. A carbon – carbon bond formation of sodium phenolate with a carbon dioxide through nucleophilic addition, proceeded to afford the corresponding salicylic acid derivatives in high yields. The anion (dianion) derived from sodium phenolate would have a nucleophilicity high enough to promote the addition reaction to $CO_2$ and being able to proceed efficiently. It is theorised that the phenolate has a low pka so that the anion(dianion) could be generated easily by treatment of a strong organic base. DBU is also a $CO_2$ transporter by forming a guanidine – $CO_2$ complex. The reactions with DBU gave the highest product yield overall (Figure 33). After deashing process, the guanidine base is removed hence the absence of peaks in NMR.

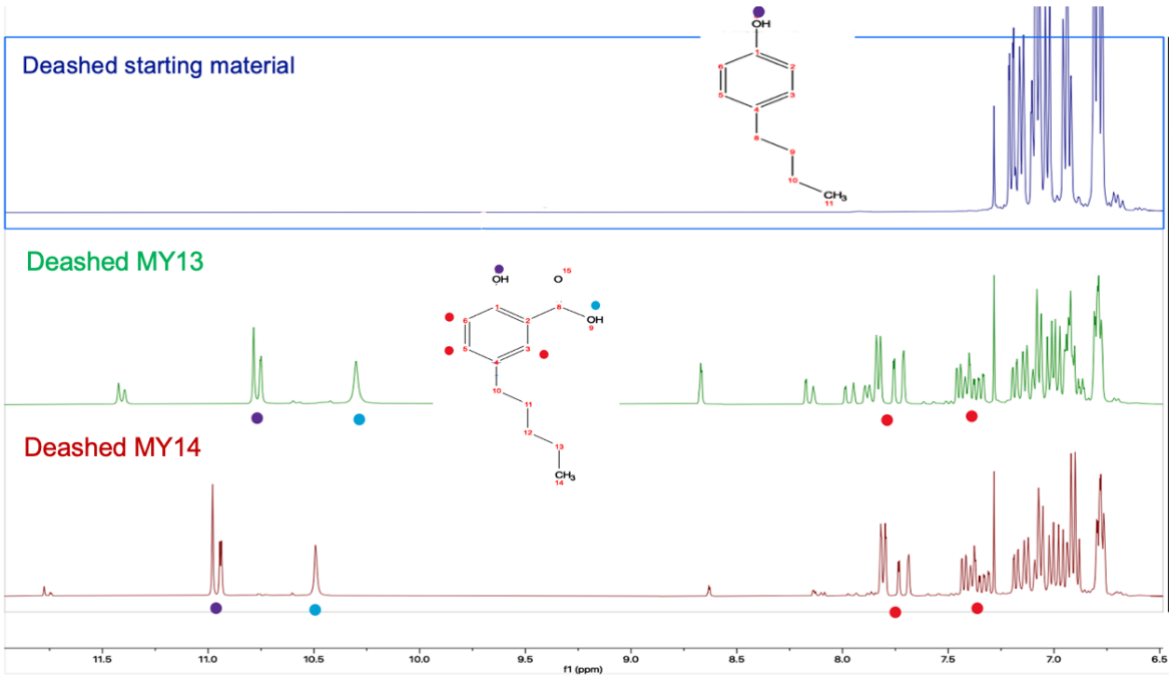
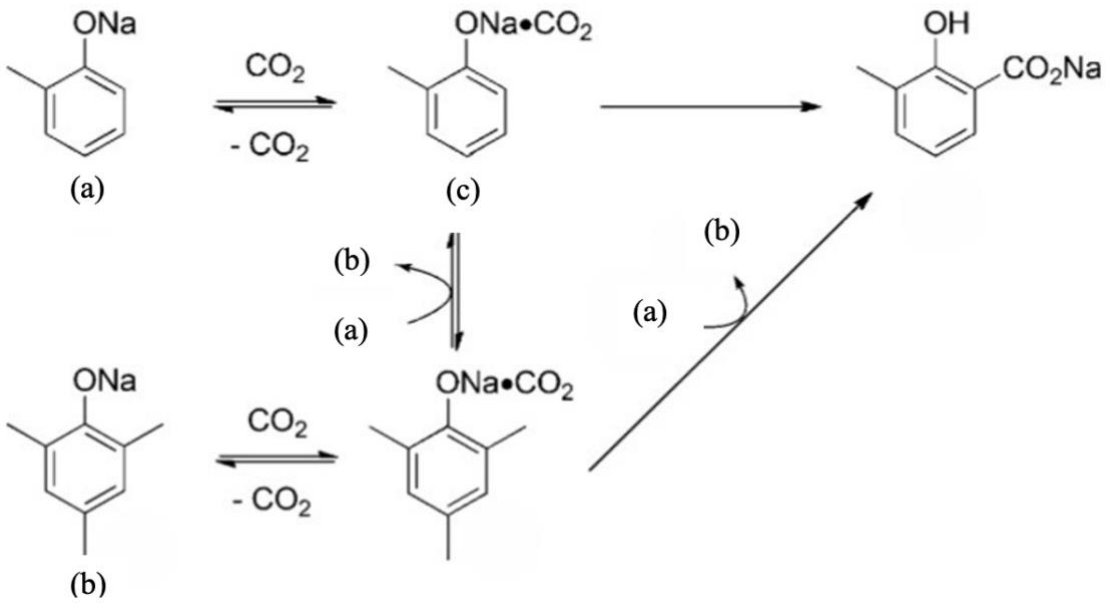



Figure 34: $^{1}H$ NMR spectra of synthesis of sodium alkyl salicylate with DBU at different pressures.

mTBD is also a strong guanidine base and has similar characteristics as DBU. The product yield from reactions with mTBD is lower than that of DBU.

**Hindered Phenolate**

Hindered phenolate is also a $CO_2$ transporter. It is suggested that only the fixed $CO_2$ is reactive in carboxylation step, not the gaseous $CO_2$. Preciado êt al proposed a mechanism that the primary role of sodium 2,4,6-trimethylphenoate 10 may be to aid $CO_2$ fixation, increasing the amount of $CO_2$ able to react in the carboxylation step.[25] Since 10 has both its ortho and para position blocked, it is not able to undergo carboxylation with the bound $CO_2$. This fixed $CO_2$ can therefore only react with 9, either by exchange to form 11 with subsequent intramolecular carboxylation, or by reacting directly with 9 in an intramolecular fashion (Scheme 6).[25]




Scheme 6: Mechanism of hindered phenolate with $CO_2$. [25]

The reactions with the hindered phenolate produced small amount product yield (Figure 35). This may be due to the remaining moisture / water present in the hindered phenolate even after intense drying of hindered phenolate. Water inhibits the carbonation of monohydric phenols and therefore should be removed from the reactants prior to the reaction. This adverse effect may be due to strong chelation of water molecules with alkali metal aryloxides, preventing the initial addition of $CO_2$.

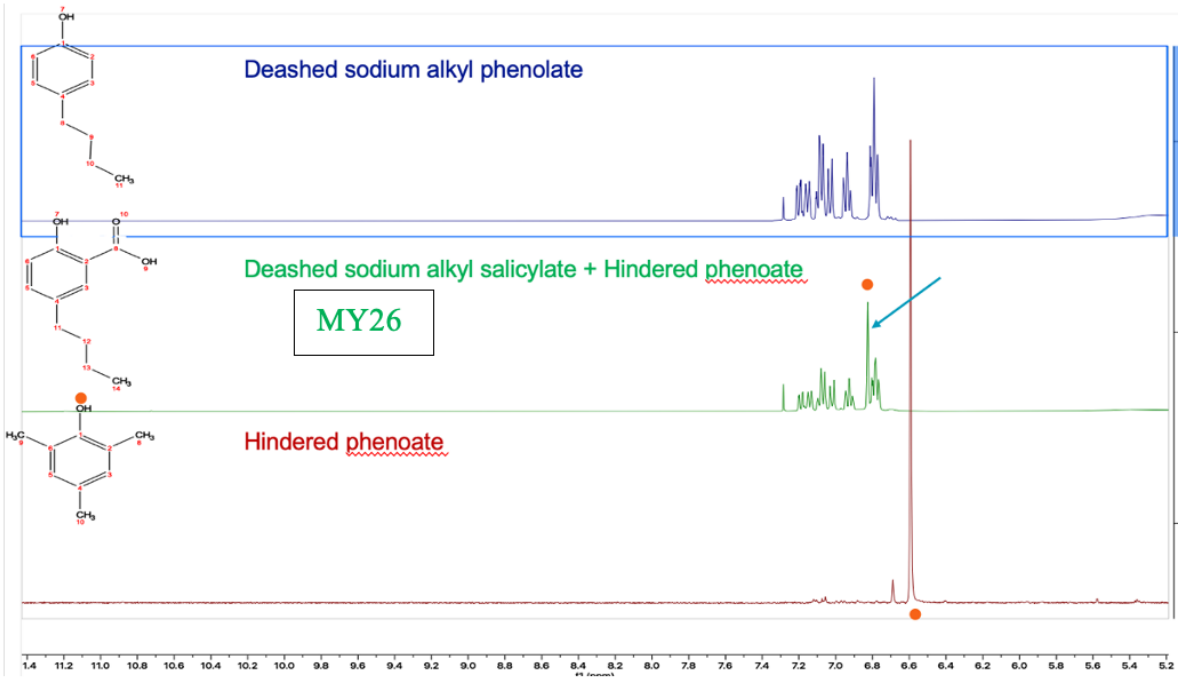



Figure 35: $^{1}$H NMR spectra of synthesis of sodium alkyl salicylate with hindered phenolate.

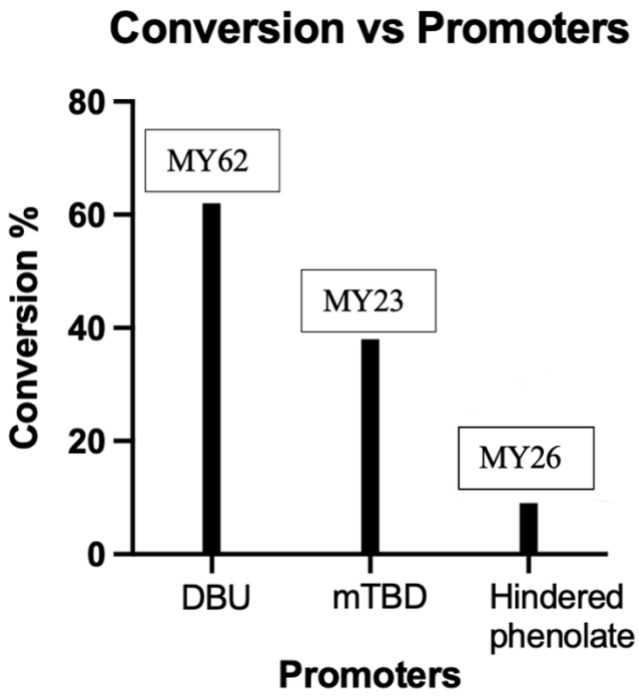



Figure 36: Graph of conversion of sodium alkyl salicylate with promoters.

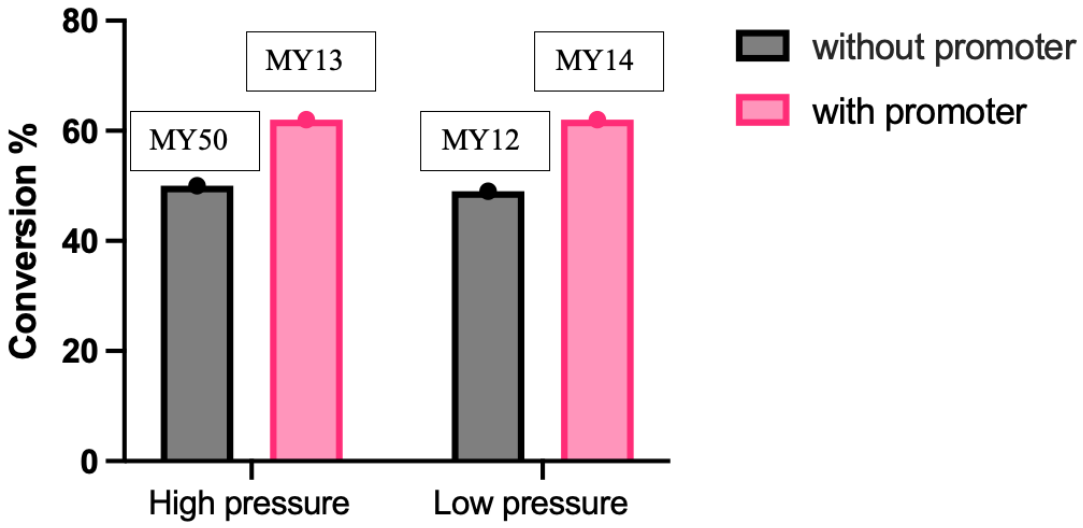



Figure 37: Graph comparison of conversion between high pressure and low pressure.

### 2.4.4 Synthesis of calcium alkyl salicylate in $scCO_2$ at high pressure

Calcium alkyl phenolate (5 g, 16.9 mmol) was added into the autoclave and the key was used to close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to the desired temperature and at 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After stabilising, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection. The reaction conditions used are summarised in Table 7.

Table 7. Reaction conditions for the Kolbe-Schmitt reaction of calcium alkyl phenolate at 4000 psi

| Sample | Temperature (°C) |
|---|---|
| MY 52 | 120 |
| MY 30 | 150 |
| MY 31 | 180 |

## Results and Discussion of synthesis of calcium alkyl salicylate in $scCO_2$

Rahim êt al reported the Kolbe-Schmitt reaction of alkaline earth metal phenoxides and the yield of calcium salicylate increased from 27% to 43% as the reaction temperature was increased from 150 °C to 200 °C at 725 psi / 50 bars. This indicates that the ortho carboxylation of calcium phenolate is possible and extreme temperatures aid the conversion of phenolate to salicylate. According to the mechanism mentioned in section 1.4.4, the last step of the Kolbe – Schmitt reaction is the rate determining step and both ortho and para routes require high activation energy. Thus, the temperature effect on the Kolbe – Schmitt reaction with calcium alkyl phenolate was investigated.

**Temperature effect**

Reaction temperature conditions 120 °C, 150 °C, and 180 °C at 4000 psi / 276 bars were studied.

The FTIR of deashed calcium alkyl salicylate should be identical to that of deashed sodium alkyl salicylate. At 120 °C, the spectra showed that the peaks of calcium alkyl salicylate are identical to the starting material, calcium alkyl phenolate. This indicates that there are no significant changes in the functional groups of calcium alkyl salicylate compared to calcium alkyl phenolate. The characteristic peak of $COO^-$ observed in the previous spectra is also absent, suggesting that the carboxylation reaction did not occur (Figure 38).

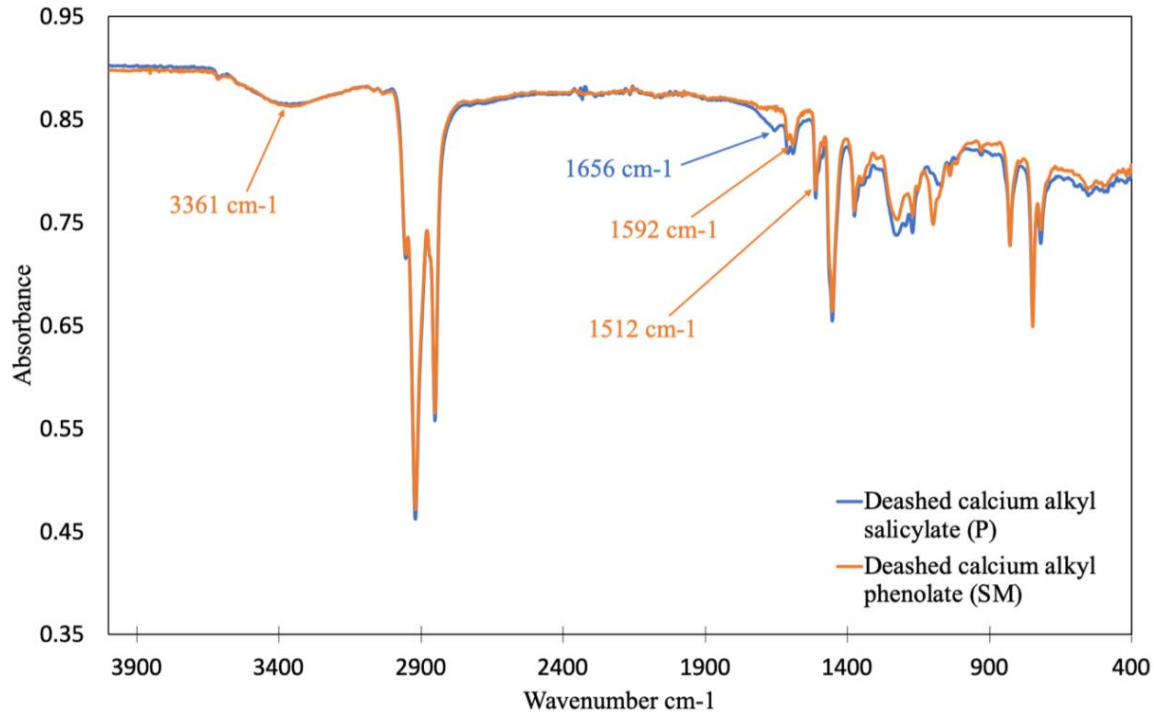



Figure 38: FTIR spectra of deashed calcium alkyl phenolate and deashed calcium alkyl salicylate.

The $^{1}H$ NMR spectra as well as the $^{13}C$ NMR spectra were a similar case as well. The spectrum of the product, deashed calcium alkyl salicylate is similar to that of the starting material. The 1512 $cm^{-1}$ peak is still present which indicates that the ortho substitution did not place at 120 °C and 4000 psi / 276 bars (Figure 39).

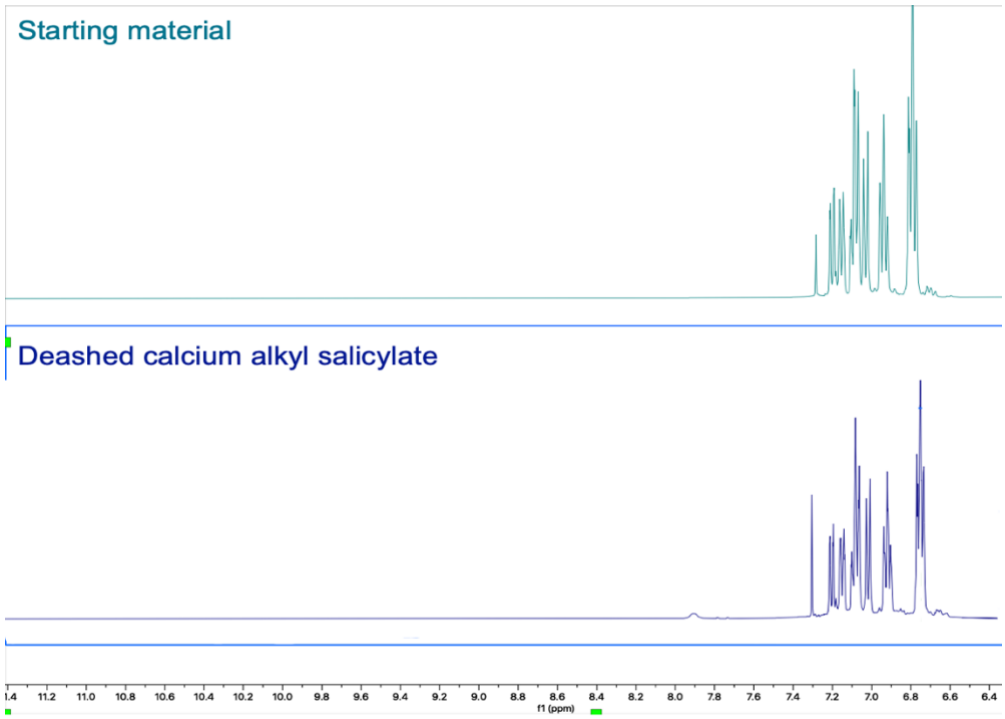



Figure 39: $^{1}$H NMR spectra of deashed calcium alkyl phenolate and deashed calcium alkyl salicylate. The two spectra are almost identical, indicating that the reaction was not successful, and the product was not produced.

For reaction temperatures at 150 °C and 180 °C, the product yields are 8% and 7% respectively. The $^{1}$H NMR spectra shows the arising peaks of -OH and -COOH, indicating that a small amount of ortho substitution took place at the higher temperatures (Figure 38). However, it is crucial to note that there is a small trace amount of sodium alkyl phenolate present in the calcium alkyl phenolate mixture from the transmetallation process of sodium alkyl phenolate to calcium alkyl phenolate (Scheme 10). Hence, part of the product yield may be from the conversion of sodium alkyl salicylate from sodium alkyl phenolate (Figure 40)

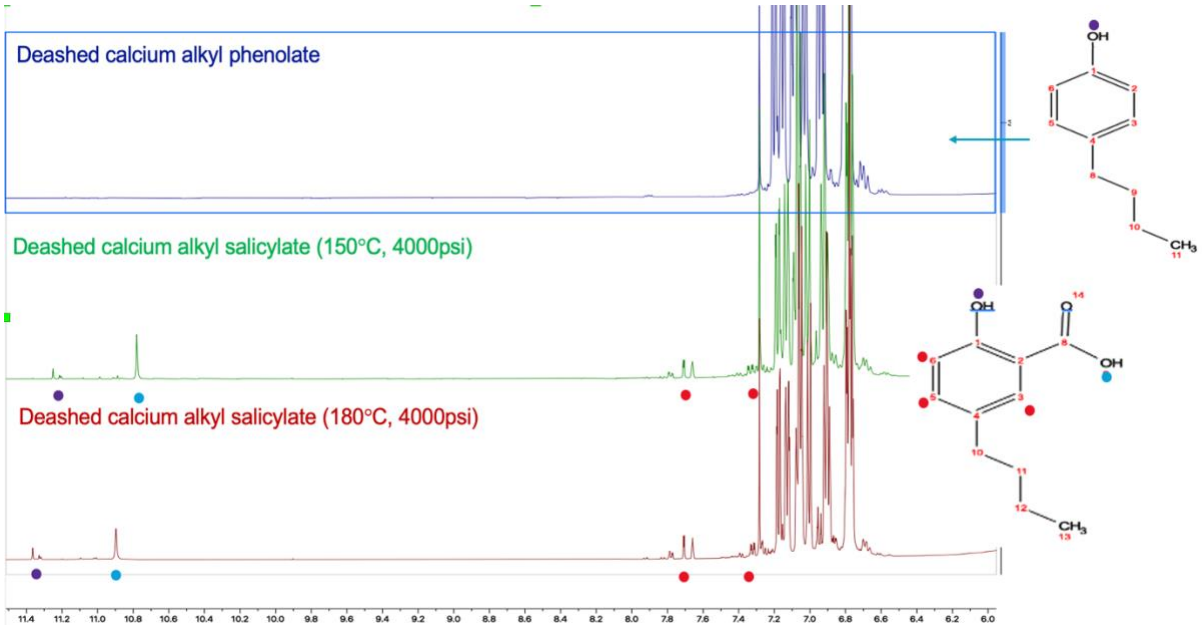
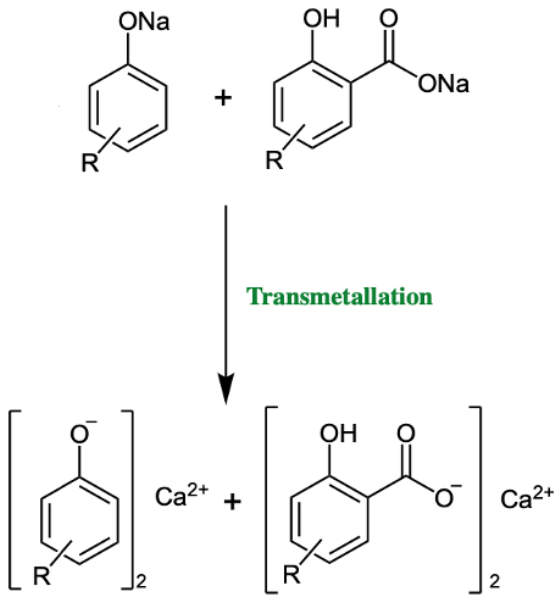



Figure 40: $^{1}H$ NMR spectra of deashed calcium alkyl phenolate and deashed calcium alkyl salicylate. The significant peaks of C-OH and -COOH are present but not obvious, suggesting that there was some conversion.




Scheme 10: Transmetallation of sodium alkyl salicylate to calcium alkyl salicylate [43]

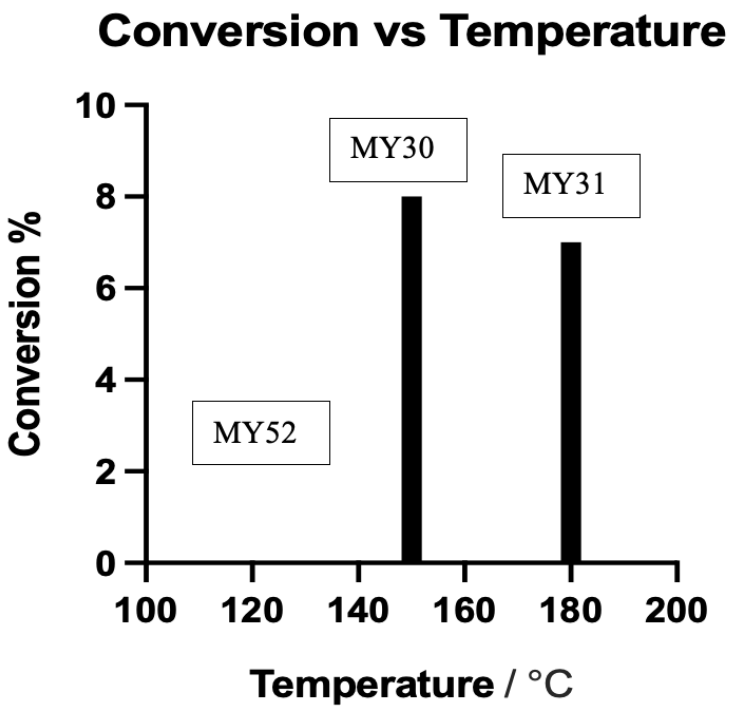



Figure 41: Graph of conversion of calcium alkyl salicylate with temperature

### 2.4.5 Synthesis of calcium alkyl salicylate in scCO$_2$ with promoters

**DBU(1,8-Diazabicyclo[5.4.0]undec-7-ene)**

Calcium alkyl phenolate (5 g, 16.9 mmol) and DBU (2.5 g, 16.9 mmol, 1eqv.) were added into the autoclave and the key was used to close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to 150 °C and 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After stabilising, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection.

**Calcium alkyl sulfonate**

Calcium alkyl phenolate (5 g, 16.9 mmol) and calcium alkyl sulfonate (1 g, 20% w/v) were added into the autoclave and the key was used to close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to 150 °C and 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After stabilising, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection. This reaction is repeated twice with 30% and 40% of calcium alkyl sulfonate instead.

**Calcium carbonate**

Calcium alkyl phenolate (5 g, 16.9 mmol) and calcium carbonate (2.5 g, 25 mmol, 50% w/v) were added into the autoclave and the key was used to close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to 150 °C and 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After

stabilising, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection.

**Calcium chloride**

Calcium alkyl phenolate (5 g, 16.9 mmol) and calcium chloride (2.5 g, 25 mmol, 50% w/v) were added into the autoclave and the key was used to close the autoclave. The pressure was then slowly increased to 700 psi / 48 bars by saturating the vessel with $CO_2$, alternating from increasing the temperature and pressure to 150 °C and 4000 psi / 276 bars. The reason for alternating between increasing temperature and pressure is because both T and P are sensitive to each other and increasing either one too quickly would cause an overshoot. After stabilising, the autoclave was left stirring at 300 rpm for 6 hours. The autoclave was then allowed to cool (<30 °C), the $CO_2$ was vented slowly. The autoclave was opened to collect the viscous dark brown product with a spatula into a vial. The average percentage yield of the product is 98% as some were lost during collection. The promoters used are summarised in Table 8.

Table 8. Promoters for the Kolbe-Schmitt reaction of calcium alkyl phenolate at 4000 psi

| Sample | Promoters |
|---|---|
| MY 32 | DBU |
| MY 42 | 20% Calcium alkyl sulfonate |
| MY 43 | 30% Calcium alkyl sulfonate |
| MY 44 | 40% Calcium alkyl sulfonate |
| MY 45 | Calcium carbonate |
| MY 46 | Calcium chloride |

## Results and Discussion of synthesis of calcium alkyl salicylate with promoters

Calcium alkyl phenolate was treated with DBU in hopes to replicate the high conversion result of sodium alkyl salicylate, but the conversion was less than 5%. Another approach was using several calcium salts (calcium carbonate and calcium chloride) and calcium alkyl sulfonate in the Kolbe-Schmitt reaction as promoters as the extra calcium atoms may assist in the conversion by separating the two phenolates that are bonded to one calcium atom. The calcium alkyl sulfonate promoted reaction gave conversions of 15%, which is the highest conversion of calcium alkyl salicylate. However, the conversion is too low for the reaction to be considered successful. Lastly, alkyl phenol was also used as a promoter but there was no product yield. So far, none of the promoters has worked to improve the Kolbe-Schmitt reaction of calcium alkyl phenolate (Figure 42). All the promoters used are summarised in Table 12.

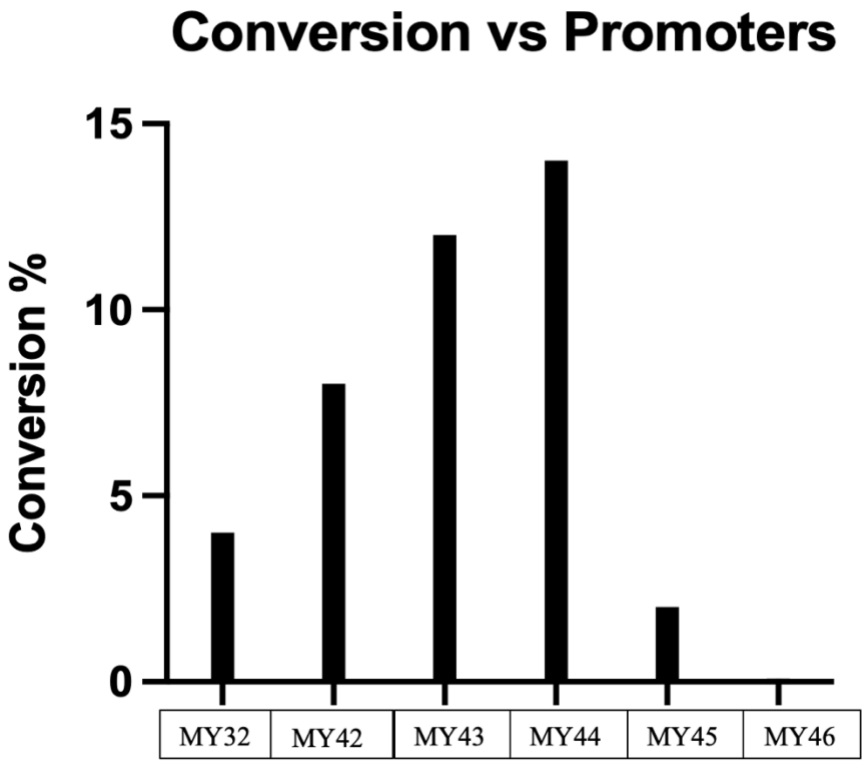



Figure 42: Graph of conversion of calcium alkyl salicylate with promoters.

Table 12: Promoters used in Kolbe-Schmitt reaction of calcium alkyl phenolate

| Sample | Promoters |
|---|---|
| MY 32 | DBU |
| MY 42 | 20% Calcium alkyl sulfonate |
| MY 43 | 30% Calcium alkyl sulfonate |
| MY 44 | 40% Calcium alkyl sulfonate |
| MY 45 | Calcium carbonate |
| MY 46 | Calcium chloride |

### 2.4.6 Kolbe-Schmitt reaction performed under Ultrasonication

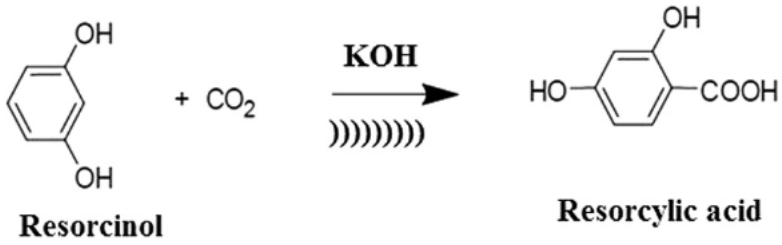
The experimental setup is shown in Figure 43. All reactions were carried out in a round bottomed flask of 100 mL capacity that was dried before use. Sodium alkyl phenolate (10 g) and toluene (5 mL) were added in the round bottomed flask. The neck of the flask was sealed with a stopper and one of the HiP needle valves connected to the $CO_2$ pipeline was inserted through a suba seal along with two short needles to ensure there is no built up of pressure in the flask. The reaction mixture was exposed to a continuous flow rate of carbon dioxide gas (25 psi / 2 bars) for a required time under ultrasonication (Model: Grant Ultrasonic bath XUBA1) (bath type sonicator). After completion of the reaction, the mixture was concentrated under vacuum.




Figure 43: Experimental setup of ultrasonication

## Results and Discussion of Kolbe-Schmitt reaction under Ultrasonication

Shanthi êt al studied a variant of Kolbe – Schmitt reaction using carbon dioxide under ultrasonic environment to obtain milder conditions instead of applying intensive high pressure and high temperature in the carboxylation process.[33] They compared the conventional Kolbe – Schmitt reaction to that of the ultrasonication and they observed that by applying ultrasound, it saves a good amount of energy. The maximum yields 30 % and 65 % were obtained in a bath type and horn type ultrasonicator respectively. The difference in yield is because the horn type ultrasonicator has a higher frequency than the bath type.




Scheme 11: Synthesis of resorcylic acid from resorcinol under ultrasonication [33]

The Kolbe – Schmitt reactions under ultrasonication were performed with two different solvents, toluene and xylene. However, there was no product yield after reaction. This may be due to the long bulky alkyl chain of sodium alkyl phenolate as Shanthi êt al used resorcinol, which is a simple phenol molecule.

**Metal Salicylate Products De-ashing**

To the salicylate product (1 g) was added t-butyl methyl ether (1 g) then HCl (2M). The organic layer was washed with HCl twice, dried ($MgSO_4$), then filtered. The solvent was removed in vacuo leaving a viscous brown liquid. The product was dried in a vacuum oven (25 °C) for 2 hours (Figure 21). The reason for the deashing procedure is to remove the metal cation (sodium and calcium) to give the salicylic acid (Scheme 8).

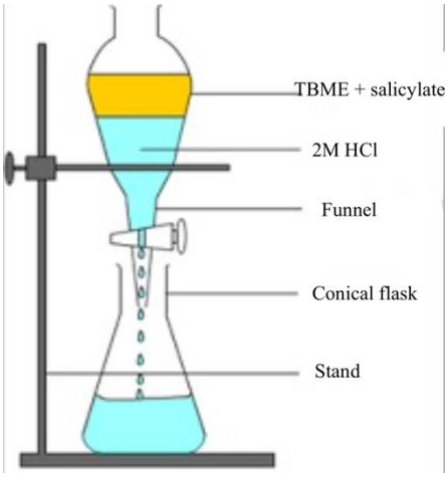
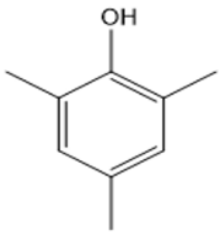



Figure 44: Experimental setup of deashing metal salicylate

**Synthesis of one of the promoters: Hindered phenolate**




Hindered phenolate

250 mL flange flask filled with 2,4,6 – trimethylphenol (10 g, 73 mmol, 1 eqv.) and xylene (11.25 g, 105 mmol, 1.5 eqv.), set up for mechanical stir and vac distillation. Stirred at 50 °C under argon atmosphere. NaOH (2.9 g, 73 mmol, 1 eqv.) added portion-wise to 65 °C, full lab vacuum (approx. 25 mmHg) applied then heated reaction mixture to 150 °C and held for 3 hours. Extra xylene was added as reaction mixture was viscous. Green viscous mixture was

obtained after reaction, collected, and dried thoroughly by grinding to a powder and dried in vacuum oven at 75 °C. – Product yield of 78% (9g collected).

Hindered phenolate produced in moles = 9g / 158.98 $gmol^{-1}$ = 56.6 mmol
Product yield of hindered phenolate = (56.6 mmol / 73 mmol) *100% = 78%

## 2.4.7 Emulsion stability

Water-in-oil emulsions were prepared by adding a saline solution at 5% w/v, as internal phase, dropwise to the mixing phase (diluent oil with salicylate) in a conical tube. Vary ratios of volume of saline and oil phase were tested. Emulsions were agitated vigorously using a magnetic stirrer at speed of 800 rpm and room temperature (18 °C) for 1 hour. The volume of the saline settled to the bottom was read from the scale on the tube at a 30-minute interval. The times taken for the emulsion to destabilise are noted and presented in Table 9.

Table 9: Time taken for emulsion to destabilise (Three repeat measurements, #1, #2, #3)

| Emulsion with surfactant | Time taken #1 / min | Time taken #2 / min | Time taken #3 / min |
|---|---|---|---|
| Phenol | 30 | 30 | 30 |
| Phenolate | 30 | 30 | 30 |
| Salicylate | 300 | 300 | 330 |

### Analysis of Emulsion Stability

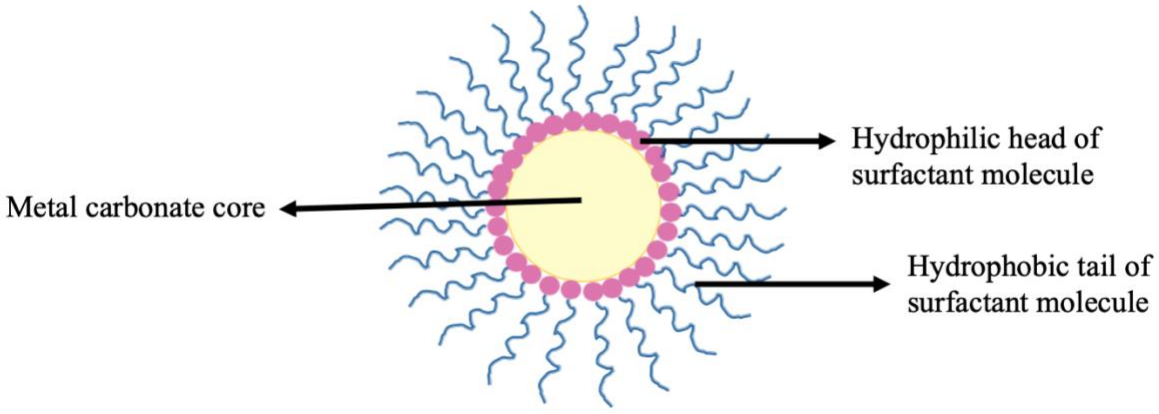



Figure 45: Schematic diagram of an over-based detergent particle.[43]

Figure 45 above illustrates a diagram of an over-based additive particle, which is an inversed micelle comprised of an amorphous metal carbonate core, stabilised by a monolayer of surfactant molecules. The inversed micelle aids in trapping water in oil to stabilise the

emulsion. Salicylates are one of the main examples of surfactants used. The emulsion stability test is to examine how effective the sodium alkyl salicylate is as a surfactant. Table 13 illustrates the time taken for the emulsion to destabilise, ie separate to two layers (Figure 44). It is expected that salicylate would be the most effective as surfactant whereas phenol and phenolate would be less effective due to the polar groups present on the molecule.

Table 13: Time taken for the emulsion to destabilise

| Emulsion with surfactant | Time taken #1 / min | Time taken #2 / min | Time taken #3 / min |
|---|---|---|---|
| Phenol | 30 | 30 | 30 |
| Phenolate | 30 | 30 | 30 |
| Salicylate | 300 | 300 | 330 |

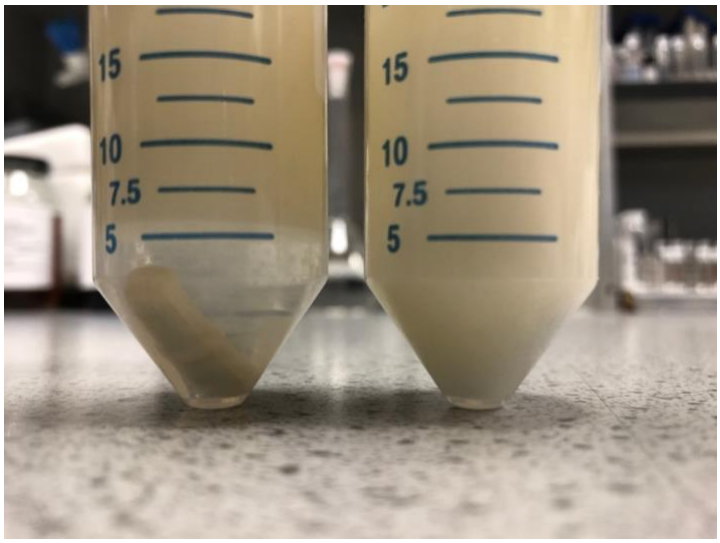



Figure 46: Left: emulsion destabilised, Right: stable emulsion.

# 3. Conclusion and future work

In conclusion, the needs of the industrial partner were positively met and based on the experiment observations they have narrowed down/eliminated most of their possible reaction conditions. They have concluded that the current operating condition is still the optimal condition and now they have a deeper understanding of the mechanism of the Kolbe – Schmitt reaction.

The Kolbe-Schmitt reaction of sodium alkyl phenolate at 4000 psi / 276 bars using 4 different reaction temperatures: 100 °C, 120 °C, 150 °C, 180 °C gave sodium alkyl salicylate with different conversion percentage (from 24% to 50%). The conversions increased (up to 50 %) as the temperature reached up to 120 °C but decreased at 150 °C and 180 °C due to the change in supercritical $CO_2$ density. The Kolbe-Schmitt reaction was also performed in the presence of three promoters: DBU, mTBD and hindered phenolate. DBU promoted reactions provided the highest conversion of all 62%, whereas mTBD and hindered phenolate gave 38% and 9% respectively. The highest conversion without any promoters is only 52%, which is around 10% less than the promoted reactions. The identity of the product was confirmed using ATR-FTIR, $^{1}H$ and $^{13}C$ NMR spectroscopy as well as quantified with the $^{13}C$ NMR Inverse Gated Decoupling method.

On the other hand, the Kolbe-Schmitt reaction of calcium alkyl phenolate at 4000 psi / 276 bars carried out at different temperatures: 120 °C, 150 °C, 180 °C, gave unsatisfactory conversion, being 8% the highest at 150 °C. Several promoters were used in the Kolbe-Schmitt reaction of calcium alkyl phenolate at 150 °C and 4000 psi / 276 bars and the highest conversion obtained was around 14%. However, it should be noted that there are traces of sodium alkyl phenolate left in the calcium alkyl phenolate mixture after the transmetallation process of sodium alkyl phenolate to calcium alkyl phenolate, which might have reacted instead of the main calcium reagent. Thus, DBU promoted reactions at high pressure is the overall best reaction condition.

Overall, this project has given a better understanding on how a complex sodium salt phenol reacts/interacts with promoters, higher temperature and in supercritical $CO_2$.

For future work, computational experiments could be carried out to understand the mechanism of Kolbe-Schmitt reaction with alkaline earth metals. Different $CO_2$ conditions

like subcritical (1000 psi) and supercritical (2000, 3000, 4000 psi) could be explored to gain a better understanding of the nature of $CO_2$ under extreme temperatures.

# 4. References


1. Bart, J. C. J.; Gucciardi, E.; Cavallaro, S., 3 - Lubricants: properties and characteristics. In *Biolubricants*, Bart, J. C. J.; Gucciardi, E.; Cavallaro, S., Eds. Woodhead Publishing: 2013; pp 24-73.
2. Booser, E. R., Lubrication and Lubricants. In *Kirk-Othmer Encyclopedia of Chemical Technology*, American Cancer Society: 2000.
3. Chapter 2 - Lubrication Chemistry. In *Tribology and Interface Engineering Series*, Pawlak, Z., Ed. Elsevier: 2003; Vol. 45, pp 11-66.
4. Bovington, C. H., Friction, wear and the role of additives in their control. In *Chemistry and Technology of Lubricants*, Mortier, R. M.; Orszulik, S. T., Eds. Springer Netherlands: Dordrecht, 1997; pp 320-348.
5. Rudnick, L. R. E., *Lubricant Additives: Chemistry and Applications*. CRC Press: 2009; Vol. Second Edition (2nd ed.).
6. George, S.; Balla, S.; Gautam, M., Effect of diesel soot contaminated oil on engine wear. 2007; Vol. 262, pp 1113-1122.
7. Hu, J.-Q.; Wei, X.-Y.; Dai, G.-L.; Fei, Y.-W.; Liu, C.-C.; Zong, Z.-M.; Yao, J.-B., Synergistic antioxidation of organic molybdenum complex with dithiocarbamate antioxidant evaluated by differential scanning calorimetry and thin film micro oxidation test. 2007; Vol. 453, pp 21-26.
8. Colyer, C. C.; Gergel, W. C., Detergents and dispersants. In *Chemistry and Technology of Lubricants*, Mortier, R. M.; Orszulik, S. T., Eds. Springer Netherlands: Dordrecht, 1997; pp 75-97.
9. Al-Sabagh, A. M.; Azzam, E. M. S.; Noor El Din, M. R., The Surface and Thermodynamic Properties of Ethoxylated Sodium Monoalkyl Sulfosuccinate Surfactants. Taylor & Francis: 2009; Vol. 30, pp 260-266.
10. Ahmed, N. S.; Nassar, A.; el menem, Y. K. A.; shazly, R. I. E., Preparation, characterization and evaluation of some metallic lube oil additives. 2014; Vol. 7, pp 56-67.
11. S.P. O'Connor, J. C., and C.Cane, "Overbased lubricant detergents - a comparative study". *Lubri. Sci.* **1994,** *6(4)*, 297-325.
12. Crawford, J.; Psaila, A., Miscellaneous additives. In *Chemistry and Technology of Lubricants*, Mortier, R. M.; Orszulik, S. T., Eds. Springer US: Boston, MA, 1994; pp 160-173.
13. Nesterenko, A.; Drelich, A.; Lu, H.; Clausse, D.; Pezron, I., Influence of a mixed particle/surfactant emulsifier system on water-in-oil emulsion stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2014,** *457*, 49-57.
14. Binks, B. P.; Desforges, A.; Duff, D. G., Synergistic Stabilization of Emulsions by a Mixture of Surface-Active Nanoparticles and Surfactant. *Langmuir* **2007,** *23* (3), 1098-1106.
15. Zou, S.; Yang, Y.; Liu, H.; Wang, C., Synergistic stabilization and tunable structures of Pickering high internal phase emulsions by nanoparticles and surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013,** *436*, 1-9.
16. Drelich, A.; Gomez, F.; Clausse, D.; Pezron, I., Evolution of water-in-oil emulsions stabilized with solid particles: Influence of added emulsifier. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2010,** *365* (1), 171-177.
17. Krtschil, U.; Hessel, V.; Reinhard, D.; Stark, A., Flow chemistry of the Kolbe-Schmitt synthesis from resorcinol: Process intensification by alternative solvents, new reagents and advanced reactor engineering. 2009; Vol. 32, pp 1774-1789.
18. Lindsey, A. S.; Jeskey, H., The Kolbe-Schmitt Reaction. *Chemical Reviews* **1957,** *57* (4), 583-620.

19. Stanescu, I.; Achenie, L. E. K., A theoretical study of solvent effects on Kolbe-Schmitt reaction kinetics. *Chemical Engineering Science* **2006,** *61* (18), 6199-6212.
20. Yan, X.; Cheng, Z.; Yue, Z.; Yuan, P., Synthesis of 3,6-dichloro salicylic acid by Kolbe–Schmitt reaction. 2. Proton transfer mechanism for the side reaction. *Research on Chemical Intermediates* **2014,** *40* (8), 3059-3071.
21. Forbeck, E. M.; Evans, C. D.; Gilleran, J. A.; Li, P.; Joullié, M. M., A Regio- and Stereoselective Approach to Quaternary Centers from Chiral Trisubstituted Aziridines. *Journal of the American Chemical Society* **2007,** *129* (46), 14463-14469.
22. Nicholls, R.; Kaufhold, S.; Nguyen, B. N., Observation of guanidine–carbon dioxide complexation in solution and its role in the reaction of carbon dioxide and propargylamines. *Catalysis Science & Technology* **2014,** *4* (10), 3458-3462.
23. Sadamitsu, Y.; Okumura, A.; Saito, K.; Yamada, T., Kolbe-Schmitt type reaction under ambient conditions mediated by an organic base. *Chemical Communications* **2019,** *55* (66), 9837-9840.
24. Pérez, E. R.; Santos, R. H. A.; Gambardella, M. T. P.; De Macedo, L. G. M.; Rodrigues-Filho, U. P.; Launay, J. C.; Franco, D. W., Activation of carbon dioxide by bicyclic amidines. *Journal of Organic Chemistry* **2004,** *69* (23), 8005-8011.
25. Luo, J.; Preciado, S.; Xie, P.; Larrosa, I., Carboxylation of Phenols with $CO_2$ at Atmospheric Pressure. *Chemistry - A European Journal* **2016,** *22* (20), 6798-6802.
26. Iijima, T.; Yamaguchi, T., Efficient regioselective carboxylation of phenol to salicylic acid with supercritical $CO_2$ in the presence of aluminium bromide. *Journal of Molecular Catalysis A: Chemical* **2008,** *295* (1), 52-56.
27. Iijima, T.; Yamaguchi, T., $K_2CO_3$-catalyzed direct synthesis of salicylic acid from phenol and supercritical CO2. *Applied Catalysis A: General* **2008,** *345* (1), 12-17.
28. Gu, M.; Yan, X.; Cheng, Z., Hybrid catalytic effects of K2CO3 on the synthesis of salicylic acid from carboxylation of phenol with $CO_2$. Springer Netherlands: 2016; Vol. 42, pp 391-406.
29. Lukić, I.; Krstic, J.; Glisic, S.; DUŠAN, J.; Skala, D., Biodiesel synthesis using $K_2CO_3$/Al–O–Si aerogel catalysts. 2010; Vol. 75.
30. Pu, Y.; Xuan, K.; Wang, F.; Li, A.; Zhao, N.; Xiao, F., Synthesis of dimethyl carbonate from CO <sub>2</sub> and methanol over a hydrophobic Ce/SBA-15 catalyst. 2018; Vol. 8.
31. Fan, Y.; Feng, J.; Yang, M.; Tan, X.; Fan, H.; Guo, M.; Wang, B.; Xue, S., $CO_2$(aq) concentration-dependent $CO_2$ fixationviacarboxylation by decarboxylase. Royal Society of Chemistry: 2021; Vol. 23, pp 4403-4409.
32. Ren, J.; Yao, P.; Yu, S.; Dong, W.; Chen, Q.; Feng, J.; Wu, Q.; Zhu, D., An Unprecedented Effective Enzymatic Carboxylation of Phenols. American Chemical Society: 2016; Vol. 6, pp 564-567.
33. Shanthi, B.; Palanivelu, K., Conversion of carbon dioxide to resorcylic acid under ultrasonication by Kolbe-Schmitt reaction. *Ultrasonics Sonochemistry* **2015,** *27* (1), 268-276.
34. Hessler, J. C., SOME RECENT WORK IN ORGANIC CHEMISTRY. *Journal of the American Chemical Society* **1907,** *29* (1), 88-99.
35. Johnson, J. R., Abnormal Reactions of Benzylmagnesium Chloride. II. The Mechanism of the o-Tolyl Rearrangement1. *Journal of the American Chemical Society* **1933,** *55* (7), 3029-3032.
36. Hales, J.; Jones, J. I.; Lindsey, A., Mechanism of the Kolbe–Schmitt reaction. Part I. Infra-red studies. *Journal of the Chemical Society (Resumed)* **1954**, 3145-3151.
37. Ayres, D. C., *Carbanions in synthesis*. Oldbourne P.: 1966.

38. Kunert, M.; Dinjus, E.; Nauck, M.; Sieler, J., Structure and Reactivity of Sodium Phenoxide-Following the Course of the Kolbe-Schmitt Reaction. *Chemische Berichte* **1997,** *130* (10), 1461-1465.
39. Kosugi, Y.; Imaoka, Y.; Gotoh, F.; Rahim, M. A.; Matsui, Y.; Sakanishi, K., Carboxylations of alkali metal phenoxides with carbon dioxide. *Organic and Biomolecular Chemistry* **2003,** *1* (5), 817-821.
40. Markovi, Z.; Engelbrecht, J. P.; Markovi, S. *Theoretical Study of the Kolbe-Schmitt Reaction Mechanism*; 2002; pp 812-818.
41. Oakes, R. S.; Clifford, A. A.; Rayner, C. M., The use of supercritical fluids in synthetic organic chemistry. *Journal of the Chemical Society, Perkin Transactions 1* **2001,** (9), 917-941.
42. Chapter 5. Supercritical Fluids. 2013; pp 115-148.
43. 4 th Year Research Project (CHEM4007).

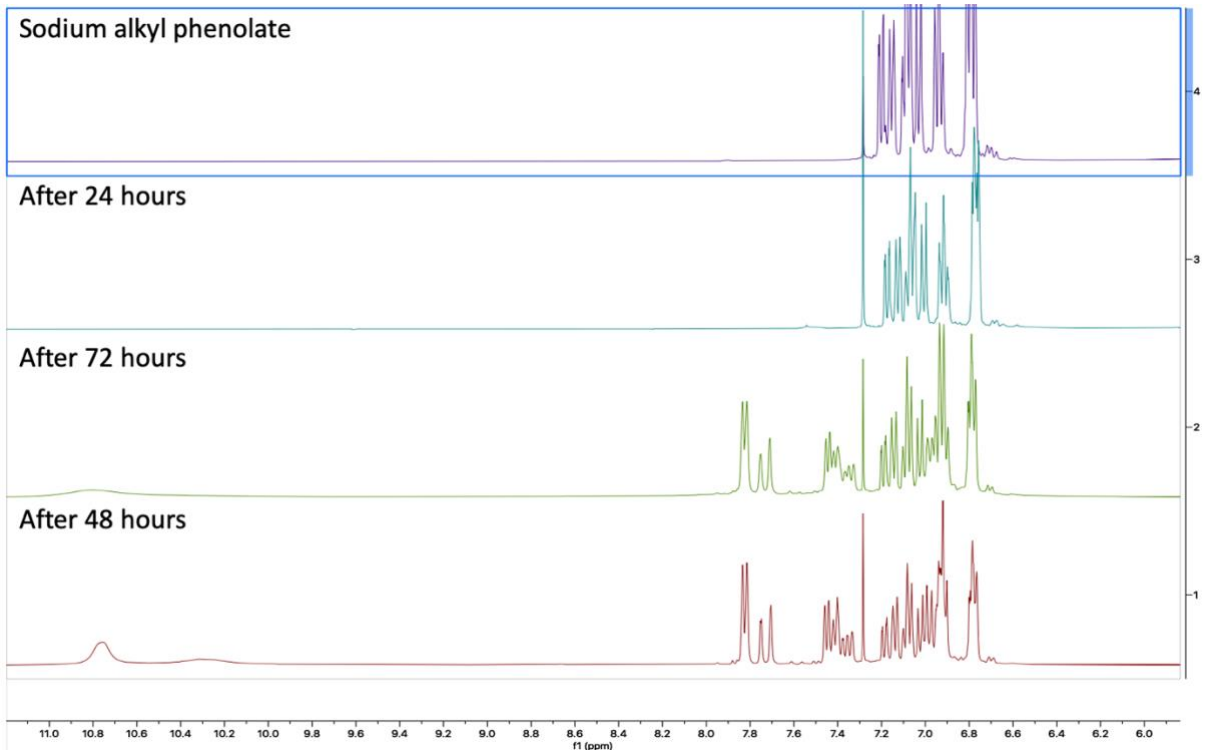
## 5. Appendix

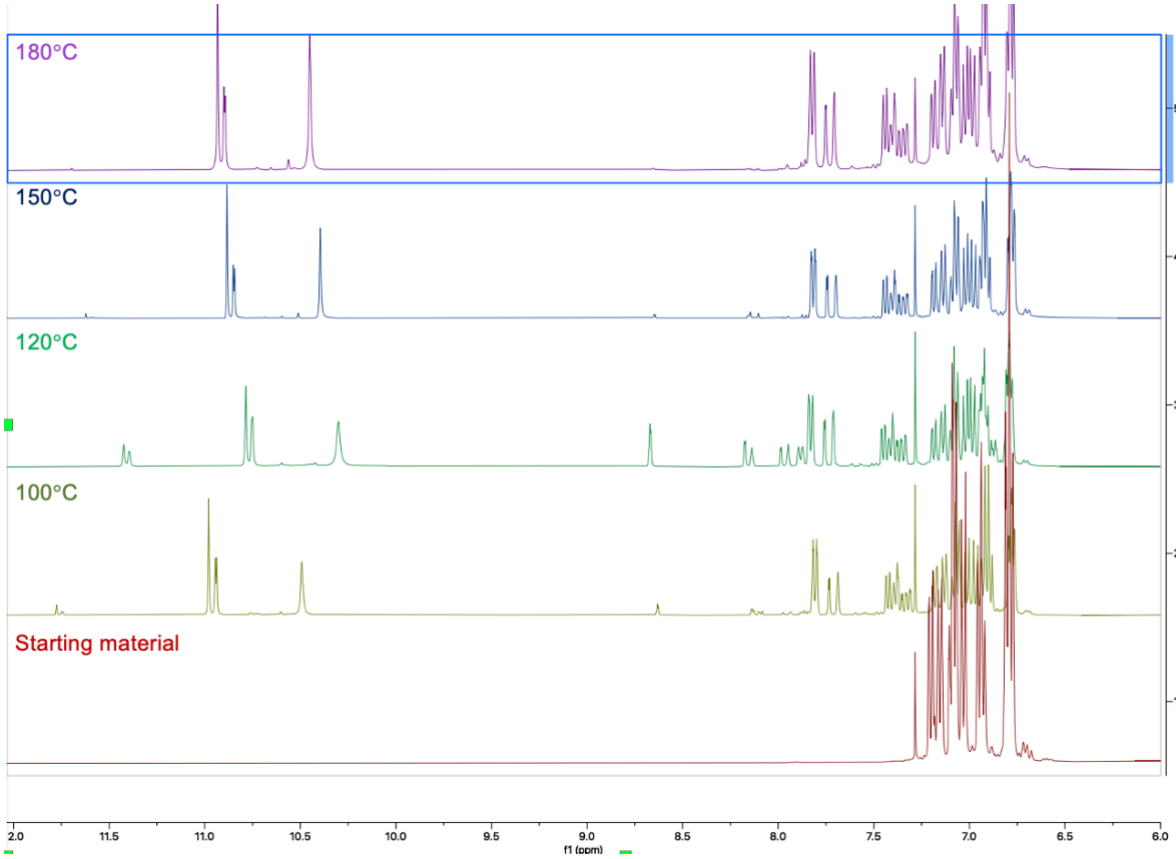
Table 10: Conversion % of all samples [ERROR?]

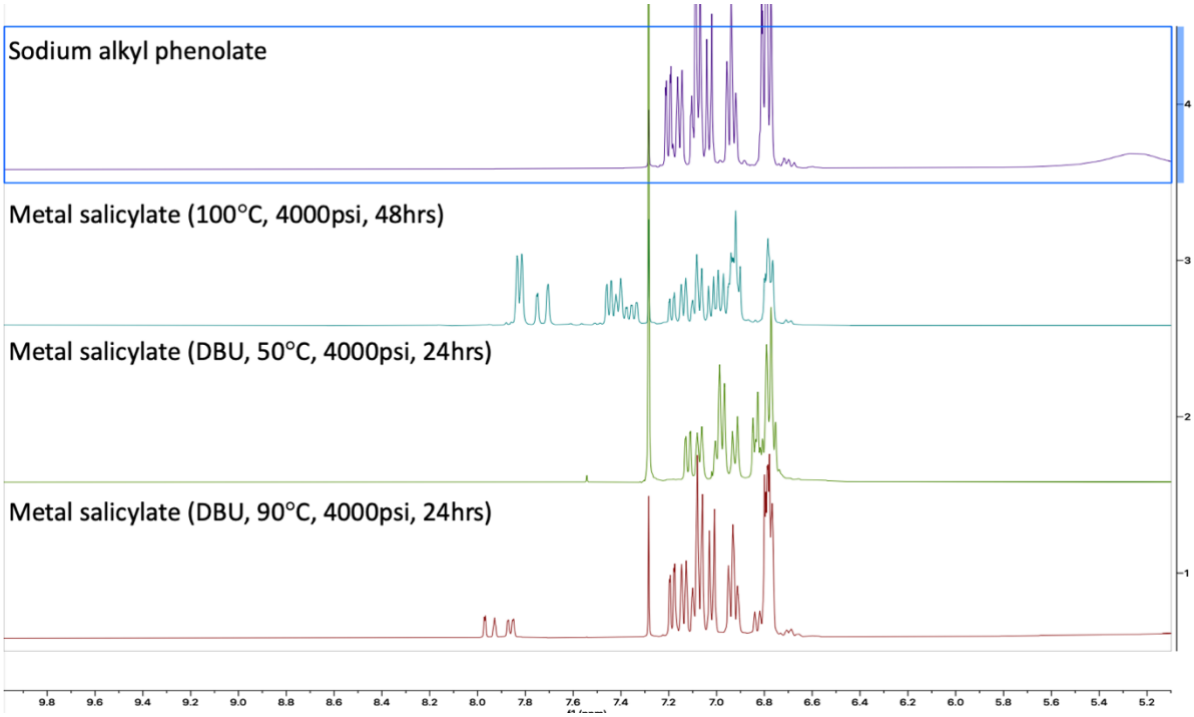
| Sample | Conditions | Conversion % |
|---|---|---|
| MY 51 | Sodium alkyl phenolate at 4000 psi, 100 °C | 30 |
| MY 11 | Sodium alkyl phenolate at 4000 psi, 120 °C | 50 |
| MY 28 | Sodium alkyl phenolate at 4000 psi, 150 °C | 30 |
| MY 29 | Sodium alkyl phenolate at 4000 psi, 180 °C | 24 |
| MY 22 | Sodium alkyl phenolate at 73 psi, 100 °C | 37 |
| MY 12 | Sodium alkyl phenolate at 73 psi, 120 °C | 49 |
| MY 34 | Sodium alkyl phenolate at 73 psi, 150 °C | 52 |
| MY 14 | Sodium alkyl phenolate with DBU at 73 psi | 62 |
| MY 23 | Sodium alkyl phenolate with mTBD at 73 psi | 38 |
| MY 26 | Sodium alkyl phenolate with Hindered phenolate at 73 psi | 9 |
| MY13 | Sodium alkyl phenolate with DBU at 4000 psi | 62 |
| MY 27 | Sodium alkyl phenolate with Hindered phenolate at 4000 psi | 2 |
| MY52 | Calcium alkyl phenolate at 4000 psi, 120 °C | 0 |

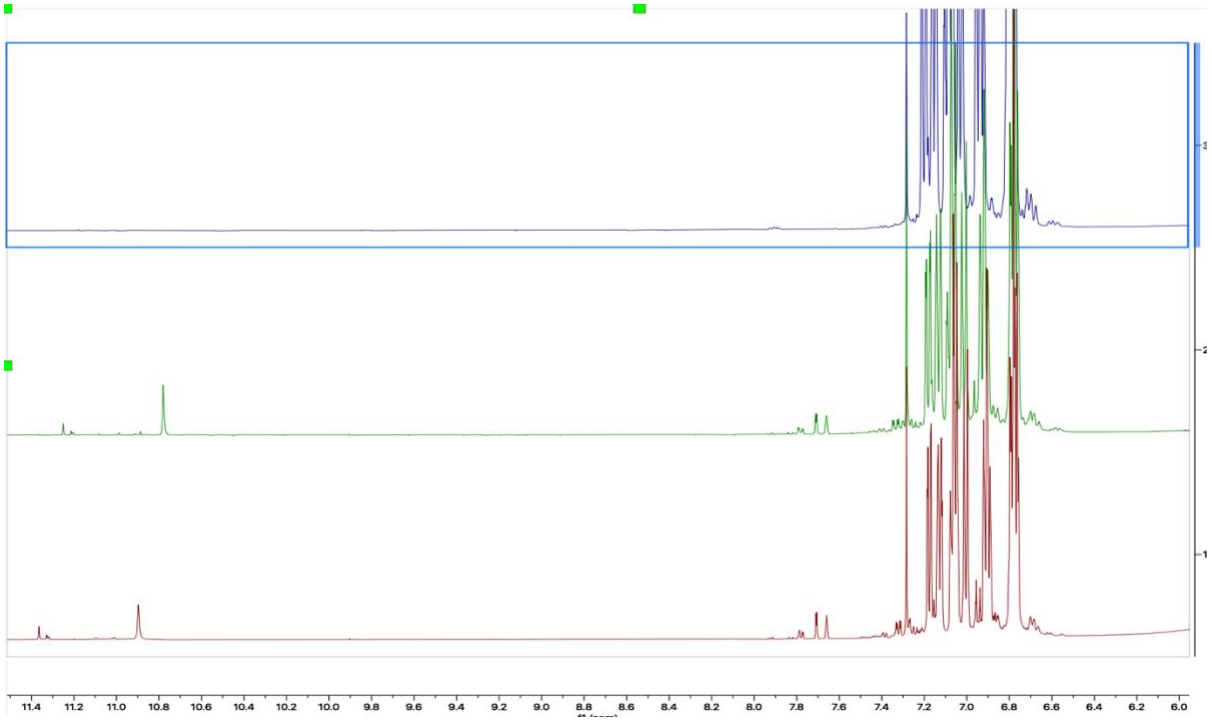
| | | |
|---|---|---|
| MY 30 | Calcium alkyl phenolate at 4000 psi, 150 °C | 8 |
| MY 31 | Calcium alkyl phenolate at 4000 psi, 180 °C | 7 |
| MY32 | Calcium alkyl phenolate with DBU | 4 |
| MY42 | Calcium alkyl phenolate with 20% calcium alkyl sulfonate | 8 |
| MY43 | Calcium alkyl phenolate with 30% calcium alkyl sulfonate | 12 |
| MY44 | Calcium alkyl phenolate with 40% calcium alkyl sulfonate | 14 |
| MY45 | Calcium alkyl phenolate with calcium carbonate | 2 |
| MY46 | Calcium alkyl phenolate with calcium chloride | 0 |

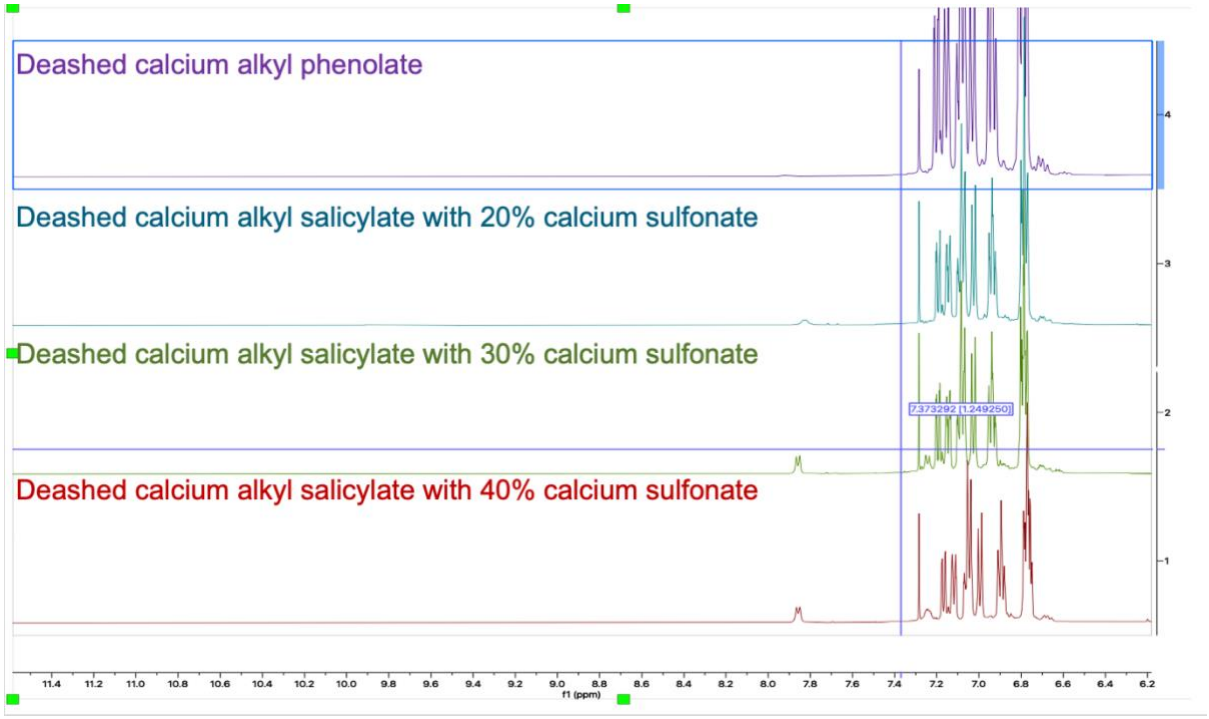
**NMR**

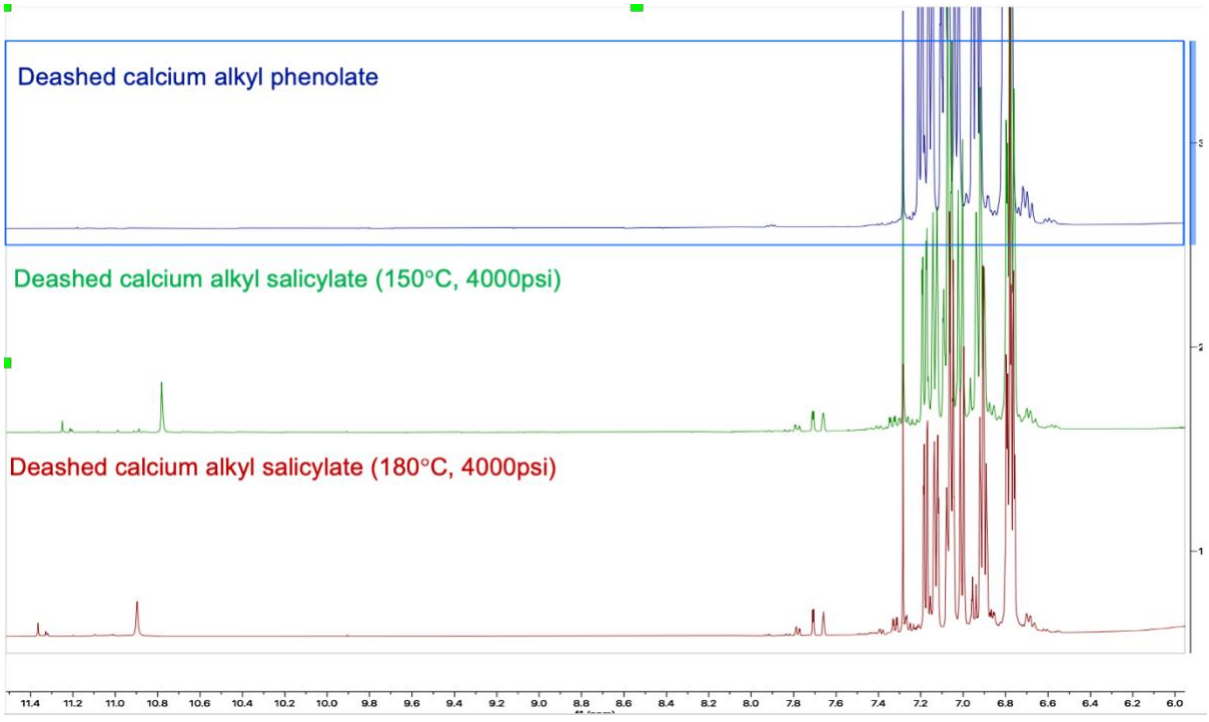

Sodium alkyl phenolate
After 24 hours
After 72 hours
After 48 hours
f1 (ppm)


180°C
150°C
120°C
100°C
Starting material
f1 (ppm)

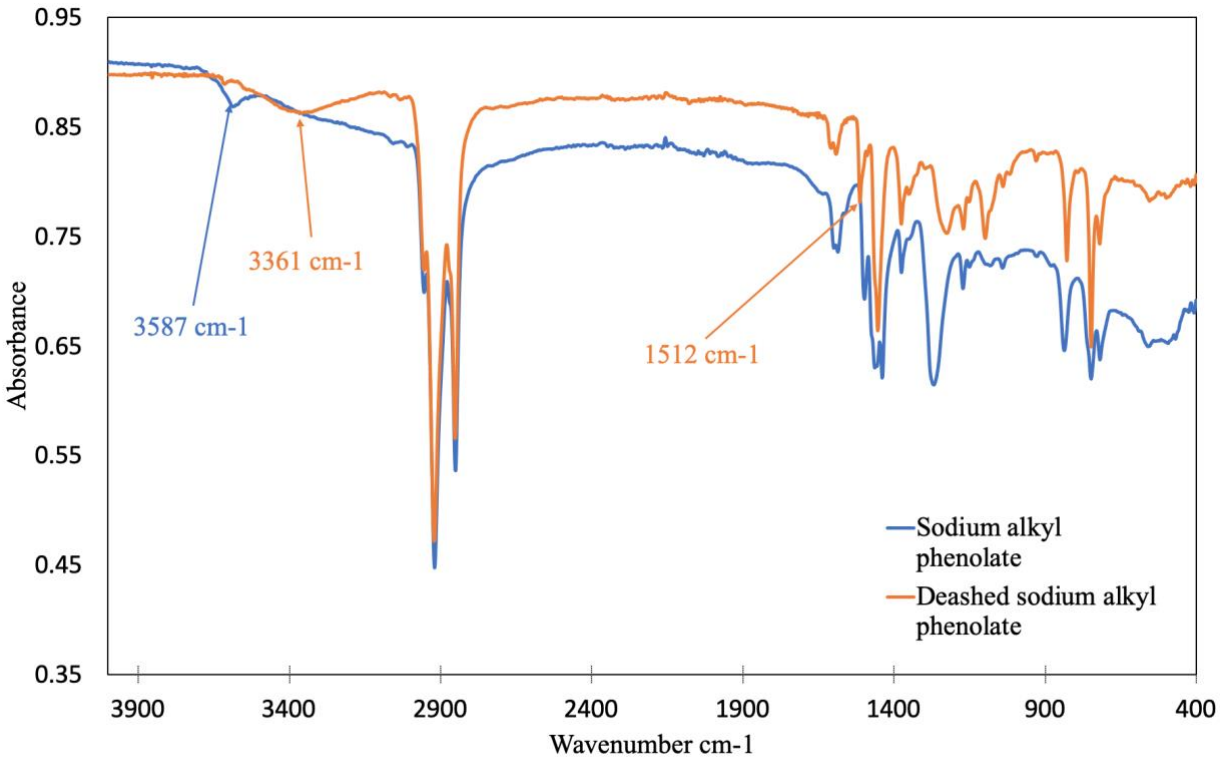

Sodium alkyl phenolate
Metal salicylate (100°C, 4000psi, 48hrs)
Metal salicylate (DBU, 50°C, 4000psi, 24hrs)
Metal salicylate (DBU, 90°C, 4000psi, 24hrs)

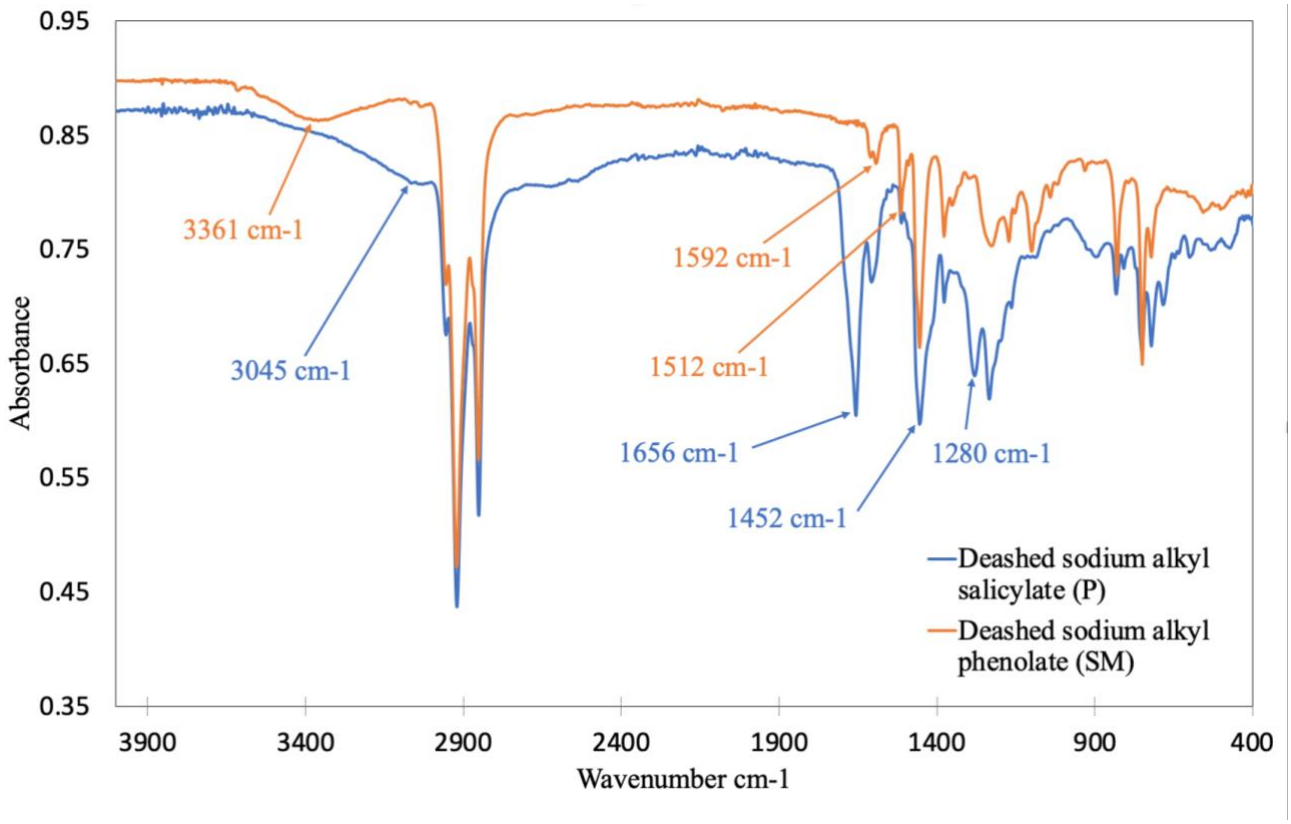


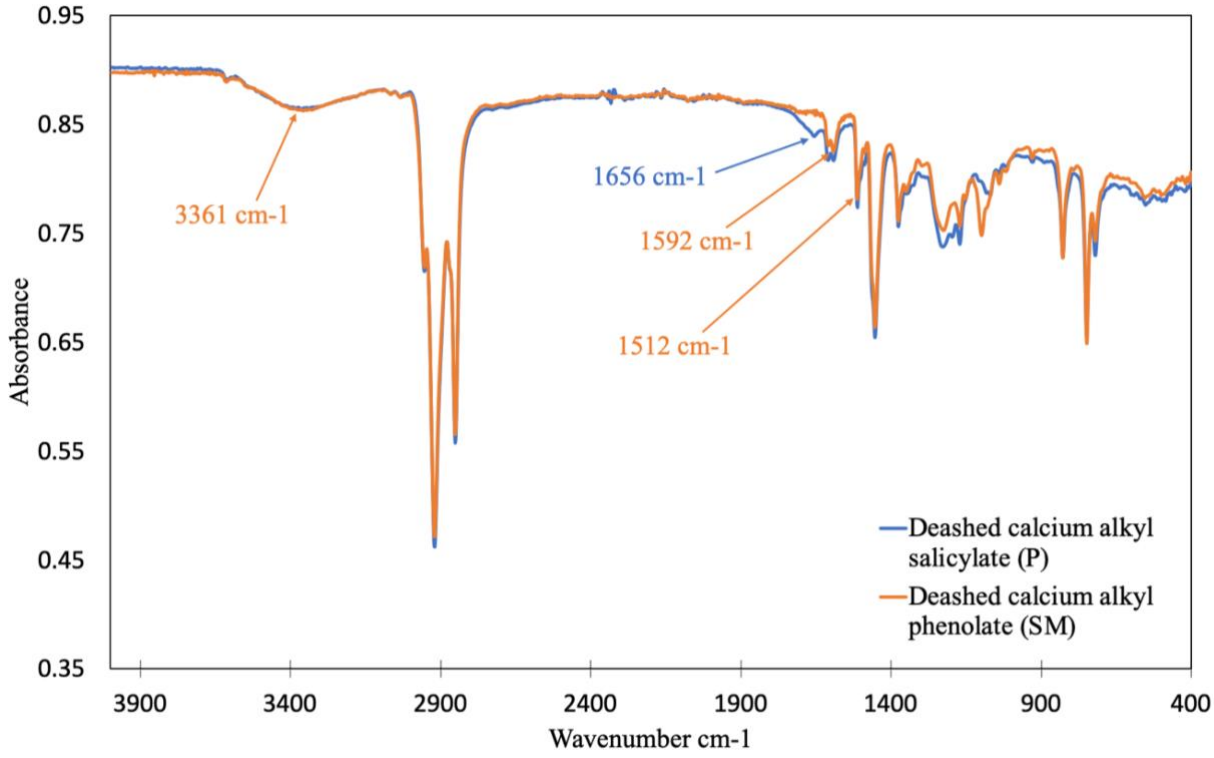

Deashed calcium alkyl phenolate
Deashed calcium alkyl salicylate with 20% calcium sulfonate
Deashed calcium alkyl salicylate with 30% calcium sulfonate
Deashed calcium alkyl salicylate with 40% calcium sulfonate
7.373292 (1.249250)
f1 (ppm)


Deashed calcium alkyl phenolate
Deashed calcium alkyl salicylate (150°C, 4000psi)
Deashed calcium alkyl salicylate (180°C, 4000psi)

**IR**


0.95
0.85
0.75
0.65
0.55
0.45
0.35
Absorbance
3900
3400
2900
2400
1900
1400
900
400
Wavenumber cm-1
3587 cm-1
3361 cm-1
1512 cm-1
Sodium alkyl phenolate
Deashed sodium alkyl phenolate


0.95
0.85
0.75
0.65
0.55
0.45
0.35
Absorbance
3900
3400
2900
2400
1900
1400
900
400
Wavenumber cm-1
3361 cm-1
3045 cm-1
1592 cm-1
1512 cm-1
1656 cm-1
1452 cm-1
1280 cm-1
Deashed sodium alkyl salicylate (P)
Deashed sodium alkyl phenolate (SM)


0.95
0.85
0.75
0.65
0.55
0.45
0.35
Absorbance
3900
3400
2900
2400
1900
1400
900
400
Wavenumber cm-1
3361 cm-1
1656 cm-1
1592 cm-1
1512 cm-1
Deashed calcium alkyl salicylate (P)
Deashed calcium alkyl phenolate (SM)