THE EXTRACTION OF PLATINUM GROUP METALS FROM CATALYTIC CONVERTERS: NON-CONVENTIONAL SOLVENTS AND PRESSURE EFFECTS

by

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DECLARATION

I, Clive Vinee O'niell Griffiths, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

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Signed

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Date

Abstract

Secondary sources of precious metals, such as catalytic converters, contain up to 200 times higher concentrations of platinum group metals (PGMs) compared to natural ores, making them increasingly important for sustainable metal recovery. Catalytic converters contain platinum, palladium, and rhodium in approximate ratios of 4:4:1, with market values in the ratio of 1:1:4, respectively. Current recovery methods using conventional organic solvents achieve high recoveries for platinum and palladium but significantly lower yields for rhodium, while also posing environmental, health, and safety concerns.

Deep eutectic solvents (DES) have emerged as environmentally benign alternatives to conventional organic solvents for metal extraction. However, their high viscosity limits mass transfer efficiency, reducing extraction kinetics and overall recovery yields. This study investigates, for the first time, the combination of DES with supercritical CO_2 (sCO_2) to overcome viscosity limitations and enhance PGM recovery from spent catalytic converters.

Conductor-like Screening Model for Real Solvents (COSMO-RS) identified choline chloride and oxalic acid as the optimal hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) pair for DES formulation. Extraction experiments were conducted using both water bath and pressure-assisted processes with compressed CO_2. The effect of water addition on DES viscosity and the influence of compressed CO_2 on extraction efficiency were systematically investigated.

The combined DES-sCO_2 approach achieved unprecedented recovery yields from the solid residue: 86.5% for platinum, 84.7% for palladium, and above 77% for rhodium. This represents the first time such high rhodium recovery has been achieved using compressed CO_2-assisted extraction. However, a significant challenge was identified in the poor absorption of metals into the DES phase, with only 17.8%, 17.3%, and 20.5% absorption for platinum, palladium, and rhodium, respectively.

This work demonstrates that while DES-sCO_2 systems can effectively leach PGMs from catalytic converter matrices, future research must focus on optimizing metal-DES complex formation to improve absorption efficiency. The findings provide a foundation for developing more sustainable PGM recovery processes and highlight the potential of pressure-assisted extraction using environmentally benign solvents.

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Dedication

I dedicate this document to my Ouma.

Contents

List of Figures

List of tables

Glossary

CO_2	Carbon dioxide
COSMO-RS	Computational Screening Model for Real Solvents
CC	Choline chloride
CA	Citric acid
DES	Deep Eutectic Solvent
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IL	Ionic Liquid
NIST	National Institute of Standards and Technology
NO_x	Nitrogen Oxides
OA	Oxalic Acid
PFD	Process Flow Diagram
PGM	Platinum Group Metal
PM	Precious Metals
p-TSA	Para-Toluene Sulfonic Acid
sCO_2	Supercritical Carbon dioxide
TBP	Tri-butyl phosphate
WB	Water-Bath
ZSM-5	Zeolite Socony Mobil–5

Chapter 1: Introduction

This work is concerned with the application of pressure assisted system, using sCO_2 (supercritical CO_2) and DES (deep eutectic solvent), towards achieving an improved yield of PGMs (platinum group metals) recovered from a secondary source. This chapter introduces the research topic, which consists of a background and context, research questions, aim and objectives, significance of the work, and the layout of the thesis.

1.1 Background to the work

Literature reports that the metal content of ores bearing precious metals is depleting (Rötzer and Schmidt, 2018) in which the grades of ore was assessed in terms of deposit types and demand, exploration changes, mine sizes and structural changes, technological developments, price, and by-products. On the other hand, the metal content of used goods such as electronic equipment and spent catalytic converters is often much higher than that of ores. Platinum ores typically contain 3-10 g/ton of PGMs (Thormann et al., 2017) and a catalytic converter typically contains 1.9 g/per kg or 1900 g/ton of PGMs (Yakoumis et al., 2018). It follows, therefore, that spent industrial and consumer goods can be viable secondary sources of precious metals.

1.1.1 The Importance of Recovering Metals from Waste

The recovery of metals has become an important exercise for several factors. These are, 1) the depletion of high-grade ores and increasing demand for metals (Chuan *et al.*, 2020), 2) higher concentrations of metal content in waste compared to primary ores (Mishra *et al.*, 2021), and 3) the recovery and recyclability of metals are essential for the future sustainable use (Shen and Akolkar, 2017). Additionally, the recovery of precious metals (PM) from waste is vital due to its importance as catalysts in industrial process and catalytic converters, and their high economic value (Vancea *et al.*, 2020).

Furthermore, the recovery of metals contributes to protecting the environment and resource conservation (Okada, Nishimura and Yonezawa, 2015). According to Kim *et al.*, (2020), the recovery of metals from industrial wastewater, known as urban mining, helps in the reduction of hazardous heavy metal emissions and promotes sustainable practices. An additional issue on the rise is the increase of electronic waste due to the rapid advancement of technology, with electronic devices having shorter life cycles.

In conclusion, the recovery of metals from secondary sources is essential in protecting the environment and economic considerations. It enables the reuse of valuable metals, reduces the need for mining of primary ores, and contributes to the circular economy.

1.2 Methods used for recovery of metals from secondary resources

The difference between primary and secondary sources is in their mode of occurrence. Primary sources of metals are found in the earth's crust and exists as ores, in forms of oxides, sulphides (Free, 2022, p. 7), whereas secondary sources of metals are found in electronics, jewellery, spent catalysts and catalytic converters. Both traditional and more modern techniques of metal recovery have been applied in recent literature to recover valuable metals from secondary resources (Firmansyah, Kubota and Goto, 2019; Peeters, Binnemans and Riaño, 2020; Lanaridi *et al.*, 2022). The more modern methods were developed to handle ores that were poorer in their content of the targeted metals. Of importance lately has also been the environmental considerations. The methods used are highlighted below.

Pyrometallurgy: Pyrometallurgy is a process whereby high temperatures are used to extract the valuable metals which includes techniques such as melting, reduction, calcination, and oxidation roasting. Pyrometallurgical techniques has a great deal of success in recovering metals, boasting recovery results of 92% for platinum and 95% for rhodium (Dong *et al.*, 2015), however these results come at a high cost. Because of the complex nature of PGMs, additional techniques are required for effective extraction (Kono *et al.*, 2018), which further adds to the cost. The chemical inertness of PGMs is an additional difficulty when using pyrometallurgy, which hinders dissolution and extraction using the conventional pyrometallurgical techniques (Mpinga *et al.*, 2015). Additionally, the inertness makes solubilization of rhodium challenging (Vasile *et al.*, 2021) and require strong acids which impacts the environmental footprint (Ikeda *et al.*, 2016). To develop eco-friendlier process, other methods have been developed.

Hydrometallurgy: Hydrometallurgy is the extraction of metals from the ores or secondary sources, using an aqueous solution (Hocking, 2005, p.413). For the recovery of metals, the techniques of used include leaching, precipitation of the metal and electrowinning (Ding *et al.*, 2019). The hydrometallurgical methods have had similar yield results and has the advantage of using lower temperatures (as low as 60°C) (Paiva *et al.*, 2022). The drawbacks of hydrometallurgical methods are the production of waste sodium cyanide, which is an environmental hazard, the toxicity of cyanide is a serious concern and the use of aqua regia produces NO_x gases as well as chlorine gas which is detrimental to both the environment and human health (Dong *et al.*, 2015). Additionally, the complexity of PGMs still hinders progress and there is a significant amount of wastewater produced (Qin, 2024).

Supercritical fluid extraction: Supercritical extraction is a process in which a supercritical fluid, a fluid deemed to be in its critical state (Brunner, 1994, p. 3), is used to extract a component from a mixture. The components that are key for extraction to take place is density, thermodynamic properties (temperature and pressure), transport properties (viscosity) and surface tension (Brunner, 1994). Supercritical extraction has many advantages which make it an excellent choice for the recovery of secondary sources. One of the drawbacks of supercritical extraction is the high capital cost.

Deep eutectic solvents (DES): DES are formed by mixing a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) in a specific ratio. DESs have gained attention because unique properties and various successes for various applications, which include CO_2 capture, extraction, separation of compounds and catalysis (Tang, Zhang and Row, 2015; Trivedi *et al.*, 2016; Li *et al.*, 2021; Liu *et al.*, 2021). The solvents are being explored for ability to selectively extract metal ions for electronic waste, which highlights its potential in recycling processes (Yuan *et al.*, 2022). Additionally, these solvents exhibit excellent leaching efficiency for metal oxides and salts compared to aqueous solutions (Zhang, 2023). The drawbacks of using DESs, is the high viscosity exhibited by these compounds.

1.3 Problem statement

PGM recovery using hydrometallurgical methods have shown recovery yields more than 90% (Saguru *et al.*, 2018; Firmansyah *et al.*, 2019; Makua *et al.*, 2019). However, its drawbacks; which include the production of nitric oxide, chlorine gas and acid fumes (Panda *et al.*, 2018), have been a cause for concern which has resulted in different methods being considered. The use of sCO_2 as a solvent with modifiers or chelating agents such as tributyl phosphate (TBP) and Cyanex 301 have shown similar successes and have less of an impact on the environment. Examples are:

- The extraction of PGMs from a spent catalytic converter using sCO_2 (Faisal *et al.*, 2008),
- The recovery of platinum and rhenium from a solid matrix using sCO_2 which was modified with Cyanex 301 (Yamini *et al.*, 2008),
- The extraction palladium from a palladium supported catalyst using sCO_2 which was modified with a polymer (Ruiu *et al.*, 2020),
- The direct extraction of palladium and silver form waste printed circuit boards powder using supercritical water oxidation and sCO_2 (Liu *et al.,* 2016).
- The recovery of palladium using sCO_2 with a chelating agent (Iwao *et al.*, 2007)

These studies indicate that the extraction of PGMs using sCO_2 in combination with a complex ion is feasible. However, two issues remain unanswered. The first being that the economic feasibility of this process at a commercial scale remains unaddressed and, second, that only palladium has been recovered, above 90% yield (Iwao *et al.*, 2007; Faisal *et al.*, 2008), while rhodium recovery remains an issue. The challenges associated with rhodium are its low solubility and inertness. Rhodium is less soluble in acids when compared to platinum and palladium (Nordberg, 2007). In addition, a common form of rhodium, Rh_2O_3, is resistant to chlorination and remains stable under a wide range of temperatures and pressures (Chen *et al.*, 2014).

For commercial viability, the existing studies validate the concept at bench-top scale, which cannot adequately answer questions regarding commercial viability. Bench-top units differ significantly from their commercial counterparts in several ways:

1. Recycle streams are often absent at a small scale, as recycling CO_2 is not prioritized.
2. Pressure generation is achieved using equipment that is not scalable to commercial levels.
3. Bench-top equipment is typically more controllable than commercial-scale equipment.

Therefore, to determine the economic feasibility, experiments must be conducted on a much larger scale. The economic feasibility however, would not be determined in this work, given that work will be conducted in a bench-top manner (shown in Chapter 3: Materials and Methods)

Given that sCO_2 is non-polar and requires a chelating agent and/or modifier to extract metals, different kinds of solvent can be used. ILs and DESs have shown successes in the extraction of all PGMs found in catalytic converters. Lanaridi, (2021) reports that there are over 50 studies that have investigated the recovery of PGMs using various forms of ILs. However it is the investigation by Lanaridi *et al.*, (2022) that is of high interest. Lanaridi *et al.*, (2022) conducted an experiment to show the recovery of PGMs using a DES, which showed high recovery yields for platinum and palladium and a recovery of above 60% for rhodium. DESs matches the recovery yields seen in hydrometallurgy and has other advantages, which include low cost and availability, biodegradability and low toxicity, and tuneable properties (Smith *et al.*, 2014).

Herewith, a question arises, can ILs or DESs in combination with sCO_2 and achieve the same results or better? Additionally, given the high viscosity associated with DESs, can the effect of sCO_2 modify the viscosity, which has limited its scalability.

To address these challenges, this study investigates the use of DESs in combination with sCO_2 for the extraction of PGMs from secondary sources. The work specifically aims to evaluate whether sCO_2 can reduce the viscosity of DESs, thereby improving mass transfer and extraction yields, particularly for rhodium. Bench-scale experiments will be conducted to assess extraction efficiency, selectivity, and the impact of sCO_2 on DES properties. The findings are expected to provide new insights into the feasibility and optimization of this combined approach for sustainable PGM recovery.

1.4 Research questions

Given the above discussion, a series of important questions arise regarding the possibility of recovering precious metals from secondary sources.

i. How does the performance of sCO_2 combined with ILs or DESs compared to other solvent extraction techniques in recovering PGMs from secondary sources?

ii. Are there specific types of ILs or DESs that demonstrate superior performance when used with sCO_2 for extracting metals?

iii. How does the combination of sCO_2 with ILs or DESs affect the extraction efficiency of different precious metals (e.g., platinum, palladium, rhodium) from spent catalytic converters?

1.5 Research aim and objectives

Based on the above problem statement, and the research questions therefrom, the overarching aim of this work was to investigate how pressure variation in sCO_2/DES (supercritical CO_2-deep eutectic solvent) systems enhances the recovery of platinum group metals (PGMs), particularly rhodium, from catalytic converters using pressure-assisted extraction.

1.5.1 Objectives

i. Screening: Selection of HBD and HBA systems with potential for high extraction yield of PGMs,

ii. Determine validity of measuring system using cheaper feed (cobalt doped zeolite catalyst) to evaluate yields (if the experimental setup is found to detecting variation of the extracted metals with a varying solvent system, then objective 3 is carried out),

iii. Perform the experiment using a sample of catalytic converter, measure the yields, and compare them with results from modern methods.

1.6 Hypothesis

It is hypothesized that, by selecting a DES system which has shown to recover PGMs, combined with the properties of sCO_2, the recovery yield could be enhanced.

i. The combination of sCO_2 with DES could result in higher recovery rates of platinum, palladium, and an improved yield for rhodium from spent catalytic converters compared to using only DESs.

ii. The use of sCO_2 will enhance the selectivity for different precious metals due to the unique solvation properties of supercritical fluids, leading to improved separation efficiencies when combined with DESs

iii. The performance (extraction efficiency and selectivity) of sCO_2 combined with specific types of DESs will outperform other solvent extraction techniques in recovering PGMs from secondary sources.

1.7 Approach

The limited literature available for the sCO_2 extraction of precious metals from spent catalytic converters coupled with the cost of catalytic converters, resulted in a careful approach to the experimental run. Firstly, it was important to determine which combination of HBAs and HBDs, in the formation of a DES, would be best suited for the recovery of PGMs. Therefore, a screening tool was used (objective 1). Thereafter, a preliminary experiment (in which a cobalt-doped zeolite was used as a feed) was performed. It consisted of conducting experiments in a water-bath (WB) and in the pressure assisted system. After the analysis of both solid and liquid samples, the validity of the experimental system was determined (objective 2). The same experiment was performed but using the catalytic converter sample, and the results were compared to those found in literature (objective 3). By performing these objectives, it would be possible to determine whether a pressure assisted system using a sCO_2 combined with DES would enhance the recovery of PGMs (aim).

There are studies that have showed promise with the recovery of metals using tri-butyl phosphate as the chelating agent and therefore it provides a great starting point. The approach is highlighted in Chapter 3.

1.8 Limitations of the study

A literature survey suggests that there is only one study that has been done for the extraction of PGMs from spent catalytic converters using sCO_2. There are, however, several studies on the supercritical extraction of palladium.

1.9 Delineation of the study

While the composition of a catalytic converter does consist of other metals, the study focused on the recovery of PGMs only, specifically rhodium, palladium, and platinum. Catalytic converters vary in size and therefore the amounts of PGM content vary as well.

1.10 The current state of knowledge and avenues for further research

By surveying literature, it can be concluded that:

- The extraction of precious metals from a spent catalytic converter is technically feasible using sCO_2. However, the feasibility is limited to the recovery of palladium and not rhodium or platinum. Due to the non-polarity of CO_2 (see Chapter 2), the process is only possible with a chelating agent or a modifier.
- The use of DES improved on the yields of both platinum and rhodium which was an issue when using sCO_2.
- The extraction of metals using both sCO_2 and an ionic liquid has been investigated in one other study (gold recovery) but not for the recovery of PGMs from a spent catalytic converter.

1.11 Organisation of the study

Table 1 Organisation of the study

Chapter	***Outline***
1: Introduction	Within this section, the work is introduced, and the problem statement is given. Additionally, the overall aim of the research work is given combined with the objectives.

2: Literature review	The literature review will provide a detailed review into the extraction of metals using sCO_2. The chapter also investigates other methods of extraction for the recovery of metals and concepts for determining the economic analysis.
3: Methods and Materials	Discusses the method and materials used for the study. Given that the feed is of an expensive nature, pre-experimental work will be explored on a pseudo metal, cobalt. Additionally, given the successes of using a DES, it will be explored as chelating agent.
4: Results	Presents the results obtained for Chapter 3. The extract sample will be sent for ICP-OES analysis to determine the metal content, and the viscosity will be analysed using a rheometer
5: Discussion	Discussed the results presented in Chapter 4 and answered the objectives.
6: Conclusion	Recommendations and conclusion to the study

1.12 Conclusion

Chapter 1 served as an introduction to the study. The problem statement highlights the importance of the study, and in the significance of the study, one of the most important aspects is the feasibility of using a DES in a pressure assisted system. The findings will contribute valuable insights into the mechanisms of metal extraction using sCO_2 combined with DES and provide a foundation for future studies aimed at optimizing these processes for commercial application.

Chapter 2: Literature review

The literature encompassing this study concerns both the fields of hydrometallurgy and supercritical fluid extraction, both of which are recent, yet developing fields. This chapter discusses how the theory in these fields is harnessed to discover a method for extracting metals from spent catalytic converters. chelating agents, their choice, and previous studies. This was used to inform the choice of reagents used in this study. The chapter also discusses the effect of DES on the recovery of PGMs.

2.1 Platinum group metals

This section will discuss the nature and significance of platinum group metals in today's economy.

2.1.1 What are platinum group metals?

Platinum group metals (PGMs) are a group of metals that are made of six elements; these are osmium, platinum, palladium, rhodium, iridium, and ruthenium (Black, 2000). These metals have similar physical and chemical properties and are found together in nature. PGMs are known to have a high resistance to corrosion, high melting points and high conductivities, and high densities (Crundwell *et al.*, 2011, p.395). These properties do however come at a high cost. According to (Daily, 2022), the price of platinum is $ 1061.85 per ounce, palladium costs $ 1778.12 per ounce and rhodium is valued at $ 12200 per ounce. To put into perspective, an ounce of gold costs $ 1918.80 (Daily, 2023). This implies that palladium is valued in a similar bracket to that of gold.

According to Matthey, (2022), the increase in price of palladium is due to the shortage of semiconductor chips in the vehicle making industry experienced in the early part of 2020. PGMs are also found in the dental industry, glass manufacturing, electronics (hard drives and LCDs), as catalysts in the chemical and petrochemical industries, and as catalytic converters for the automobile industry. PGMs are highly recyclable, with various techniques showing recovery yield of more than 90% (Dong *et al.*, 2015; Ding *et al.*, 2019; Chidunchi *et al.*, 2024). As industries move towards greener technologies, the demand for PGMs is expected to rise even further.

In summary, PGMs play a significant role due to their unique properties and diverse applications across various sectors.

2.1.2 Industrial uses of PGMs

One of the most important uses of PGMs is in catalytic converters for automobiles. Platinum is used in various sectors of the industry, these include dentistry and biomedical, electrical, and electronic appliances, the chemical industry, the glass industry, petroleum, and pollution control (Matthey, 2022). Palladium is used in the automotive, jewellery, industrial sectors, and the automotive industry makes up more than 80% of the total demand. Rhodium is used in used in the automotive industry, which accounts for more than 95% of the demand, and other sectors include glass manufacturing, specifically fibre glass. Another major use of PGMs is in the jewellery industry. Platinum is often used in high-end jewellery, particularly in engagement rings, due to its durability and natural white colour (Black, 2000, p.2). Palladium is also used in jewellery and is becoming an increasingly popular alternative to white gold.

PGMs are rare and are primarily mined in South Africa and Russia. According to a report by Matthey, (2022), in 2021, South Africa is the largest producer of platinum, accounting for about 75% of global production. Russia is the second largest producer, followed by Canada, the United States, and Zimbabwe. In addition to mining, PGMs are recovered from secondary materials, such as spent catalysts and spent catalytic converters.

2.1.3 Conventional catalytic converter

There are various alternative technologies that are being tested; these include (1) improving the design of the engine, (2) using alternative fuels and fuel additives, (3) pre-treating the fuel, and (4) better tuning of the combustion process (Patel, Subedar and Patel, 2022). However, none of these technologies do the job as efficiently as the catalytic converter.

Internal combustion engines, such as those used in vehicles and trucks, have a catalytic converter fitted in its exhaust system. Catalytic converters consist of a stainless-steel housing and two ceramic honeycomb structures, which are kept in place by a heat blanket. The ceramic structure placed at the entrance of the catalytic converter has a rhodium chloride coating, with the latter structure coated with hexachloroplatinic (IV) acid ($H_2PtCl_6 \cdot 6H_2O$) and palladium chloride (Moldovan, Gömez and Palacios, 1999).

The primary goal of a catalytic converter is the conversion of products; NO_x, carbon monoxide (CO) and hydrocarbons (HC), produced by an engine, to breathable gases. The chemical reactions that occur is the oxidation of CO to CO_2 and HC to CO_2 and water, and the reduction of NO_x gases to nitrogen and oxygen. The reduction reaction occurs first, and the oxygen gained is used for the oxidation reaction. The process is shown below in equations 1, 2 and 3:

$$2NO \rightarrow N_2 + O_2 \text{.................... Equation 1}$$

$$2NO_2 \rightarrow N_2 + 2O_2 \text{.................. Equation 2}$$

$$2CO + O_2 \rightarrow 2CO_2 \text{...................Equation 3}$$

There are various combinations of the coating however, Moldovan, Gömez and Palacios, (1999) does note that the total amount of PGMs on catalytic converters do not exceed 0.1% of the total content.

According to Yakoumis *et al.*, (2018), the size of a typical catalytic converter is highly dependent on the power of the engine, date in which the vehicle is manufactured, type of fuel the engine uses and whether the converter is manufactured by the vehicle supplier or by an aftermarket supplier. Typically, a catalytic converter contains almost 1500 mg/kg of PGMs (Moldovan, Gömez and Palacios, 1999). By comparison, PGM ores contain 4 – 6 grams of platinum/ton and spent converters would potentially contain 1500 grams of PGM/ton.

Despite their effectiveness in reducing emissions, catalytic converters face challenges such as catalyst poisoning from impurities in fuels that can diminish their performance over time. Poisons such as phosphorus (Kaleli, 2001), sulfur (Bergman *et al.*, 2020) and alkali metals such as sodium and potassium (Williams *et al.*, 2014; Williams *et al.*, 2011) have shown to affect catalyst performance. However, as regulations become more stringent globally regarding vehicle emissions, ongoing research into enhancing catalytic converter technology remains essential for meeting environmental standards.

2.2 Current technologies used for extracting PGMs from spent catalytic converters

Currently there are at least two methods that have been used for the purpose of extraction of PGMs from their ores, which are combinations of pyrometallurgy and hydrometallurgy (Crundwell *et al.*, 2011). PGMs are extracted from two sources, from a primary source, from ores, and from secondary sources, from spent catalytic converters. For the extraction from ores, pyrometallurgical methods are used. This method works when the content of metal is significant enough to form a trickle of pure metal extract from the solid rock. Given that metal content in the catalyst in this work is at most 0.1% of the composition of the catalytic converter (Jimenez De Aberasturi *et al.*, 2011), and hence too little to extract using this method. The nature of this work is the recovery of PGMs from a secondary source, and thus pyrometallurgy does not form part of the scope.

Hydrometallurgical methods involve the leaching of ore or concentrates to dissolve the metal in aqueous solution (Free, 2022, p. 145), from where the metal, or a mixture of different metals, will be selectively extracted in their pure form.

2.2.1 Hydrometallurgy

This section explained the different methods within hydrometallurgy in the recovering of PGMs from secondary sources. The extraction of PGMs from catalytic converters were the only sources that were considered. A typical hydrometallurgical extraction process involves leaching the PGM concentrate by using hydrochloric acid (HCl) or cyanide leaching.

2.2.1.1 Types of extraction

This section will discuss how hydrometallurgical methods are used in the extraction of PGMs from secondary sources.

2.2.1.1.1 Pre-concentration PGMs by dissolving

For this process, the pre-treating is done for the removal of organic substance and the removal of carbon deposition on the surface. Kim, Woo and Jeon, (2000) reported that PGMs can be recovered by using the cementation process; a process of extracting a metal based on the electrochemical reaction between the cementing metal and the ion of the precipitated metal (Havlik, 2008, p. 255), by using aluminium powder as the reducing agent. In a study by Mishra, (1987) a spent catalytic converter was pressure leached by sulphuric acid.

2.2.1.1.2 Leaching in HCl and oxidants

The process involves leaching PGMs in a hydrochloric acid, HCl, solution with a certain oxidizing agent, which could either of the following, HNO_3, Cl_2, $NaClO_3$ and H_2O_2 (Grumett, 2003; De Sá Pinheiro *et al.*, 2004; Marinho *et al.*, 2011; Sun and Lee, 2011). The reactions with HCl produce a chloro-complex ($[PtCl_6]^{2-}$, $[PdCl_4]^{2-}$, $[RhCl_6]^{3-}$). Investigations have reported that the inclusion of a pre-treatment (oxidization or reduction roasting) is used to destroy any organic substances on the surface of the spent catalysts or change the supporter forms (Fornalczyk and Saternus, 2009; Jimenez De Aberasturi *et al.*, 2011). In a study conducted by Jafarifar, Daryanavard and Sheibani, (2005), the recovery of platinum was found to be 98.3%. The study leached platinum from a bimetallic catalyst using microwave radiation with aqua regia with a liquid/solid ratio of 2 for 5 minutes. To increase extraction efficiency, the leaching of Pt and Rh from a spent catalytic converter using aqua regia and $AlCl_3$, the recovery was found to be 95% and 82%, respectively (Bolinski and Distin, 1992). In the study it was found that the Rh dissolution was raised slightly with the addition of $AlCl_3$. Angelidis, (2001) reported that in a process which used methods of reductive leaching (using H_2SO_4 and $N_2H_6SO_4$), oxidative leaching (using NaClO, HCl and $AlCl_3$), leaching with HCl, and neutralisation with a metallic Al, the recovery yields for Pt and Rh was found to be 94% and 89%, respectively. In a study by Harjanto *et al.*, (2006), PGMs were extracted from a spent catalyst residue and recorded yields of 77, 88, and 99% for Rh, Pl and Pd, respectively. The process consisted of leaching with HCl and H_2O_2, followed by substituting the HCl with NaClO which aimed to lower the acidity of the solution without affecting the dissolution efficiency of PGMs. An environmentally friendly electro-generated chlorine leaching technique for removing PGMs from used automotive catalysts was developed by Kim *et al.*, (2013) and Upadhyay *et al.*, (2013). The produced Cl_2 was added to an HCl solution to produce Cl_2(aq), Cl_3^-, and HClO. According to Chen *et al.*, (2014), the extraction rate increased from 56 to 82% with by using a hydrogen reduction pre-treatment with parameters of 300°C for 3 hours and a flow rate of 150 – 200 ml/min.

2.2.1.1.3 Cyanide leaching

The use of cyanide to recover PGMs from spent catalysts has been studied (Gary B. Atkinson, Robert J. Kuczynski, 1992; Chen and Huang, 2006). For the process, sodium cyanide is used to react with a spent catalyst in an alkaline solution to extract PGMs. The use of the alkaline solution forms stable complexes with PGMs. For the separation of PGMs from the solution, the following processes can be used, cementation on zinc dust, carbon absorption or by solvent extraction and precipitation (Sparrow and Woodcock, 1992). In the study by Desmond *et al.*, (1992), whereby a spent catalytic converter was leached with sodium cyanide, the recovery of all PGMs was found to be 90%. The process consisted of leaching the samples twice with a 1% sodium cyanide at 160°C for one hour. In the recovery of Pt from a spent dehydrogenation catalyst, using sodium cyanide, 85% was recovered which consisted of running the process under optimum conditions of 140 - 180°C, pH of 8 – 9 for one hour (Shams, Beiggy and Shirazi, 2004). Chen and Huang, (2006) reported recovery yields of 95 – 96%, 97 – 98% and 90 – 92% for Pt, Pd and Rh, respectively, in the leaching of a spent catalytic converter. The process consisted of pre-treating the spent sample for two hours, followed by two stages of pressure cyanide leaching for one hour, with parameters of 15 bar, 160°C and a solid: liquid ratio of 1:4.

2.2.1.2 Issues with Hydrometallurgy

However, there are limitations associated with hydrometallurgical recovery of PGMs. Traditional methods, such as acid dissolution and chemical separation, can be complex, lack selectivity, and involve numerous recycling streams and refining steps, leading to inefficiencies in the process (Firmansyah *et al.*, (2019). Additionally, some hydrometallurgical techniques may result in the loss of valuable metals, such as lithium, in slag, and can have high energy and chemical reagent consumption (Cerrillo-Gonzalez *et al.*, 2020). The recovery of PGMs from spent automotive catalysts using hydrometallurgical methods may also be energy-intensive (Liu *et al.*, 2014). Moreover, while hydrometallurgical processes offer advantages over smelting in terms of reduced operating costs, they may still require significant energy consumption (Thethwayo, 2018).

In addition issues are cause for concern, those are that the transition of these metals to a larger scale have been slow, waste management (liquid washes and gas emissions produced), time factor of the process, cost and nature of the reagents used (Saguru *et al.,* 2018). Additionally, hydrometallurgical methods produce sodium cyanide as a waste (Razmakhnin and Vasiljuk, 2022), which is an environmental hazard.

In conclusion, hydrometallurgical methods represent a viable approach for recovering PGMs from spent catalytic converters. While these techniques demonstrate significant potential through various leaching processes—often yielding high recovery rates—they also present challenges related to chemical safety and operational complexity. Ongoing research into optimizing these methods is essential to enhance efficiency and minimize environmental impacts associated with PGM recovery.

2.2.2 Supercritical fluid extraction

Supercritical extraction of valuable materials from solid substrates has been around for more than decade, and large-scale processes in the food industry include the decaffeination of coffee beans and black leaves, and the production of hops extracts (Brunner, 1994, p. 178).

2.2.2.1 What is a supercritical fluid?

A supercritical fluid (SCF) is a pure component that is in its supercritical state, whereby both its temperature and pressure is above the critical values (Brunner, 1994, p. 3) which is shown in Figure 1. The critical point is the highest point, in terms of its temperature and pressure, in which a fluid exists. At this point, the fluid exists neither in a distinct liquid nor a gaseous phase.

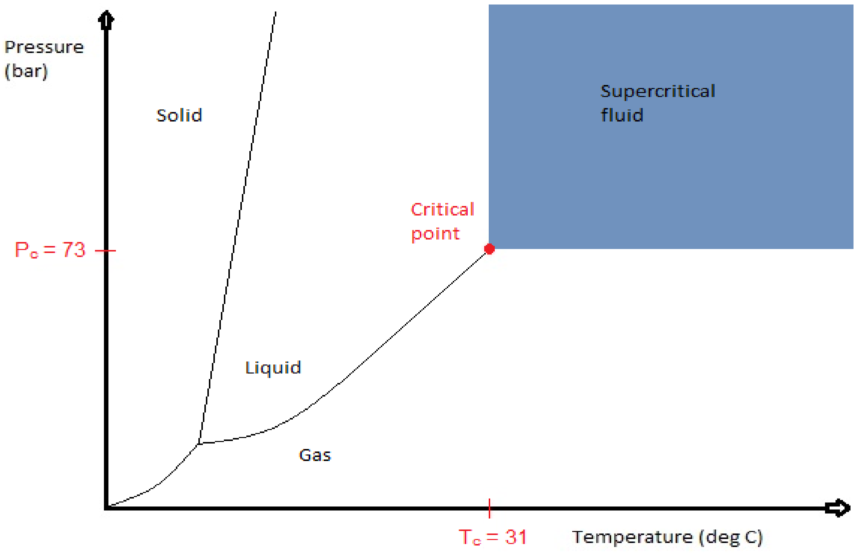


Figure 1 Phase diagram of CO_2

Error! Reference source not found. illustrates the critical points for carbon dioxide, which is 7.3 MPa or 73 bar and 31°C. Carbon dioxide was chosen as the supercritical fluid because of its low critical points compared to other compounds, shown in **Error! Reference source not found.**, and there are other advantages over other fluids. These are discussed in a latter section of the chapter. **Error! Reference source not found.** lists critical points of pure compounds and of these, sCO_2 and supercritical water, scH_2O, are the most used fluids (Braeuer, 2015, p. 2). However, looking at **Error! Reference source not found.**, the critical points are vastly different, whereby scH_2O has a critical pressure 221.2 bar and critical temperature of 647.3 K compared to that of sCO_2. Given these differences, sCO_2 is generally the more favourable option, except in cases where specific applications require the unique properties of supercritical water. Supercritical water is more corrosive than sCO_2, therefore is used to test corrosive properties (Šípová *et al.*, 2023).

Table 2 Critical points for pure compounds (adapted from Brunner, (1994))

Pure Compounds	T_c (K)	P_c (bar)
Helium	5.2	2.3
Hydrogen	33.0	12.9
Neon	44.4	27.6
Nitrogen	126.2	33.9
Carbon monoxide	132.9	35.0
Argon	150.8	48.7
Carbon dioxide	304.2	73.8
Propylene	365.0	46.0
Methanol	512.6	81.0
Ethanol	513.9	61.0
Water	647.3	221.2

2.2.2.2 Advantages of using supercritical extraction

In SFE, carbon dioxide (CO_2) is the most used solvent and given its non-toxicity, it can provide a sustainable way of extracting natural products and be recycled. Other benefits of CO_2 are that it is inexpensive when compared to other solvents, it has a lower critical pressure and temperature than other solvents, and it is non-flammable and has the highest critical density of all solvents. CO_2 also has the distinct advantage whereby it has a tuneable solvent power (Brunner, 2018), allowing for the manipulation of thermodynamic properties by changing the process parameters. Furthermore, according to Clark, Ricciardo and Weaver, (2016), CO_2 allows (1) for the customizing of the properties to target specific molecules, and (2) the complete recycling of CO_2 avoids the necessity of energy-intensive recovery processes.

Other solvents have been used, such as water, methanol, and ethanol. However, these other solvents, except water, are expensive, toxic, and flammable (Passos *et al.*, 2010). It does beg the question, are there any disadvantages to using CO_2? Most of the successes achieved have been done at laboratory scale level, and there is a delay in the technology transfer to commercial scale due to the high operating costs and lack of technical data to perform a process scale up (Duba and Fiori, 2015; Montañés *et al.*, 2018). Regarding metal extraction using CO_2, the main challenge lies in its polarity. However, this issue can be addressed by incorporating a chelating agent or a modifier.

2.2.2.3 How does supercritical extraction work?

Supercritical fluid extraction (SFE) is a technique in which the solvent used to extract a soluble compound is maintained above its critical temperature and pressure. The properties of supercritical fluids change significantly depending on its state and these changes form the basis for numerous applications. Pressure, temperature and volume are vital for gas extraction (Brunner, 1994, p. 6). Gas extraction from solids has two process steps, the extraction from the solid and the separation of the extract from the solvent (Brunner, 1994, p. 180). For the extraction process, the supercritical fluid flows through the loaded sample and dissolves the extractable content of the solid. According to Brunner, (1994, p. 180), the direction of flow of the solvent can be upwards or downwards and that the influence of gravity can be seen as negligible when at high solvent ratios. For the separation step, the loaded solvent is fed to a separation vessel and within this vessel; the extract is separated from the solvent. The following properties were looked at, density and transport properties.

2.2.2.3.1 Density

The density of sCO_2 is closer to that of the liquid CO_2, which is shown in

, and increases with the increase of pressure at a constant temperature. However, when pressure is constant and there is an increase in temperature, the density decreases. The dissolving effect of the supercritical fluid is dependent on the density, and therefore it is a key parameter. Both (Sodeifian *et al.*, 2022) and (Ushiki *et al.*, 2023) showed that an increase in density, increased the solubility.

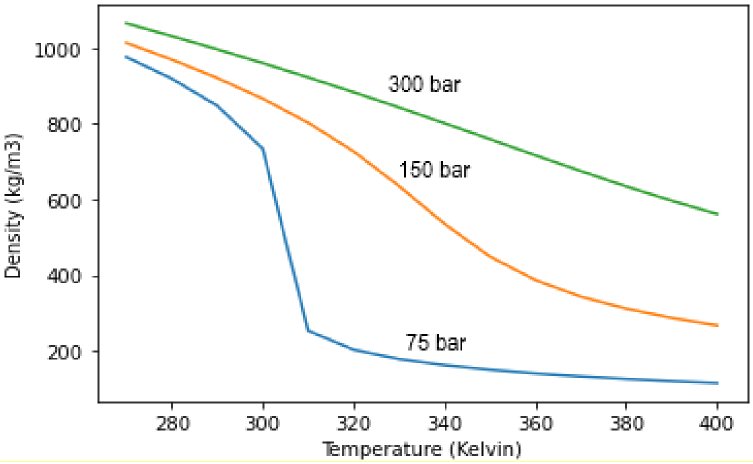


Figure 2 Change in density compared with the change in Temperature at various pressures (data retrieved from NIST, (2023))

Error! Reference source not found. illustrated the variation in density of CO_2 with respect to temperature at a constant pressure. For all chosen values of pressure, at the initial temperature of 270 K, the densities were all close to 1000 kg/m^3. However, at that point, the fluid was still in liquid phase and therefore a high density was expected. For all selected values, the density decreases as the temperature increases. There was a rapid decrease in density for 75 bar, and as soon as the temperature increased to beyond the critical point, the rapid nature of the change stopped.

highlights the similarities shared by gases and liquids, and sCO_2. The data suggests that sCO_2 has liquid-like properties in terms of both its density and diffusion, and the viscosity of sCO_2 resembles that of a gas. Thus, SCF has properties of both gases and liquids, for example, it has the diffusion properties of a gas and solvating power of a liquid (Vardanega, Cerezal-Mezquita and Veggi, 2022) (Vardanega and Osorio-tob, 2022).

Table 3 Comparison of different properties of carbon dioxide in various phases (data retrieved from NIST, (2023))

Substance	Density (kg/m^3)	Viscosity (g/cm·s)	Diffusion (cm^2/s)
Gas	10^{-3}	10^{-4}	10^{-1}
Liquid	1.0	10^{-2}	10^{-5}
Supercritical CO_2	0.3 - 1	$10^{-3} – 10^{-4}$	$10^{-4} – 10^{-6}$

2.2.2.3.2 Transport properties

This section discusses the impact of viscosity and the diffusivity coefficient properties on supercritical CO_2.

Viscosity

Viscosity is defined as the coefficient of the shear stress of a slowing fluid and is calculated using the following linear expression (Mukhopadhyay, 2000, p. 84):

$$\tau = -\eta \frac{\partial u}{\partial z} \text{………………Equation 4}$$

In which tau, τ, is the shear stress caused by applying the velocity gradient, $\frac{\partial u}{\partial z}$, by the viscosity, η. Viscosity is dependent on both temperature and pressure. The increase in viscosity because of pressure happens at isothermal conditions, and the decrease in viscosity due to temperature, happens at isobaric conditions. Viscosity rapidly increases when pressure is beyond the critical pressure. The relationship of viscosity and pressure of CO_2 was shown in Figure 3. An important aspect that was clearly visible in Figure 3, was the considerable difference in viscosity at a lower temperature (310 K), above 80 µPas, compared to the highest temperature (350 K), which was less than 50 µPas. Additionally, for all three temperatures, viscosity was less than or close to 20 µPas at 60 bar, and soon after the critical pressure was reached, the change in viscosity differs substantially.

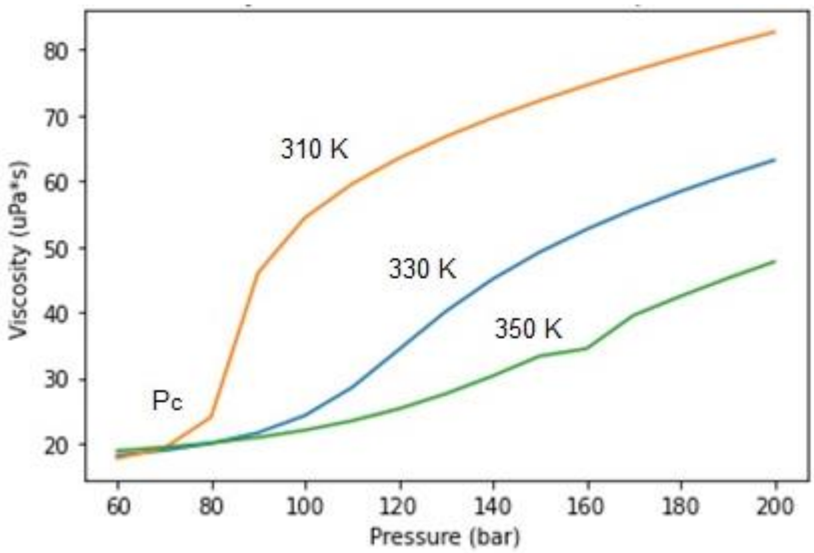


Figure 3 Viscosity vs Pressure graph at constant Temperature (310, 330 and 350 K) (data retrieved from NIST, (2023)*)*

Figure 4 showed how viscosity changes with temperature at a constant pressure of CO_2. The data suggests that there was a gradual decrease in viscosity as temperature increases. One difference of note was the rapid decrease in viscosity at 80 bar. As soon as critical temperature was reached, the viscosity rapidly stops decreasing.

Given that Figure 2 and Figure 4 compared density and viscosity with temperature at a constant pressure, a similar impact was seen. An assumption that can be made is that temperature has the same impact for both properties. Thus, at constant pressure, both density and viscosity decrease with temperature.

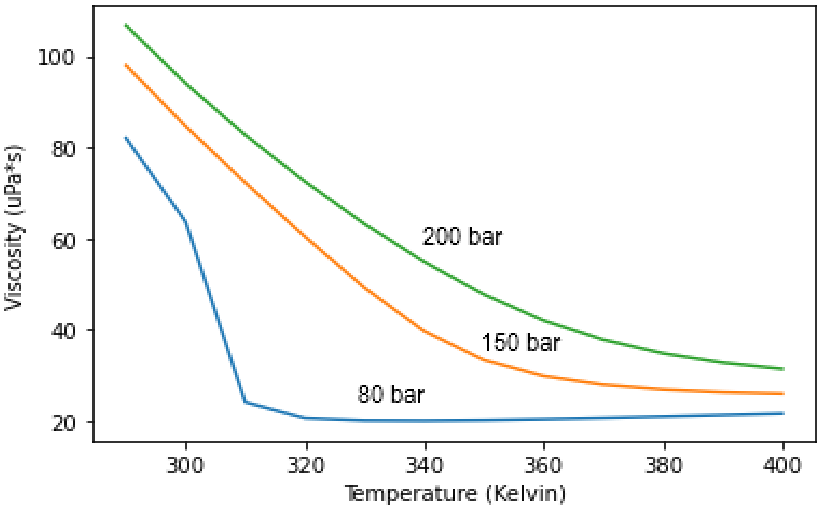


Figure 4 Viscosity vs Temperature at constant Pressures (80, 150 and 200 bar) (data retrieved from NIST, (2023)*)*

2.2.2.4 Chelating agents and Modifiers

The extraction of metals using only sCO_2 is not possible (Faisal *et al.*, 2008) due to the non-polarity of the CO_2 molecule, and the polarity of metalling ions. This is overcome using a chelating agent and/or a modifier. Many literature sources indicate the feasibility, in principle, of extracting PGMs using sCO_2.

The way the chelating agent or modifier is used may vary depending on the specific molecular characteristics of the complex form between the metal and the chelating agent. In cases where the polarity of the complex formed is sufficiently low, a modifier may not be necessary. However, when the residual charge of the complex is significant, then a modifier such as methanol or ethanol may be required.

There are various techniques with which the supercritical extraction can be carried out. These include the sCO_2 extraction combined with a chelating agent only (Zhang, Anawati and Azimi, 2022a), (Kunanusont *et al.*, 2021) using only a modifier (Pitchaiah *et al.*, 2019) and using both modifiers and chelating agents (Shamsipur, Ghiasvand and Yamini, 2001; Shaofen and Chiu, 2008; Golzary and Abdoli, 2020). According to Shaofen and Chiu, (2008), the results show a recovery of 94.7% of copper using the Cyanex 302 chelating agent. A modified sCO_2, combined with methanol, was used for the study, and showed to have a higher yield compared to the results found in the study by Wang, Debelak and Roth, (2008). The yield extraction results show that in principle, the combination of both a modifier and chelating agent will yield better recovery results.

However, even though this may be the case for copper, other metal extractions with only a chelating agent and sCO_2 has been effective. For the supercritical extraction of neodymium, results show that both tri-ethyl phosphate, TEP, (Kunanusont *et al.*, 2021) and tributyl phosphate, TBP, (Sinclair *et al.*, 2018) were both able to extract more than 90% of neodymium. For the extraction of palladium (Iwao *et al.*, 2007), the results show that the effectiveness of TBP is less compared to that found in the extraction of neodymium. The study found that TBP extracted less than 60% of the palladium. These results are different from those reported in a later study. According to Faisal *et al.*, (2008), TBP was able to extract 96% of the palladium from a spent catalytic converter. The conditions for both studies were within a similar range; 200 bar and 80°C. The difference in the studies was the methods in extracting the palladium. A summary of metal extractions using sCO_2 have been shown in ***Error! Reference source not found.*** below.

Error! Reference source not found. outlines the studies in extraction of metals using a supercritical fluid. There is however, one concern in that the extraction of PGMs. These are, the extraction of rhenium and platinum from spiked filter paper using a modified sCO_2 (Yamini, Saleh and Khajeh, 2008), extraction of palladium from a spent catalyst using sCO_2 combined with different modifiers (Iwao *et al.*, 2007), and the extraction of PGMs from a spent catalytic converter using sCO_2 modified with a chelating agent (Faisal *et al.*, 2008).

All the aforementioned studies indicate a high extraction yield, above 90%, however the operating conditions are different, specifically the temperature. The difference in temperature between the studies has a range of 20°C. This uncertainty changes the approach for the extraction process. For this study, the parameters will be initially tested on a Zeolite ZSM-5 catalyst of which a metal will be adsorbed onto it. Given the economic value of PGMs, a pseudo metal will be used.

2.2.2.5 The influence of process parameters

As far as the solvent power of sCO_2 depends on its density, which in turn depends on the temperature and pressure conditions, each of the following process parameters influence the yield of the product. Furthermore, other parameters such as particle size and solvent ratio will be discussed.

2.2.2.5.1 Temperature and pressure

The effects of temperature and pressure was tested on the extraction of eugenol from clove leaves using sCO_2 (Frohlich et al., 2019). The data gathered showed that the best yield was achieved at 220 bar and 40°C, and yet a temperature of 60°C was run with the same pressure of 220 bar and yielded fewer effective results. Similarly, for the sCO_2 extraction of Indonesian raw propolis (Fachri et al., 2020), the temperature and pressure for the highest yield, was found to be 50°C and 250 bar, respectively. Other experiments with higher temperature conditions, with the same pressure, yielded poorer results. The results show a similar trend in other studies (Rudyk and Spirov, 2017). This trend is to be expected and is related to the solvating power of the solvent. The solvating power is affected by the density of the solvent, which rises when the pressure is increased in an isothermal process, decreases when there is an increase in temperature in an isobaric system (De Azevedo, Kopcak and Mohamed, 2003). According to Brunner, (1994, p. 192), the capacity of the solvent increases with an increase in pressure, and temperature increases the rate of extraction; only at a higher pressure. Brunner, (1994, p. 193) also states that an additional reason in how temperature allows for greater extraction, is the increase in mass transfer rates.

2.2.2.5.2 Solvent ratio

According to (Brunner, 1994, p. 193), after determining the temperature and pressure, the solvent ratio is the most important parameter. When the solvent ratio low, the extract in the solid substrate is high, and at medium solvent ratios, the extraction ability is at its highest. The influence of the solvent ratio also has an impact on the economics of the process. A higher solvent ratio results in shorter extraction times, but the equipment needed to handle a higher ratio will be more expensive (Brunner, 1994, p. 195).

2.2.2.5.3 Size of the solid particles

In many circumstances, the transport rate in the solid phase has a significant impact on mass transfer when gas is extracted from solid substrates. The length of the transport path determines mass transport in the solid phase. In general, when particle size decreases, the extraction rate rises.

2.2.3 Deep Eutectic Solvents (DES)

Deep eutectic solvents or DES is a compound made up of two or more components and has a melting point of less than 100°C. DES are made of a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA). One of the most used compounds in constituting a DES is choline chloride (Smith, Abbott and Ryder, 2014). DES share similar properties to that of ionic liquids, which include, low toxicity, non-flammibility, low vapor pressure two or more components that form a eutectic mixture which has a melting point which is lower than the individual melting point (Yuan *et al.*, 2022). The eutectic mixture is a mixture of two components in a specific mass ratio to achieve the lowest possible melting point of the mixture. The melting point is called the eutectic point.

The melting point lower than either of the components on their own. Glucose has a melting point of 146°C and citric acid has a melting point of 156°C, and yet the DES of citric acid and glucose, with a molar ratio of 1:1, has a melting point of less than 80°C (Pisano *et al.*, 2018).

Other advantages of DES include possibility of constituting them from natural components. Choline chloride, a popular choice in DES, is used as an ingredient in animal feed, sucrose is more commonly known as sugar, is also used as a component in DES (Yuan *et al.*, 2022). Others include glucose, fructose, tartaric acid, glycerine, and urea (Yuan *et al.*, 2022). Additionally, DES have tuneable properties, which include changing the polarity, density, viscosity, and solubility (Dai *et al.*, 2015). This is done by adding water in a weight of DES: weight of water ratio (w/w). The viscosity of the DES decreased by almost 50% with the addition of a water content of 25% w/w (Dai *et al.*, 2015).

One of the key motivators for using DES was its ability to selectively extract metal compounds. Chang *et al.*, (2022) experimented with a DES made of choline chloride and oxalic acid to selectively extract transition metals from a spent Li cathode. It was found that the DES was able to selectively extract NiO, Co_3O_4 and Mn_3O_4 from the cathode, at yields of 99.1%, 95.1% and 95.3%, respectively. There were intermediary methods used to assist with the extraction process. These include adding a diluent, dimethyl sulfoxide to decrease the viscosity, and then extract nickel. Thereafter water was added to dilute the filtrate extract cobalt, and lastly the pH was adjusted to 12 to extract manganese. DES has been successfully utilized for the recovery of PGMs from secondary sources. Lanaridi *et al.*, (2022) investigated the extraction of PGMs using both a DES and IL and were able to fully extract the platinum and palladium with a ±60% recovery for rhodium. This research showed the effectiveness of DES for these metals, providing an alternative to conventional hydrometallurgical methods.

One of the disadvantages of using a DES is the high viscosity in most of the solvents. This can be overcome by adding a percentage of water to the DES however it may affect the properties of solvents. In summary, DES represent a promising alternative to the conventional methods, which include lower toxicity, biodegradability, and its cost-effectiveness. The promising success shown towards PGM recovery bolds well for future experiments.

2.2.3.1 COSMO-RS

The question now becomes, how would one find the solvent that can be specifically designed to extract the desired metal?

The accurate computational modelling od DESs is important for solvent selection and process optimization in chemical engineering and related industries. The BP86 generalized gradient approximation (GGA) functional combined with the TZ2P basis set, used within the Amsterdam Density Functional (ADF) software, is widely recommended as a standard computational approach for producing quantum chemical input data for COSMO-RS. COSMO-RS (Conductor-like Screening Model for Real Solvents) is a molecular model that utilizes both quantum mechanical calculations and statistical thermodynamics to predict various physicochemical properties of substances (Klamt, 2011; Parnis *et al.*, 2020; Klajmon, 2022).

This model was found to be accurate and efficient in predicting properties such as activity coefficients, solubility, and the distribution of species in different systems (Masuch *et al.*, 2011; Abramov, Loschen and Klamt, 2012; Soares and Gerber, 2013).

The fundamentals of COSMO-RS incorporate the use of density functional theory (DFT) to calculate the molecular electrostatic properties within a solvation model, which enables the estimation of bulk thermodynamic properties based on the properties of the solute and solvent molecules (Klamt, 2011; Parnis *et al.*, 2020; Klajmon, 2022). By utilizing quantum chemical calculations and surface polarization charge densities, COSMO-RS can forecast a wide range of properties for various substances, including organics, polymers, ionic liquids, and pharmaceutical compounds (Loschen and Klamt, 2015; Liang *et al.*, 2023; Dai *et al.*, 2024). The method has been utilized to predict interfacial tension, redox potentials, and screen ionic liquids as green solvents (Namazian, Lin and Coote, 2010; Ramalingam, Rajendran and Ganesan, 2018; Zemánková *et al.*, 2023).

Wojeicchowski *et al.*, (2021) tested 1372 different combinations of DES on the extraction of antioxidants from rosemary. The use of the COSMO-RS model, it was determined that the best combination of DES was a mixture that consisted of 15 wt% of tetrapropylammonium chloride, 55 wt% 1,2-propanediol and 30 wt% water.

2.2.3.1.1 BP86 GGA Functional and T2ZP basis set

The BP86 functional is a widely used generalized gradient approximation (GGA) functional in density functional theory (DFT). It combines Becke's 1988 exchange functional and Pardew's 1986 correlation functional. The BP86 functional is among the most established GGA functionals for routine molecular calculations, including for calculations in COSMO-RS solvation models (Franke and Hannebauer, 2011).

The BP86 functional provides and good compromise between computational efficiency and accuracy, which provides reliable molecular geometries and energentics for systems such as hydrogen bonding and electrostatic interactions found in DES (Franke and Hannebauer, 2011).

Triple-zeta with two polarization functions (TZ2P) basis set is a high quality basis designed for accurate quantum chemical calculations (Materials, 2024b). In addition, the TZ2P basis set optimizes core and valence descriptions which ensures flexibility to describe both electron density and subtle charge rearrangements occurring in hydrogen bond systems like DESs (Materials, 2024b).

Multiple studies have demonstrated the use of BP86 in combination TZ2P (Afridi *et al.*, 2024; Asubonteng *et al.*, 2025; Van Eygen *et al.*, 2025)

Table 4 Metal ion extraction studies

	Authors	***Source (Matrix)***	***Metal ion (s)***	***Chelating agent (CA) or Modifier (M)***	***Optimum Parameters***	***Extraction efficiency***
1	Glennon *et al.*, (1997)	Spiked filter paper	Fe^{3+}	perfluorooctanohydroxamic acid (CA), heptafluorobutyrichydroxamic acid (CA), N-Methylheptafluorobutyrichydroxamic acid (CA) N-methylhydroxylamine hydrochloride (CA)	304 bar, 70˚C	97% extraction for PFOHA
2	Laintz *et al.*, (1992)	Aqueous Cu (NO) adsorbed on silica	Cu^{2+}	Lithium bis(trifluoroethy1) dithiocarbamate (LiFDDC) (CA)	75.8 bar, 35.8˚C	Above 70% extraction of Cu^{2+}
3	Wang et al., (2008)	$MgCl_2 \cdot 6H_2O$ was dissolved onto filter paper	Cu^{2+}, Mg^{2+}	Ammonium carboxylate perfluoropolyether (PFPE) (CA) and water	Mg^{2+}: 220 bar, 120˚C Cu^{2+}: 250 bar, 60˚C	Mg^{2+}: 65% Cu^{2+}: 73%
4	Wang and Chiu, (2008)	Wood samples	Cu, As, Cr	Cyanex 302, Dibutyldithiocarbamate ammonium salt (DBDC) (CA), Sodium diethyldithiocarbamate (NADDC)	304 bar, 60˚C 5% MeOH modified	Cyanex 302 Cr: 50.3% Cu: 94.7% As: 66.3%
5	Golzary and Abdoli, (2020)	PCB waste	Cu^{+}	Methanol, ethanol and propanol as modifiers and cyanide 301, 302 and TBP as chelating agents. A combination of both ligands and modifiers were used. The best pairing was cyanide 301 and methanol	200 bar, 60˚C	97%

6	Park *et al.*, (2013)	Sea sand and coarse soil	Cd^{2+}, Co, Zn	Used Cyanex 272 and diethylamine (DEA) together	Conditions not specified	100% extraction of cadmium
7	Wai *et al.*, (1996)	Metal dithiocarbamates	Hg^{2+}, Cu, Zn	FDDC (CA), Sodium diethyldithiocarbamate (NaDDC) (CA), ammonium pyrrolidinedithiocarbamate (APDC) (CA)	233 bar, 60˚C	95%
8	Wang *et al.*, (2009)	Stock solution of Co^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+}, Mn^{2+} at 1mg/mL	Ni^{2+}	bis(2-(2-butoxyethoxy) ethyl)-2,2 bipyridine-4,4'-dicarboxylate (CA), bis(2-(2-ethoxyethoxy) ethyl)-2,2 -bipyridine-4,4 –dicarboxylate (CA),	250 bar, 40˚C	100% (Ni with PFOAT additive) >50% (Ni without PFOAT additive)
9	Shamsipur *et al.*, (2001)	Study the supercritical fluid extraction of uranium from cellulose based filter papers, as a model for biological samples such as plants and animal tissues, in the presence of several different co-extractants.	U	bis(2-ethylhexyl) hydrogen phosphate (HDEPH), tri-n-octylphosphine oxide (TOPO), dicyclohexyl-18-crown-6 (DC18C6), dibenzoylmethane (DBM), 8-hydroxyquinoline (HOX), diphenylaminesulfonic acid (DPASA) 1,4-bis-[4-methyl-5-phenyl-2-oxazolyl] benzene (DMPOPOP) and TBP (All compounds are CA)	250 atm, 60ºC	97% with HDEPH $scCO_2$ modified with 5% w/w MeOH
10	Quach *et al.*, 2014)	Separation of U (uranium) from other actinides from nitric acid solution	U^{4+}	Tri-butyl phosphate (TBP) (CA)	200 bar, 40˚C	1 M of nitric acid: 93.3% 0.1 M of NO_2- 92.4%
11	Pitchaiah *et al.*, (2019)	Uranium and plutonium from chloride salt matrices	U^{2+}	Methanol (Modifier)	200 bar, 50˚C	99% (including neat uranyl chloride (UO2Cl2))

12	Song *et al.*, (2021)	Dynamic extraction of REEs from AMD in sCO_2	Various ions, La, Nd and Ce	Metal ions coagulated in HNO_3 TBP used as chelating agent	200 bar, 60˚C, 0.104 mL/min of scCO_2	La: 40.1% Nd: 58.2% Ce: 41.8%
13	Duan *et al.*, (2019)	A series of poly functional open-chain crown ether diphosphates modified with varying length of ethylene oxide bridge and different ester side chains	Lanthanide metal ions	Various chelating agents used; best performing CA was tripropylene glycol bis (2-ethylhexyl) dimethyl diphosphate (TPGEH). Only CA were used	200 bar, 40˚C	La^{3+}: 92% Ce^{3+}: 94% Pr^{3+}: 93%
14	van Dyk *et al.*, (2022)	Surface tailings, sand dumps, and slime dams left behind by gold mining operations	Au^{2+}	Various chelating agents compared; best performing CA was betaine bis(trifluoromethylsulfonyl) [Hbet][TF2N]	100 bar, 40°C Extraction time 24h	>80%
15	Park *et al.*, (2020)	Sea sand and real sand	Cs^+	CA 1: carbamate-conjugated catechol CA 2: NEt4PFOSA (perfluoro-1-octanesulfonic acid tetraethylammonium salt) Chelating agents were used simultaneously	210 bar, 40˚C	27 experiments performed, with best performing experiment extracting 99.9%
16	Leybros *et al.*, (2016)	Extracting caesium from contaminated soils	Cs^+	pentadecafluoro-n-octanoic acid (HPFOA) (CA)	270 bar, 61˚C	95.9%

17	Hung *et al.*, (2016)	Then, dynamic extractions with supercritical carbon dioxide were carried out on sulphuric acid solutions containing molybdenum and impurities like iron and zirconium	Mo^{2+}	Trioctylamine (TOA) and 2-ethylhexyl 2-ethylhexylphosphonic acid Both CA's	250 bar, 40˚C	99% in TOA after 30 min
18	Zhang *et al.*, (2022)	Waste fluorescent lamps	Y^{3+} Eu^{3+}	TBP-HNO_3 (CA)	None given	>95% for both
19	Bouali *et al.*, (2021)	We highlight the importance of properly understanding how cerium nitrate is adsorbed on the cellulose-based substrate as a matrix model by showing how this affects measured extraction efficiencies	Ce^{3+}	EtOH/water and IPA/water in ratios of 70/30, 96/4 (EtOH/H_20) and 95/5 (IPA/H_20) Both modifiers	250 bar, 40˚C	Various extraction yields, with the best performing EtOH/water (70/30) at 82%
20	Jafari Nejad *et al.*, (2011)	Metal cations (La^{3+}, Ce^{3+}, Sm^{3+})	Ce^{3+}, La^{3+} and Sm^{3+}	Cyanex 301 (CA) and TBP (CA) used as co-extractant	250 bar, 40˚C 4ml/min	42.2% for La^{3+} 71..1% for Ce^{3+} 93.5% for Sm^{3}

21	Kunanusont *et al.*, (2021)	Neodymium (Nd) from an end-of-life NdFeB magnet	Nd^{+}	Triethyl phosphate (TEP) (CA), tri-n-butyl phosphate (TBP) (CA), tri-butyl phosphine oxide (TBPO) (CA), and tri-octyl phosphine oxide (TOPO) (CA)	207 bar, 55°C	>90%
22	Reisdörfer *et al.*, (2020)	Neodymium from hard disk drives (HDDs)	Nd^{3+}	Roasted and unroasted tested. Used malic and citric acid as co-solvent	90°C, 120 bar (unroasted) 90°C, 100 bar (unroasted)	Unroasted: 99.4% Roasted: 99.5%
23	Sinclair *et al.*, (2018)	Neodymium and holmium nitrate	Nd^{3+}	TBP (CA)	280 bar, 60°C	90.7%
24	Chou *et al.*, (2008)	Gallium (III) ions from synthetic etching wastewater of the semiconductor industry	Ga^{3+}	thiopyridine (PySH) (CA), thenoyltrifluoroacetone (TTAH) (CA), acetylacetone (AcAcH) (CA).	207 bar, 70°C	Above 80%
25	Chou and Yang, (2008)	Indium(III) ions from synthetic etching wastewater of semiconductor and optoelectronic industries	In^{3+}	B-diketone (AcAcH) (CA), fluorinated β-diketone (TTAH) (CA), thiopyridine (PySH) (CA), and piperidinyldithiocarbamic acid (NCS$_2$H) (CA)	AcAcH: 70°C, 138 bar TTAH: 60°C, 138 bar NCS$_2$H: 60°C, 138 bar	NCS$_2$H: 90.7% PySH: above 80% TTAH:above 70% AcAcH:below 50%
26	Yamini *et al.*, (2008)	Re (VII) and Pt (IV) from a solid matrix such as a spiked filter paper	Pt^{4+} Rh	Cyanex 301 (CA) in methanol (M)	45°C, 203 bar	105% of Pt 95% of Rh

27	Iwao *et al.*, (2007)	Palladium catalyst containing 0.5% palladium	Pd	Cyanex 302 (CA), TBP (CA) and Acetyl acetone (M)	80 bar to 200 bar, and 40˚C to 80˚C.	99%
28	Faisal *et al.*, (2008)	Pure sample of the catalytic converter	Pd Pt Rh	TBP (CA)	200 bar, 60˚C	96% of Pd

Table 4 highlights the following:

- The versatility of studies focusing on metal extraction, which include transition metals, rare earth metals and precious metals.
- The role of chelating agents and modifiers within supercritical extraction and how its effectiveness varies with each metal.
- The optimized conditions for extraction range between 100 to 300 bar and 40°C to 80°C, which suggests that the efficiencies are influenced by both temperature and pressure.
- Several studies show high recovery rates, demonstrating the feasibility of using sCO_2.

2.3 Conclusions

For the extraction of PGMs, hydrometallurgical methods have been widely used. The method has shown to be effective in extracting PGMs from secondary sources. The use of hydrometallurgical methods has recovery yields of above 90% in many studies (Bolinski and Distin, 1992; Jafarifar *et al.*, 2005; Harjanto *et al.*, 2006). However, it does indicate that it can be energy intensive and produce harmful gases.

Compared to hydrometallurgical methods, the use of sCO_2 is that its non-toxic, it is inexpensive when compared to other solvents and it has a tuneable solvent power. The use of sCO_2 has shown to match the recovery yields shown in hydrometallurgy. The same can be said about DESs, in that it maintains the high recovery yields. However, the environmental impact is less than compared to hydrometallurgy.

The use of a DES presents an opportunity to test whether it has the same effect when exposed to a supercritical fluid. Literature shows that the increase in temperature improves the yield for the products, however none have shown the impact a change in pressure has.

Chapter 3: Materials and Methods

In this chapter, the methodologies that investigates whether the effect of sCO_2 improves the recovery yield of PGMs are outlined. The study encompasses a series of experiments and simulations using the COSMO-RS model, a water bath experiment, pressure assisted experiment, the effects on the viscosity and recovery yield.

3.1 Introduction

The selected method is largely based on the work presented by Lanaridi *et al.*, (2022). Their work was carried out at laboratory scale and used DES and ILs to recover PGMs from a spent catalytic converter (SCC). Lanaridi *et al.*, (2022) used a method which consisted of subjecting the SCC to an oxidizing agent, and then DES, to improve the recovery of rhodium. The mixture was stirred for four hours at a constant speed, at atmospheric pressure and 80°C. Once the process completed, the sample was centrifuged, and the DES phase was analysed using ICP-OES to determine the PGM content.

For this work, the key difference was the exposure to compressed CO_2. This work will use similar conditions set out by Lanaridi *et al.*, (2022), however the sample will be subjected to compressed CO_2 at 100 bar for 1 hours at 80°C. After which the sample will be shaken using a vial shaker to get rid of excess CO_2. Thereafter, the sample will be centrifuged and both DES phase and solid residue samples were analysed using ICP-OES analysis. It is important to note that in the work by Lanaridi *et al.*, (2022), further processing of the extract sample to recover rhodium and separate the metals from the DES solution, which is not the case in the work.

The experimental work was done in four parts. In Part I (screening), the COSMO-RS model was used to screen for the most suited DES for PGM recovery. In Part II, the effect of water on viscosity was analysed. Samples were subjected to both water bath (WB) and compressed CO_2 conditions without the solid sample present. In Part III, the WB experiment was performed. And finally, in Part IV, the compressed CO_2 experiment was performed. For each of the extraction experiments, the effect of two DESs were compared, along with 3 varying water content % (0%, 10% and 20%). The extracts phases, DES phase and solid phase, were recovered a stored in a 5°C fridge before being sent for analysis.

The experiment was carried out in vials (bench-top scale) in a pilot plant system in a batch setup. This was to measure the effects of each DES system with varying water content percentages.

These parts are explained in greater detail below.

3.2 Materials

This section highlights the materials used for the experiment.

3.2.1 Catalytic converter

The catalytic converter used in this work was purchased from Springbok Toyota (South Africa). The converter came with the exhaust assembly.

3.2.2 Chemicals and Reagents

All the chemicals and reagents in the method development were of analytical grade, unless otherwise stated. These chemicals and reagents are shown in ***Error! Reference source not found.***

Table 5 List of chemicals and reagents used

Chemical Name	Function	Purity (%)	Supplier
Choline chloride	HBD	≥98	Sigma-Aldrich
Oxalic acid	HBA	98	Sigma-Aldrich
Toluenesulfonic acid	HBA	≥98	Sigma-Aldrich
Carbon dioxide	Solvent	99.99	Air Liquide

3.3 Equipment

Calculations were performed using both instrumentation and software.

3.3.1 Instrumentation

This section provides an overview of the instruments and analytical techniques employed in this study, focusing on the use of a rheometer, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and microwave digesters. The selection and use of these instruments were integral to obtaining precise and accurate measurements, ensuring the reliability of the experimental data.

3.3.1.1 Rheometer

A Paar-Physica MCR-51 rotary rheometer was used for determining rheological characteristics of different materials which ranges from sludges to sewage suspensions, showing its range. Rheological measurements were performed on the prepared DES samples using an Anton Paar MCR51 rheometer equipped with a parallel-plate geometry (CP50, 50 mm diameter, 1 mm gap). This configuration was selected for its suitability in handling viscous, non-Newtonian fluids such as DESs. The instrument operated at a minimum torque sensitivity of 250 µNm. Measurements were conducted in controlled shear rate mode, with the shear rate linearly decreased from 1000 s^{-1} to 0 s^{-1} over a 2-minute interval. Each sample was tested in duplicate, and 30 data points were recorded per run, with each point measured over a 5-second interval. All DES samples were tested at ambient temperature (25 ± 1 °C) without additional conditioning.

3.3.1.2 ICP-OES

Liquid samples acidified to 2% HNO_3 solutions or digested solid samples are introduced into the instrument via auto sampler by peristaltic pump. The sample passes through the nebuliser which produces a fine aerosol. The large droplets are removed by a spray chamber and small droplets then pass through to the plasma. In ICP-MS, the plasma torch is positioned horizontally and is used to generate positively charged ions rather than photons. In fact, every attempt is made to stop the photons reaching the detector because they have the potential to increase signal noise. It is the production and detection of large quantities of these ions that gives ICP-MS its characteristic ultra-trace detection capability - about three to four orders of magnitude better than ICP-OES.

3.3.2 Software

3.3.2.1 Amsterdam Suite (AMS)

Amsterdam Suite, which is by Software for Chemistry and Materials (SCM), was used to perform the COSMO-RS screening and utilize the ADF modelling tool (‘Software Chemistry & Materials,’ 16/12/2024). This section provides an overview of the Amsterdam Suite's functionalities, focusing on its application in the present research. The software's capabilities in terms of data visualization, statistical analysis, and simulation are described in detail. A 12-month license was purchased.

3.3.2.2 ADF Modelling

The Amsterdam Density Functional (ADF) program is a computational tool widely used in the field of chemistry for performing density functional theory (DFT) calculations.

3.3.2.3 COSMO-RS

The software was used to calculate the sigma potential and sigma profile of each of the compounds used in the experiment. The COSMO-RS program has a wide selection of compounds but for those that are not found within the database, it can be generated using ADF Modelling by selecting the COSMO-RS task. Once the task is chosen, the software selects the minimum specifications to perform the task.

3.3.3 Supercritical Pilot Plant

A SAPAREX SFE-5 Pilot plant was used for the pressure assisted process. The plant was designed for the purpose of separating of both solids and liquids using supercritical carbon dioxide, sCO_2. The plant consists of two extraction vessels, a high-pressure feed pump, a co-solvent pump, a chiller, a heat exchanger, three separators and column. The extraction vessels, A40 and A41, are pressure rated for 700 bar at 150°C and 400 bar at 250°C. Both the extraction vessels have a volumetric capacity 5 L. The cyclonic separators, S50, S51 and S52, are pressure rated at 200 bar at 100°C the separators have a volumetric capacity of 0.6 L. The SAPAREX CO_2 pump can operate at a maximum pressure of 300 bar at a flow rate of 0.3 kg/min and the co-solvent pump is pressure rated at 700 bar at 0.5 mL/min. The heat exchanger, HE3000, operates by using direct electrical heating and has a maximum temperature output of 250°C. A PFD of the plant is shown in **Error! Reference source not found.**.

3.4 Method

There are two methods described in this section consist of ADF modelling, screening of the best solvent, synthesizing the DESs, dismantling the catalytic converter and the extraction of PGMs from the converter.

3.4.1 ADF Modelling

All geometry optimizations and COSMO calculations were carried out using density functional theory at the BP86/TZ2P level, in conjunction with the relativistic scalar ZORA correction for heavier elements. The COSMO surface was constructed using the Delley approach, utilizing established atomic radii, and the resulting surface screening charges were used as input for the COSMO-RS model to predict thermodynamic properties and sigma-profile analyses. Calculations adhered to the default COSMO-RS parameterizations recommended in the original methodology and were executed using ADF 2024.1 and AMS 2024.1 (Materials, 2024a).

3.4.2 DES screening using COSMO-RS

The screening of potential DESs was performed using the COSMO-RS computational method (Materials, 2024b), following the procedure outlined below:

i. Compilation of DES Candidates - A comprehensive list of DES combinations was generated based on an extensive literature survey of commonly used HBDs and HBAs,
ii. Compound Identification - Each compound in the generated list was searched within the COSMO-RS database. For compounds not present in the database, corresponding ADF models were generated to enable their inclusion,
iii. Input Preparation – Compounds were added to the COSMO-RS software either by selecting from the existing compound list, inputting SMILES strings, or by loading the generated ADF models,
iv. Simulation and Output Analysis - COSMO-RS was used to calculate relevant solvent properties, analyse sigma profiles and potentials to predict solvent behaviour.

3.4.3 DES synthesizing

All DESs investigated in this study were choline chloride-based, and thus the synthesis method remained consistent across samples. Two DESs were synthesized and compared, both using a molar ratio of 1:1. DES1 comprised choline chloride and toluene sulfonic acid, while DES2 consisted of oxalic acid and choline chloride, showed in Table 6. Although the molar components differed, the synthesis method was adapted from Lanaridi *et al.*, (2022).

In each case, 500 mL of natural deep eutectic solvent (NADES) was prepared. The required masses of each component, calculated according to their molar ratio (see Appendix 1), were transferred to a 2 L round-bottom flask. The mixture was stirred using a rotavapor at 40 rpm and maintained at 80 °C for one hour. The reaction was monitored until the formulation resulted in a viscous liquid

Table 6 Composition of DESs used

DES	HBA	HBD
1	Choline chloride	p-Toluene sulfonic acid
2	Choline chloride	Oxalic acid

3.4.4 Catalytic converter removal and preparation

Reliable and accurate quantification of the PGMs present in the input car catalyst sample was the cornerstone of the research project, since it would serve as a reference for subsequent determination of PGM extraction efficiencies. Additionally, full characterization of the car catalyst was performed to allow assessment of PGM separation from other metals in subsequent experiments.

3.4.4.1 Dismantling the catalytic converter

The ceramic catalyst must be removed from the catalytic converter. It was removed by grinding through the steel housing. The catalytic converter is shown in ***Error! Reference source not found.***.

Figure 5 Catalytic converter before dismantling (the ceramic catalyst is contained in the part shown by the arrow)

The metal housing was removed by using a grinder, which is shown in Figure 6.

Figure 6 Steel structure housing the catalytic converter

Once the 2nd incision was made, the steel structure was completely removed, shown in Figure 7.

Figure 7 Catalytic converter before final steel housing removal

The steel structure was removed, and fabric lining (white material) was removed and discarded. The final feed material is shown in Figure 8.

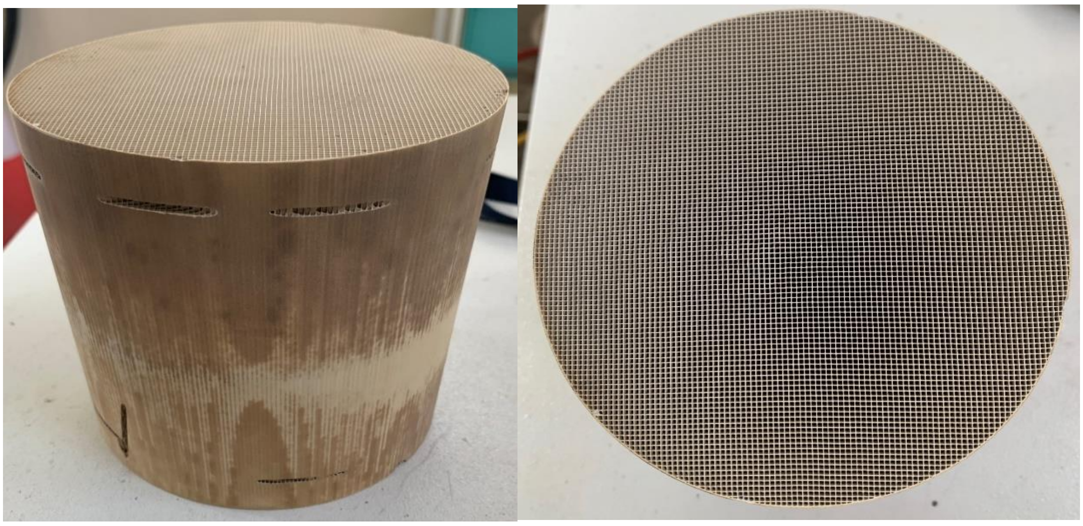


Figure 8 Catalytic converter removed from steel structure

The next step was removing enough material for experiment. The feed sample was crushed, using a pastle and mortar, and then sieved to the desired size.

3.4.5 Size reduction and sieving

The desired size for the experiment was less 0.175 mm or less. To achieve this, the sawed-off feed was broken into smaller pieces using a pastle and mortar, shown in Figure 9. Thereafter, it was placed in in a sieve tray to separate the different sizes and capture the required size for the experiment, shown in Figure 10. The arrangement for the sieves were as follows, a 1 mm size at the top, followed by a 0.35 mm sieve, thereafter the 0.175 mm and the capture tray. The range used for the experiment was less than 0.175 mm. Finally, an amount of approximately 2 g per sample was weighed and placed in 50ml vials shown in Figure 11.

Figure 9 Size reduction using a pastel and mortar

Figure 10 Sieving of the CC

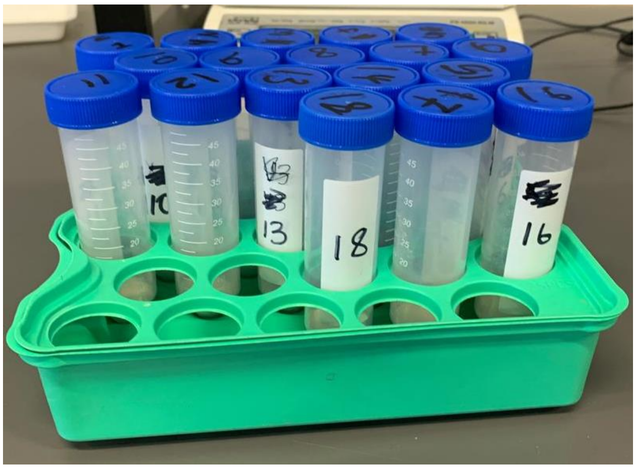


Figure 11 Placement of samples in vials

3.4.6 Characterization of the catalytic converter sample

Samples weighing 1 gram each were prepared for microwave digestion. Each sample was placed into a digestion vessel containing a mixture of hydrochloric acid (5 mL, 32 %), nitric acid (20 mL, 65 %), and sulfuric acid (2 mL, 98 %) for the extraction of trace metals. 5 mL of 2 % nitric acid was dispensed through the opening of the tube cover into the central tube of the sealed digestion vessels. The vessel was capped and placed in a heating block, and digestion was carried out at 200 °C for 2 hours. After digestion, the vessels were allowed to cool to room temperature. The digested solutions were then filtered. Subsequently, 1 mL of the filtered digested solution was diluted with 9 mL of 2% nitric acid. The resulting solutions were analysed using ICP-OES.

3.4.7 Water bath (WB) experiment

For the WB experiments, a similar method used by Lanaridi *et al.*, (2022) was followed, which includes preparation of the DES, experimental conditions used, type of DES used, and the S:F (solvent: feed) ratio of 5: 1.

The feed and DES preparation were done prior to the experiment and placed in separate vials. The experimental procedure was as follows:

i. The container containing the DES was placed in a water bath which was set to 80°C,
ii. Once the DES become less viscous, it was removed from the WB,
iii. The vials containing the feed sample were put on a scale and the DES amount was added according to a S:F ratio of 5:1,
iv. As soon as the DES was added the sample was placed into a beaker, in the WB,
v. The samples were shaken for 1 minute every 30 minutes for 4 hours,
vi. Thereafter, the samples were centrifuged at 5500rpm for 30 minutes,
vii. Once the phase separation was achieved, a sample of the DES phase was poured into a 15 ml vial,
viii. The solid extract was rinsed with deionized water and dried in an 80°C. Thereafter the dried sample place in a vial and stored in a dry area at room temperature.

3.4.8 Pressure assisted process

3.4.8.1 Procedure before the experimental run

After the milling procedure, DES is added to the sample. Thereafter the sample is added to a 50 ml vial and added to the extraction vessel, A41. The system was utilized in a batch process setup, thus P210, A40, S50, S51, S52 and, F53 were not utilized (Figure 12 PFD of the plant).

3.4.8.2 CO_2 conditioning

The CO_2 used for the experiment was conditioned such that it assumed the supercritical phase. The CO_2 was transferred from the cylinder and cooled by means of a condenser, CE2000. The purpose of doing this was to phase change CO_2 from a gas to a liquid. Once in the liquid phase it was pumped via a piston pump, P200, to the heat exchanger. The pump increased the pressure of the liquid CO_2 before

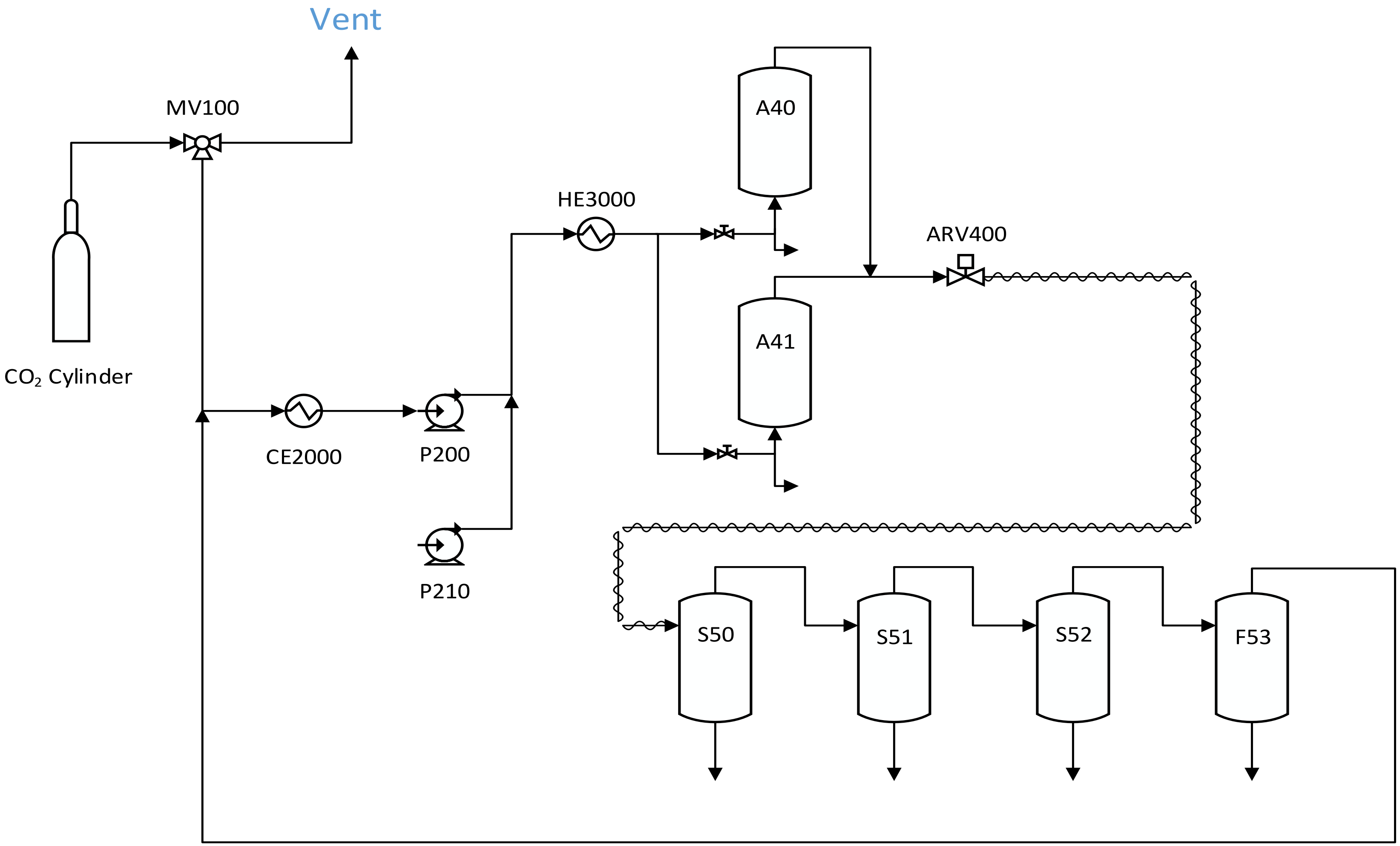


Figure 12 PFD of the plant

it reaches the heat exchanger, HE3000. The liquid CO2 was heated to above its critical temperature of 31.1oC, and changes to the supercritical phase.

3.4.8.3 Experimental conditions

Lanaridi *et al.*, (2022) showed that the optimum temperature for the recovery of PGMs was 80°C. Therefore 80°C was used as the reference temperature. There are no studies that investigated the combined use of a pressure assisted system using sCO_2 and DES for the extraction of PGMs. However, van Dyk *et al.*, (2022) investigated the recovery of gold from gold tailings using an sCO_2 and an IL and used a pressure of 100 bar. Therefore, for this work, the same pressure was used. These conditions were used as the basis for the start of the experiment however a varying amount of water content was used and different DESs to determine which has a better yield. All the vials containing different DESs and water content, were placed in the vessel and run as 1 experiment. All water bath samples were assumed to be ambient pressure, equivalent to 1 bar for the purpose of the experiment. These are shown in ***Error! Reference source not found.***. The water bath runs and sCO_2 runs were on separate days, with the water bath samples run first. The samples were stored in a 5°C fridge until it was taken for analysis.

Table 7 Experimental and DES parameters

Sample number	***Temperature (°C)***	***Pressure (bar)***	***DES used***	***Water (%wt)***
1	80	1	No DES	NA
2	80	100	No DES	NA
3	80	1	DES1	0
4	80	1	DES1	10
5	80	1	DES1	20
6	80	100	DES1	0
7	80	100	DES1	10
8	80	100	DES1	20
9	80	1	DES2	0
10	80	1	DES2	10
11	80	1	DES2	20
12	80	100	DES2	0
13	80	100	DES2	10
14	80	100	DES2	20
15	80	1	DES1	10
16	80	100	DES1	10
17	80	1	DES2	10
18	80	100	DES2	10

3.4.9 Vial shaking

Once the run has completed, the sample vials are shaken for 10 minutes each, using a vortex mixer, to get rid of the excess CO_2 within the sample.

3.4.10 Centrifugation

After vial shaking, the sample is centrifuged at 5000rpm for 30 minutes, to enable the decanting a clarified supernatant liquid. The sample was placed in a 5°C fridge until the analysis.

3.4.11 Sample analysis

3.4.11.1 Viscosity analysis

The samples of both the water bath and sCO_2 were analysed using the rheometer. An identical run was done after the first experiment which had 3 differences:

- No feed sample present, only the DES was exposed to WB and CO_2 experiments,
- Samples not sent for centrifugation, and
- Samples not sent for ICP analysis.

The viscosity analysis demonstrated that the presence or absence of the feed sample did not significantly affect the viscosity of the system. Therefore, the viscosity measurements were conducted without the feed sample to save time. Additionally, since only the DES phase was present in the second run, centrifugation was deemed unnecessary. Finally, as the chemical formulae of the DESs do not inherently contain PGMs, it was unnecessary to perform ICP analysis on the DES alone. These modifications streamlined the experimental process without compromising the integrity of the results

3.4.11.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Samples of the feed, extract and DES phase were sent for analysis to determine the composition.

3.5 Chapter outcomes

For Objective 1, literature indicated that oxalic acid and toluene sulfonic acid were HBDs for PGM extraction, and citric acid was found to be the strongest performing HBD in terms of its extraction abilities towards metal extraction. Choline chloride was found to be the best HBA. To fulfil Objective 2, a Students t-test was performed on a sample of cobalt-doped zeolite to establish the validity of the experiment. For the requirements of Objective 3, the samples were analysed using ICP-OES analysis and compared to conventional methods by comparing the recovery yields.

Chapter 4: Results and Discussion

The chapter presents the results derived from analysing the data. The results answer the objectives highlighted in Chapter 1. Objective one was aimed using a screening tool to determine whether which compound will be most effective as an HBA or HBD. The second objective was to determine the validity of the measuring system using a sample of the feed to evaluate yields, by performing a Students t-test. Objective three was to use the same system to perform the main experiment, on condition that the system was found suitable. The analysis included ICP-OES to measure how much of the PGMs remained on the feed.

4.1 Computational modelling (objective 1)

For the modelling of deep eutectic solvents (DES), the Amsterdam Modelling software package provides a comprehensive database of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA). This database allows users to explore a wide range of combinations, potentially exceeding 2000 unique DES systems based on the available data.

4.1.1 ADF Modelling

The AMS database did not contain toluene-sulfonic acid (TSA) and choline chloride (CC). Therefore, the models of these compounds were generated using the ADF modelling tool and shown in Figure 13.

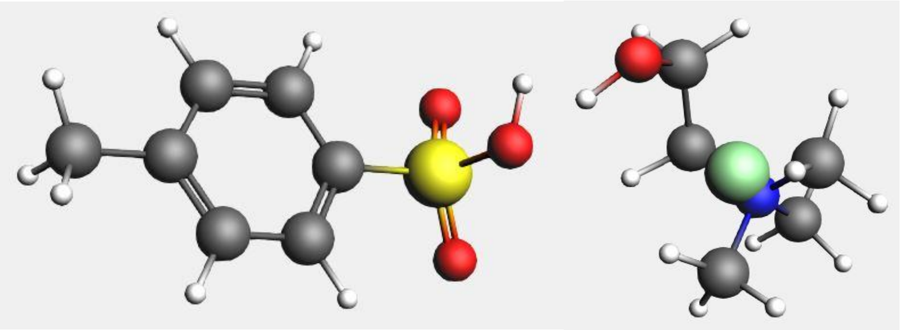


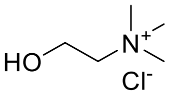
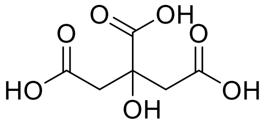
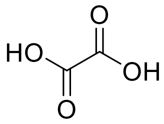
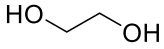
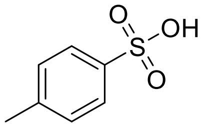
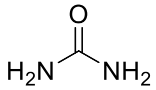
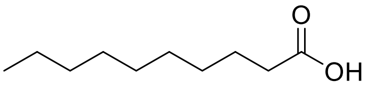
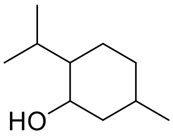
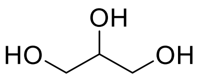
Figure 13 The structures of toluene sulfonic acid (left) and choline chloride (right)

4.1.2 COSMO-RS

In the formation of DESs, some molecules can act as both HBAs and HBDs due the electronegative atoms, including oxygen and nitrogen, which can donate and accept hydrogen bonds (Neni *et al.*, 2024). The selection of suitable HBAs and HBDs, one must consider the chemical structure and composition of DESs and PGMs (present in the catalytic converters). According to Kurzman *et al.*, (2013), the PGMs in catalytic converters typically can vary in terms of their oxidation states. Platinum can form platinum (II) chloride ($PtCl_2$) and platinum (IV) oxide (PtO_2), palladium primarily exists as palladium (II) chloride ($PdCl_2$) and rhodium as rhodium (III) chloride ($RhCl_3$) (Kurzman *et al.*, 2013).

Therefore, this DES was used as the standard and DESs were compared in terms of its sigma profile and sigma potential. The possible combinations are shown in Table 8. Table 8 also showed the molecular structure for each of the compounds. The classification of compounds as HBD or HBA in this table reflects their predominant role in the specific DES systems studied. These roles may vary depending on the interacting species.

Table 8 List of HBAs and HBDs

List of compounds	***Molecular Structure***
Choline chloride	
Citric acid	
Oxalic acid	
Ethylene glycol	
p-Toluene sulfonic acid	
Urea	
Decanoic acid	
Menthol	
Glycerol	

According to Lanaridi *et al.*, (2022), the DES that had the highest yield was toluene sulfonic acid and choline chloride (DES 1), in a molar ratio of 1:1.8. Therefore, this combination was used as a starting point to evaluate the sigma profile and sigma potential analysis.

4.1.2.1 Sigma profile

The sigma profile describes the distribution of the charge density on the surface of the solvent, which influences the solubility and the selectivity for different compounds (Pour *et al.*, 2024). The sigma profile of a DES is derived from the combination of HBD and HBA compounds. The effectiveness of a

DES is determined by its advantageous sigma profile. This profile is a key factor in shaping the solvent's solubility, selectivity, and thermodynamic characteristics. To create efficient and environmentally friendly solvents for diverse applications, it is essential to fine-tune these profiles (Ivanović *et al.*, 2022). This optimization process involves the meticulous selection and blending of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) components.

The range of the sigma profile is critical for understanding the solvent's behaviour in various applications. According to Mullins *et al.*, (2008), the sigma profiles of most molecules typically fall within the range of approximately −0.025 e/Å to +0.025 e/Å, with the HBD zone from -0.025 e/Å to -0.0084 e/Å and the HBA zone from +0.0084 e/Å to +0.025 e/Å. This range is indicative of the electrostatic interactions that characterize the affinity of HBA and HBD components within the DES.

A range of compounds were chosen, and their different sigma profiles were compared.

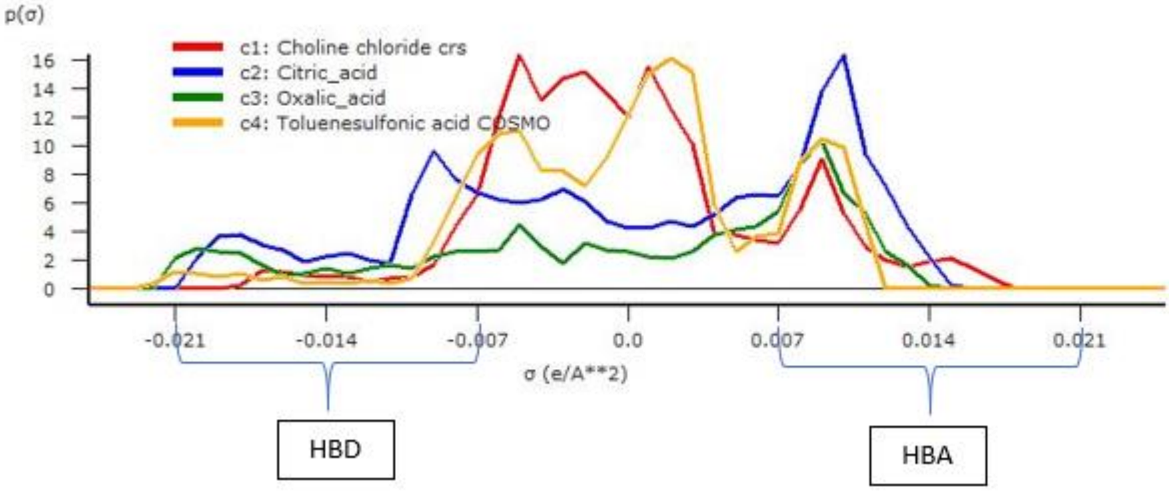


Figure 14 Sigma profile for pure compounds

4.1.2.1.1 Citric acid summary

The data from Figure 14 suggests that citric acid was best suited as an HBA and an HBD. It showed a peak of ± 16 in the HBA zone and a peak of ± 10 in the HBD zone, suggesting a stronger HBA.

4.1.2.1.2 Oxalic acid summary

Oxalic acid showed a peak of ± 10 in the HBA region, suggesting it would make an effective HBA. It further should a low peak in the HBD region, around 3, suggesting that it would not be suitable as an HBD.

4.1.2.1.3 Toluene sulfonic acid summary

From Figure 14 Toluene sulfonic acid (p-TSA) shows a peak of ± 10 in the HBD zone, and it has a peak of ± 10 in the HBA zone. This suggests that p-TSA is suited as both an HBA and HBD.

4.1.2.1.4 Choline chloride summary

Figure 14 suggests that choline chloride shows a peak of ± 9 in the HBA region and a peak of less than 2 in the HBD region.

In conclusion, both choline chloride and toluene sulfonic acid are excellent choices as a hydrogen bond acceptor in the formation of deep eutectic solvents. Its ability to form stable and effective mixtures with various hydrogen bond donors, coupled with its biocompatibility and low toxicity, makes it a valuable component in the development of sustainable and green solvent systems.

4.1.2.1.5 Sigma Ratio Variations in Mixed DES Systems

Based off the summaries, combinations of DESs were generated. Figure 15 exhibits peaks in both the HBA and HBD regions, notably near ±8 e/Å², suggesting a DES that is balanced. These features do not represent direct additive enhancements from individual components (e.g., CC's peak at +10), but rather a redistribution of surface polarity due to the intermolecular interaction's characteristic of DES formation.

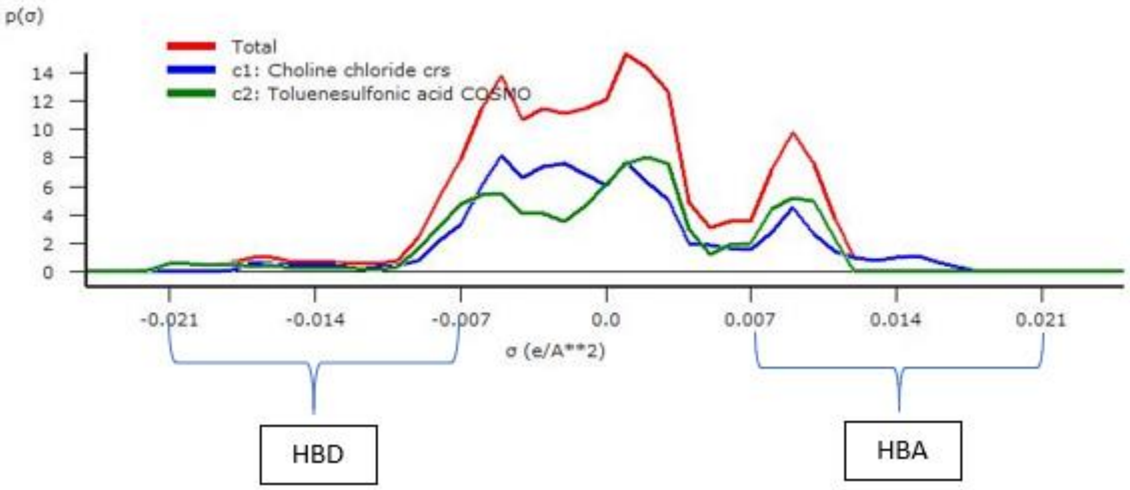


Figure 15 Sigma profile of p-TSA and CC

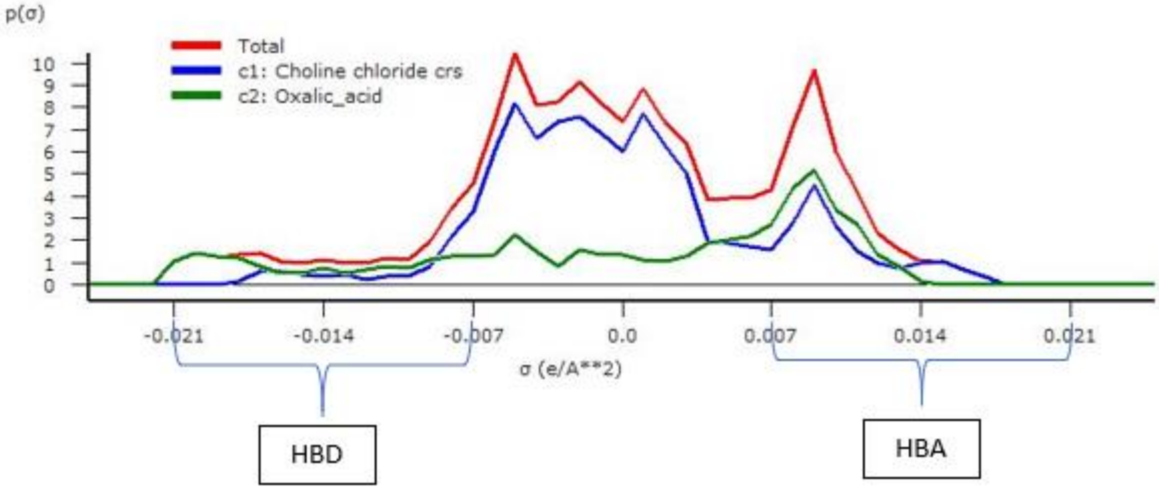


Figure 16 Sigma profile of OA and CC

Figure 16 illustrated the sigma profile for the DES which was made up of OA and CC. The sigma profile demonstrates that the DES formed from OA and CC exhibits interaction strength in both the HBA and HBD regions, with pronounced activity in the HBA zone. In the HBD region, the peak was found to be 4 e/Å² and the HBA region was 10 e/Å². For this combination of DES, the values of the peaks in both zones are not aligned, and this DES would have strong capabilities as an HBA and not as much as an HBD.

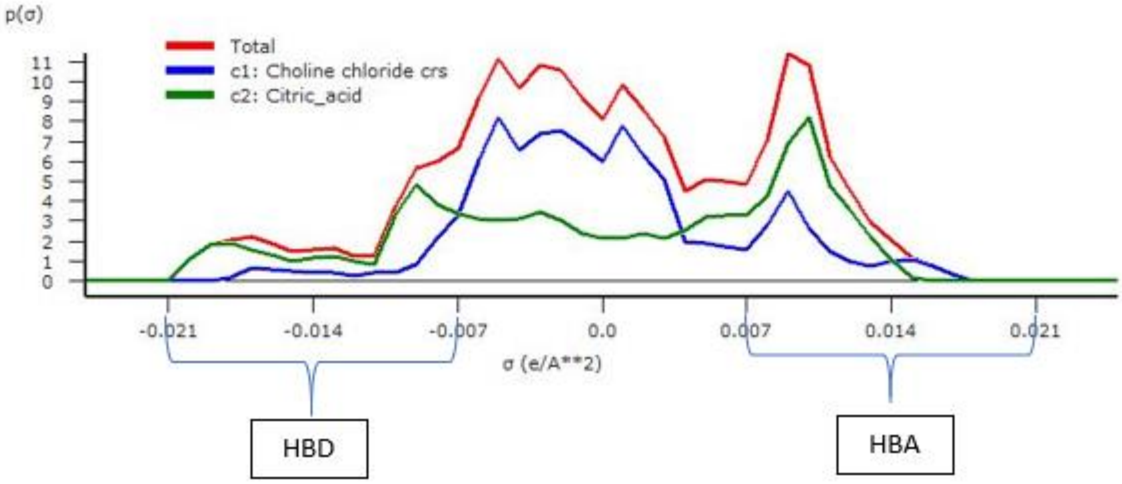


Figure 17 Sigma profile of CA and CC

Figure 17 showed the DES of CA and CC. It showed a value of 6 e/Å² in the HBD region and in the HBA region, the value was found to be 11 e/Å². As a DES, it indicated a strong overall polarity balance. The next set of sigma profile results measured the effect of adding water to the DES. The water content additions ranged from 10 – 20wt% of the DES, while still maintain the 1:1 molar ratio of the DES. Figure 18 shows the effect of adding 10wt% of water to the DES made up of p-TSA and CC. The effect of water lowers the peak in the HBA region from ± 10 to ± 5.5. The same effect on the peak in not seen in the HBD region, with the peak remaining ± 2. By adding 10wt%, it balances the overall strength of the DES.

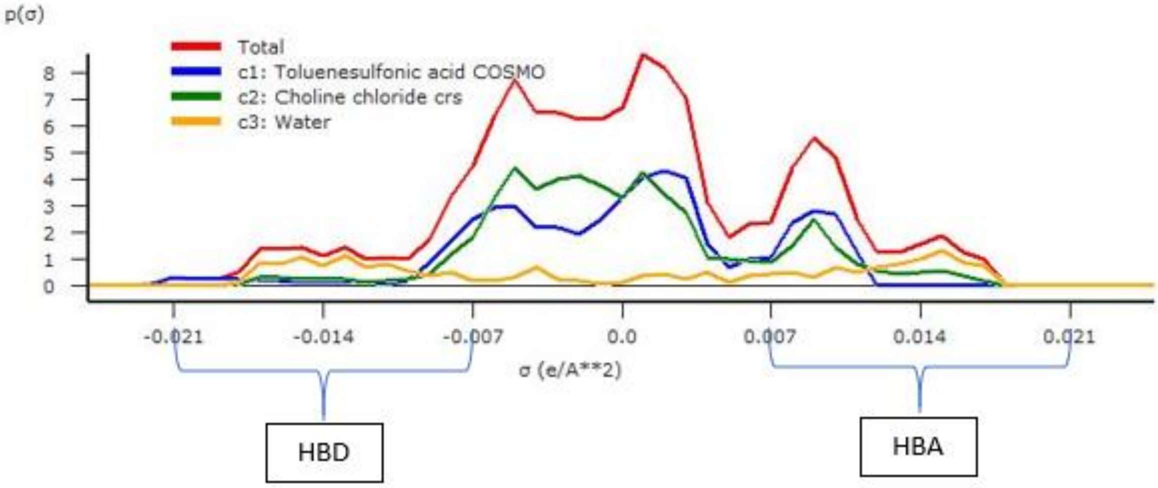


Figure 18 Sigma profile of CC and TSA with 10wt% water

For Figure 19 shows the effect of adding 20wt% of water to the DES made up of p-TSA and CC. The effect of water lowers the peak in the HBA region from ± 5.5 to ± 4, with an additional peak forming. Within the HBD region, the peak remained lower than 2. The addition of 20wt% water lowered the peaks even further. It does slightly affect the overall balance of the DES.

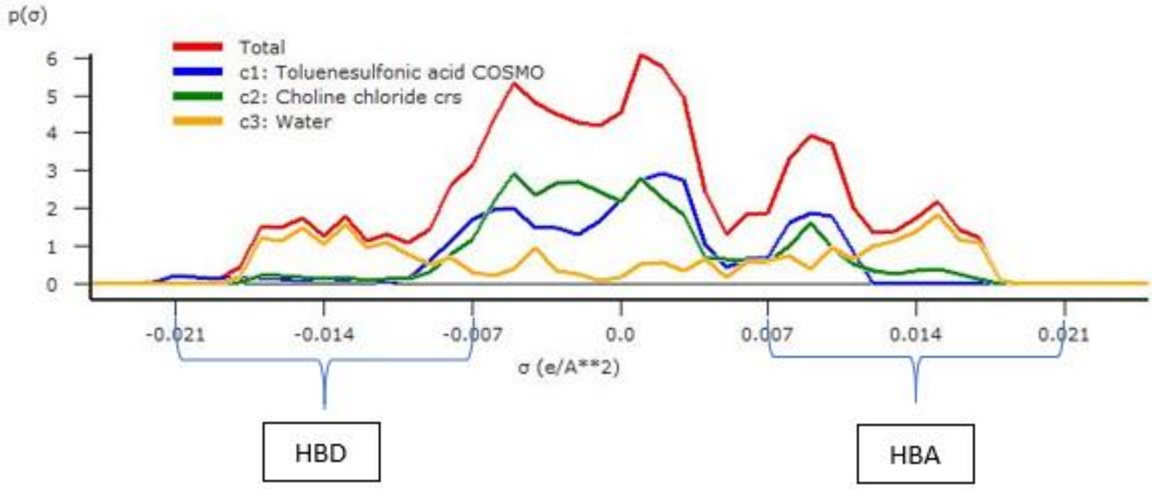


Figure 19 Sigma profile of CC and TSA with 20wt% water

Figure 20 shows the effect of adding 10wt% of water to the DES made up of OA and CC. The effect of water lowers the peak in the HBA region from ± 10 to ± 6, decreasing the peak by almost 40%. No effect was seen in the HBD region, with the peaks remaining below ± 2. By adding 10wt%, the overall balance of the peaks is not seen as with the p-TSA based DES.

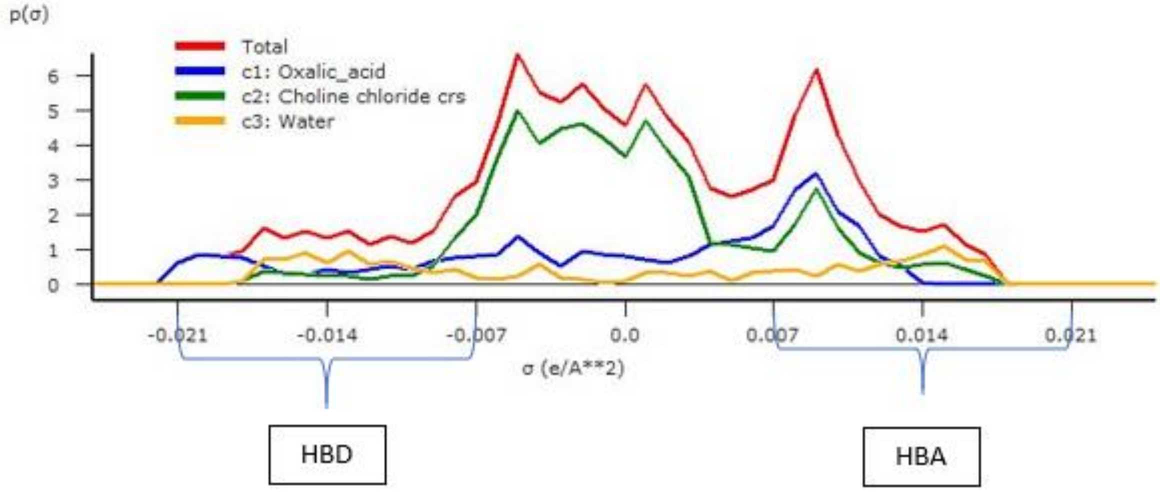


Figure 20 Sigma profile of CC and OA with 10wt% water

Figure 21 shows the effect of adding 20wt% of water to the DES made up of OA and CC. The effect of water lowers the peak in the HBA region from ± 6 to ± 4.8, decreasing the peak by almost 20%. The same effect on the peak was seen in the HBD region, with the peak decreasing from ± 3 to 2.4, again a 20% decrease. By adding 20wt%, the overall balance of the peaks is not seen as with the p-TSA based DES.

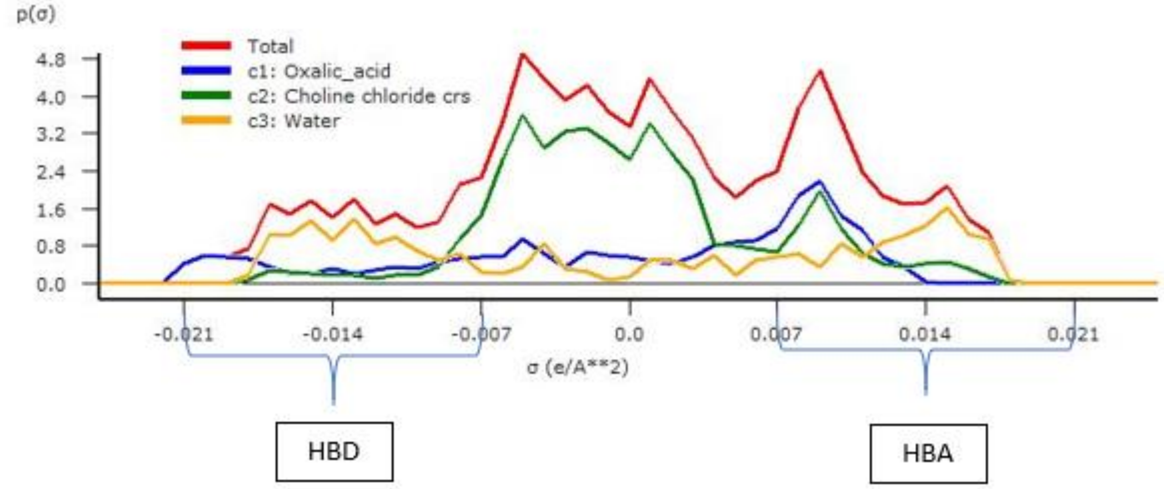


Figure 21 Sigma profile of CC and OA with 20wt% water

The overall conclusion for the DES samples made up of p-TSA and CC is that the addition of water lowers the peaks of shown in both regions, however affecting the HBA region more. However, adding water balanced the two regions, causing the peaks to be closer. The trends for the OA-based DES the trend is much more defined than the p-TSA based DES. An addition of 10wt% water decreased both peaks by 40% and the addition of 20wt% water further decreased both peaks by 20%. The addition of water did not have an impact on the HBD region, which remained ± 2.

4.1.2.2 Sigma potential

The sigma potential was applied to evaluate the affinity of molecular surface segments exhibiting specific polarities, namely the HBD zone, HBA zone, or neutral region, within a given type of solvent (Benabid *et al.*, 2021). It provides an insight into the solvation behaviour in the mixtures or solvents. The results of the pure components were shown in Figure 22.

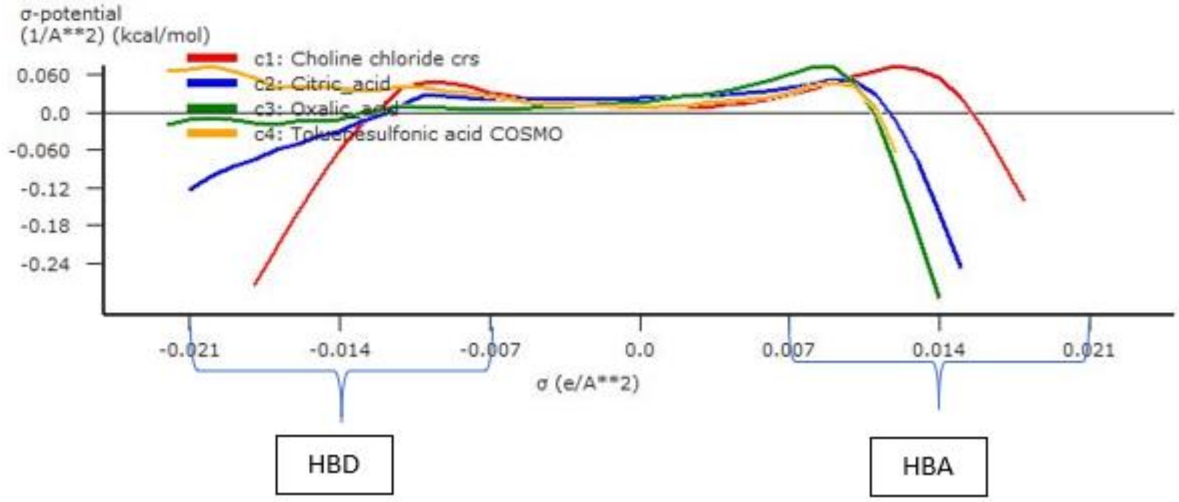


Figure 22 Sigma potential analysis for all pure compounds

The results showed that OA had the highest affinity towards HBAs followed by CA, thus it would be better suited as an HBD. CC showed an affinity towards HBDs followed by CA, which indicates that it would be better suited as an HBA. Toluene sulfonic acid showed a low HBA affinity. Therefore, the best possible combination for a DES would be choline chloride and oxalic acid (HBA: HBD). In addition, the combination of toluene sulfonic acid and choline chloride was also used as a DES.

4.2 Viscosity analysis

Given the viscosity issues related to DES, it is important to investigate effect of compressed CO_2 on the viscosity of DES. The viscosity of all the samples were measured and compared.

4.2.1 Water bath experiments viscosity analysis

To determine whether compressed CO_2 influences the viscosity, it was compared to an identical sample that was not subjected to compressed CO_2. The results are as follows:

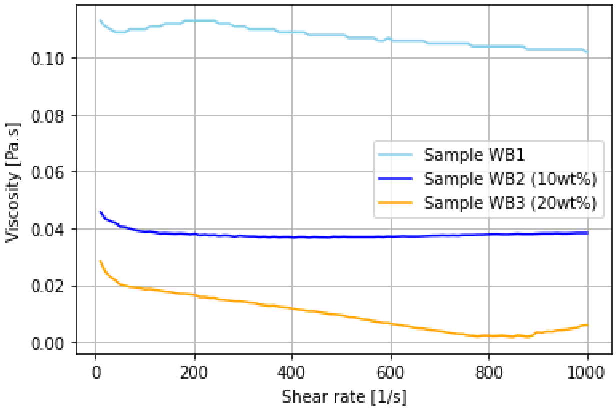


Figure 23 Viscosity of DES1 with varying water content at ambient pressure and 80°C

Figure 23 highlighted the impact of adding water to the DES, showing that with increasing water content, the viscosity drops. WB1 is the water-bath sample with no water, WB2 is the same DES with 10%wt water and WB3 is the same DES with 20%wt water. The water content decreased the viscosity of WB1 by at least 60% and adding a further 10wt% of water decreased the viscosity by 50% from WB2 to WB3. Additionally, the data suggests that Sample WB2 was more of a Newtonian fluid by maintaining the viscosity just below 0.04 Pa.s. Sample WB3 once more showed a decrease in viscosity with increasing water content. However, Figure 24 shows that with an increasing shear rate the viscosity did not maintain the Newtonian fluid properties.

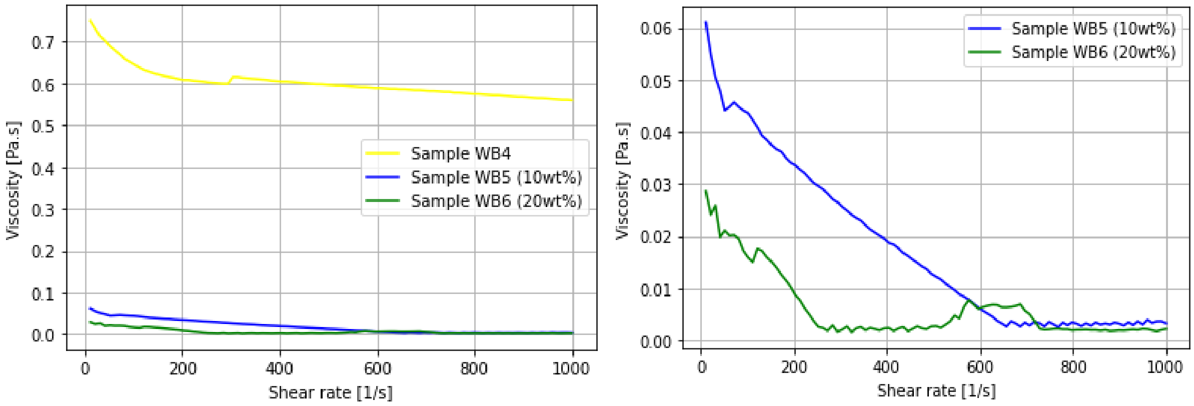


Figure 24 Viscosity of DES2 with varying water content at ambient pressure and 80°C.

Sample WB4 is a DES made up of oxalic acid and choline chloride, with varying water content in sample WB5 (10wt%) and WB6 (20wt%). There is a considerable difference after the water is added, from around 0.6 Pa.s for WB4 to less than 0.1 Pa.s, almost a 90% drop in viscosity. When the two DES are compared, it is more pronounced in the 2nd DES with the same amount of water added.

In summary, the addition of water to a DES results in a decrease in viscosity due to the disruption of hydrogen bonding networks and the inherent low viscosity of water. This property is crucial for enhancing the mass transfer capabilities of DESs in various applications, although careful consideration of water concentration is necessary to maintain the desired characteristics of the solvent.

4.2.2 Compressed CO_2 viscosity analysis

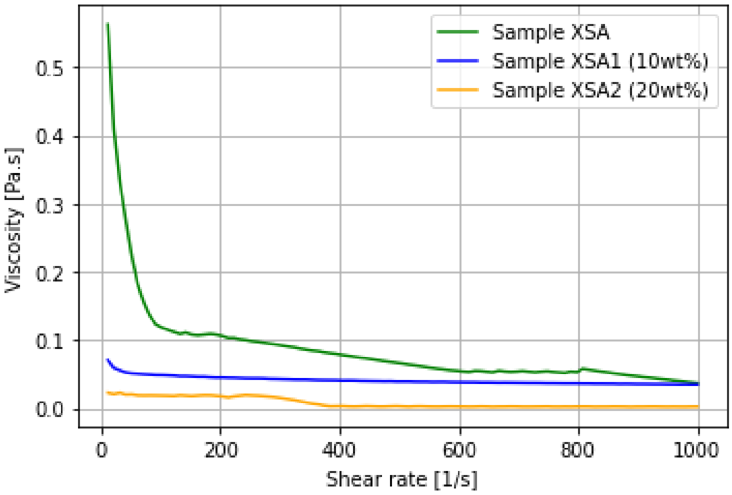


Figure 25 DES 1 with varying wt% of water exposed to compressed CO_2

Figure 25 shows the effect of compressed CO_2 on the viscosity of DES 1 with varying water content percentages (XSA – no water content, XSA1 – 10%wt water content and XSA2 – 20wt% water content). Sample XSA showed a high initial viscosity, above 0.5 Pa.s, and as the shear rate increased, the viscosity dropped ± 0.05 Pa.s. Sample XSA exhibited shear thinning properties with increasing shear rate, whereas XSA1 exhibited almost no shear thinning and XSA2 showed shear thinning but after 400 s^{-1}, no more shear thinning was seen. The effect of the shear thinning is not as severe for all samples after 600 s^{-1}. The effect of compressed CO_2 on DES 2, in Figure 26, are similar to that in Figure 25. There is a similar drop in shear thinning exhibited after 600 s^{-1}, however a major difference is that for samples XOA1 and XOA2, their viscosities do not differ. In fact, after ± 500 s^{-1}, the viscosities are the same value. There is a significant drop in viscosity of XOA from ±2.5 Pa.s to less than 0.5 Pa.s before a shear rate of 100 s^{-1}.

In Figure 26, two samples of DES 2 were compared, one subjected to compressed CO_2 conditions and the other WB conditions. Sample WB1 exhibited Newtonian properties by remaining ± 0.1 Pa.s without changing by the application of shear rate. Additionally, Figure 26 a), shows the samples which contained water, XOA1 and XOA2, maintained its Newtonian fluid characteristics. However, on closer inspection, Figure 26 b), it does not exhibit these properties before 400s^{-1}.

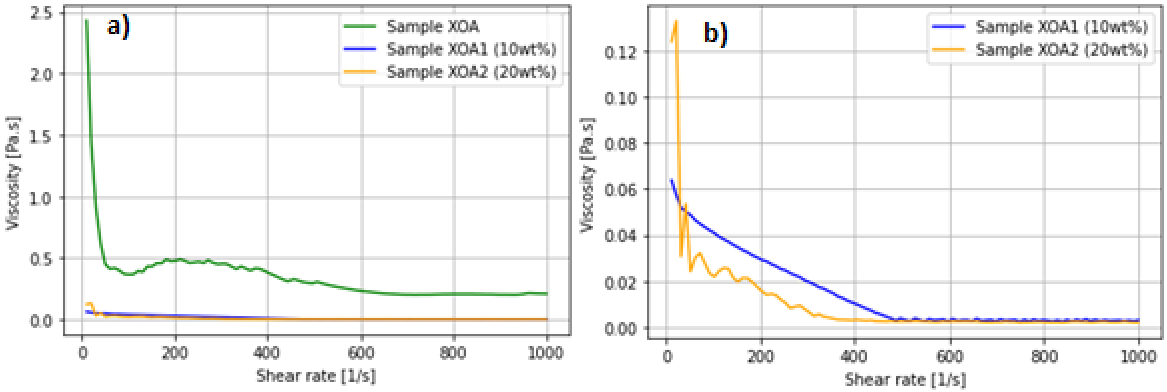


Figure 26 DES 2 with varying wt% of water, a) XOA – no water content, XOA1 – 10wt% water and XOA2 – 20wt% water, and b) XOA1 and XOA2, exposed to compressed CO_2

4.2.3 Comparison of compressed CO_2 and water bath samples

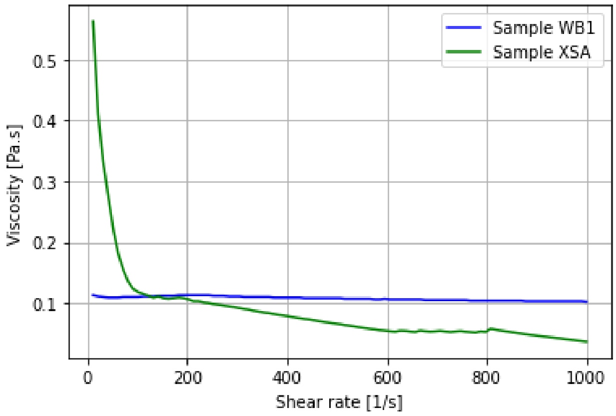


Figure 27 Comparison of DES 1 samples, one exposed to compressed CO_2 and the other not, with no water content

Figure 27 - Figure 30 shows the compares the effects of the samples that have the same DES and water content in both water bath conditions and compressed CO_2. The data suggests the effect of

compressed CO_2 on viscosity in not universal, with Figure 28 showing that sample WB2 has a lower viscosity than XSA1. In addition, sample XSA1 showed shear thinning and its opposite sample remained consistent with increasing shear rate. Samples WB3 and XSA2 experienced sheer thinning, however XSA2 was more rapid and WB3 was a linear decrease.

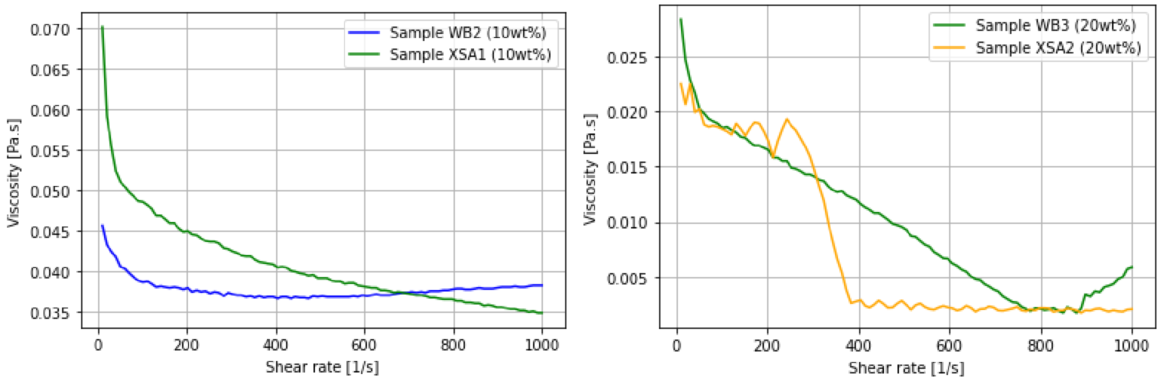


Figure 28 Comparison of DES 1 samples, one exposed to compressed CO_2 and the other not, with 10wt% water content (left) and 20wt% (right)

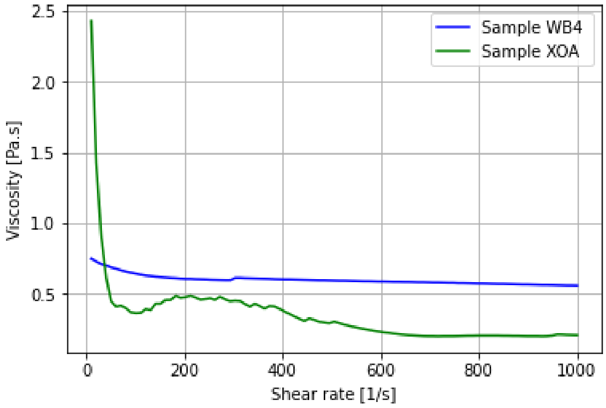


Figure 29 Comparison of DES 2 samples, one exposed to compressed CO_2 and the other not, with no water content

Figure 29 observed an initial high viscosity reading, almost 2.5 Pa.s, and then rapidly thinning as the shear rate was increased. Sample XOA experienced shear thickening from ± 100 s^{-1} until 300 s^{-1}. Thereafter, sheer thinning occurs until 600 s^{-1} and then the viscosity remains unchanged at ± 0.2Pa.s. Viscosity comparison of DES 2 samples. WB4 was placed in the water bath and XOA was subjected to compressed CO_2.

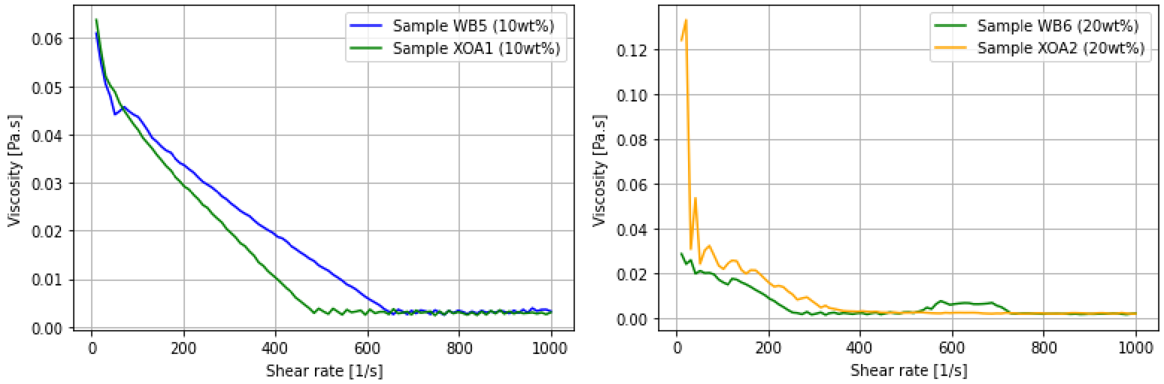


Figure 30 Comparison of DES 2 samples, one exposed to compressed CO_2 and the other not, with 10wt% water content (a) and 20wt% (b)

In Figure 30 (a), the difference in viscosity is not significant. Both samples, WB5 and XOA1, experience sheer thinning at the start of the measurement. Between a sheer rate of 400 – 600, sample settles at a viscosity of between 0.00 and 0.01 Pa.s and remains in this range until the end of the measurement. The sheer thinning for sample WB5 stops after 600 s^{-1} and remains at a viscosity between 0.00 and 0.01 Pa.s. Therefore, one can conclude that for these two samples, the impact of compressed CO_2 stops the shear thinning process at an earlier shear rate. On the graph on the right, the same pattern was seen. An initial shear thinning of both samples and then it stabilized.

In conclusion, while the initial effect of compressed CO_2 on a DES is typically a decrease in viscosity, cooling the system can lead to an increase in viscosity due to the reformation of hydrogen bonds, reduced molecular mobility, and potential changes in the chemical composition of the solvent. This complex interplay underscores the importance of considering both temperature and pressure conditions when evaluating the rheological properties of DESs in the presence of CO_2.

4.3 Extract analysis

4.3.1 Preliminary experiments (objective 2)

This was a preliminary investigation focused on establishing whether exposure to compressed CO_2 had any measurable effect. Due to financial constraints, only a subset of DES samples was selected for water bath experiments, specifically three matched sets under compressed and ambient conditions. These comprised DES 2–0, DES 1–0, and DES 2–20, with each set divided between water bath and supercritical CO_2 conditions. In contrast, DES 1–0, DES 1–10, and DES 1–20 were only exposed to supercritical CO_2. The results of each are shown in Figure 31.

Table 9 Summary of DES Formulations Used in This Study

DES Code	HBA	HBD	Molar ratio
DES1	Choline chloride	p-Toluenesulfonic acid	1:1
DES2	Choline chloride	Oxalic acid	1:1

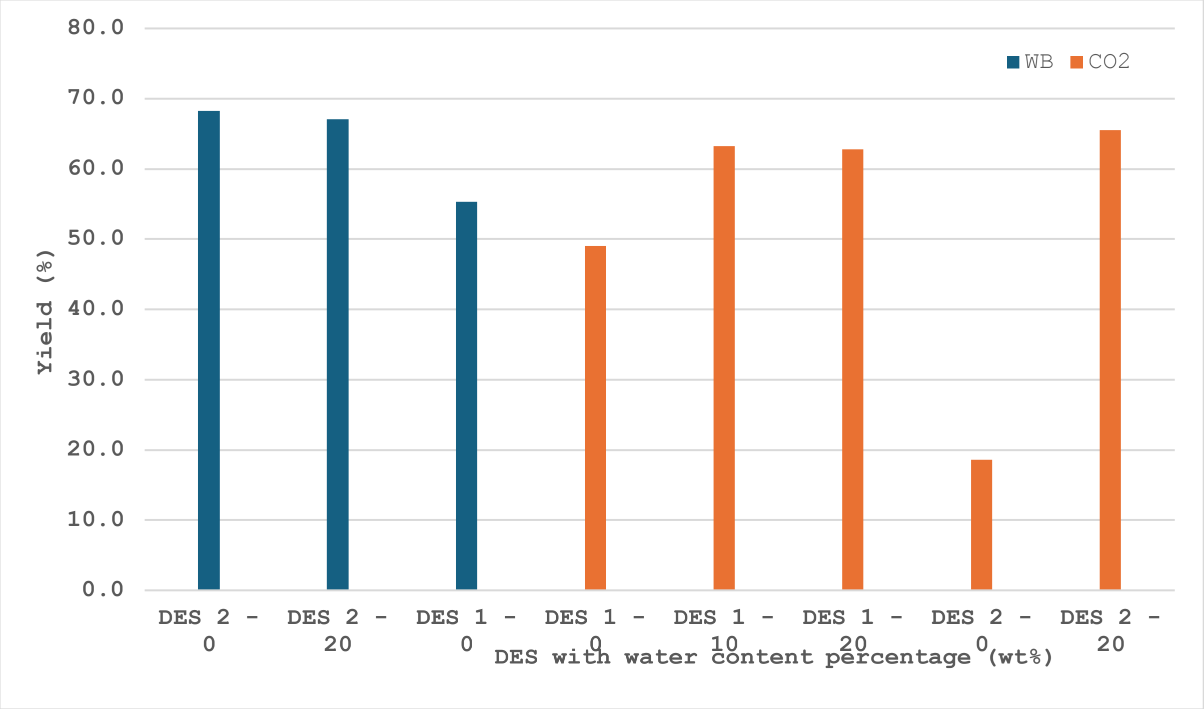


Figure 31 Concentration of cobalt in the ZSM-5-cobalt catalyst extracts

To validate the experimental method and assess its ability to measure the effect of CO_2, two preliminary DES systems were investigated, as summarized in Table 9. A cobalt-doped zeolite was used as the feed material to examine how compressed CO_2 influences the system. The DES samples analysed included: DES 1, composed of choline chloride and p-toluenesulfonic acid (p-TSA), and DES 2, composed of choline chloride and oxalic acid (both prepared with varying water content percentages). Figure 31 presents the results, where blue bars indicate experiments conducted using a conventional water bath, and orange bars represent experiments performed under pressure-assisted conditions. For clarity, the naming convention used in this study refers to the water content percentage in each DES sample. For example, DES2-0 contains 0% added water, DES2-20 contains 20% added water, and so forth.

The effect of using different DES systems on cobalt extraction efficiency of the DES system was assessed. Figure 31 shows that the DES 2-0 recovered the most cobalt, which was 68.3%. DES 2-20, recovered marginally lower than DES 2-0, with 67.1%. The results suggest that the addition of water for DES 2 in the WB did not make a significant difference. DES 1-0 recovered 55.3% of the cobalt in the WB and did not perform as well as DES 2. In the CO_2 experiment, DES 1-0 recovered 49% of the cobalt and increased when water was added. DES 1-10 recovered 63.2% and DES 1-20 recovered 62.8%. This suggests that the addition of water increase however, too much water did not yield any further improvements. For DES 2 in CO_2, sample DES 2-0, recovered 18.6% cobalt and when 20% water was added, the recovery yield improved to 65.6%. Once more, in CO_2, the addition of water did increase the yield of cobalt. DES 2-0 performed the best in the WB and the worst in CO_2, which suggests that the effect of CO_2 has an impact on that DES. However, both DES 2-20 samples performed fairly equally in both WB and CO_2 conditions.

In conclusion, the addition of water to a DES can alter both its physical properties and extraction capabilities. While it can enhance the mobility and solubility of certain metal complexes, it may also lead to decreased extraction efficiency for specific metals due to complexation and phase separation. Understanding these interactions is essential for optimizing metal extraction processes using DESs. One can hypothesize that for the PGM experiments, increasing water content to 10% would yield the best results, however, much of that is dependent on the DES used. In addition, the experimental conditions for the supercritical CO_2 experiments showed to be effective. Both the optimized water content and supercritical CO_2 conditions were incorporated into the PGM extraction experiments.

4.3.2 PGM results (objective 3) – residue results

For the experimental run on PGM recovery, Figure 32 highlights the recovery yields for PGMs using DES 1 for both experiments in the WB and compressed CO_2. The results looked at each metal separately in each environment.

For platinum (Pt) the following was determined:

i. For the WB experiments, the increase of water content increased the recovery yield for the 20wt% sample, with an increase in yield of ± 5% from 84.52% to 88.38%. The 10wt% sample had a marginal effect on the yield when compared to the 0% sample, increasing from 84.52% to 85.23%. The trend using DES 1, in the WB, suggests that increasing water content does improve the yield.

ii. For the compressed CO_2 samples, the increase of water had the opposite effect on the yield. The 0wt% water sample had a recovery yield of 86.47% and it decreased to 66.45% for the 10wt% sample, however, improved to 69.16% for the 20wt% sample. The trend suggests that adding water to the sample lowers the recovery yield.

iii. The 0wt% sample in CO_2 showed a better yield than the same sample in the WB conditions. While all other samples performed worse when subjected to CO_2.

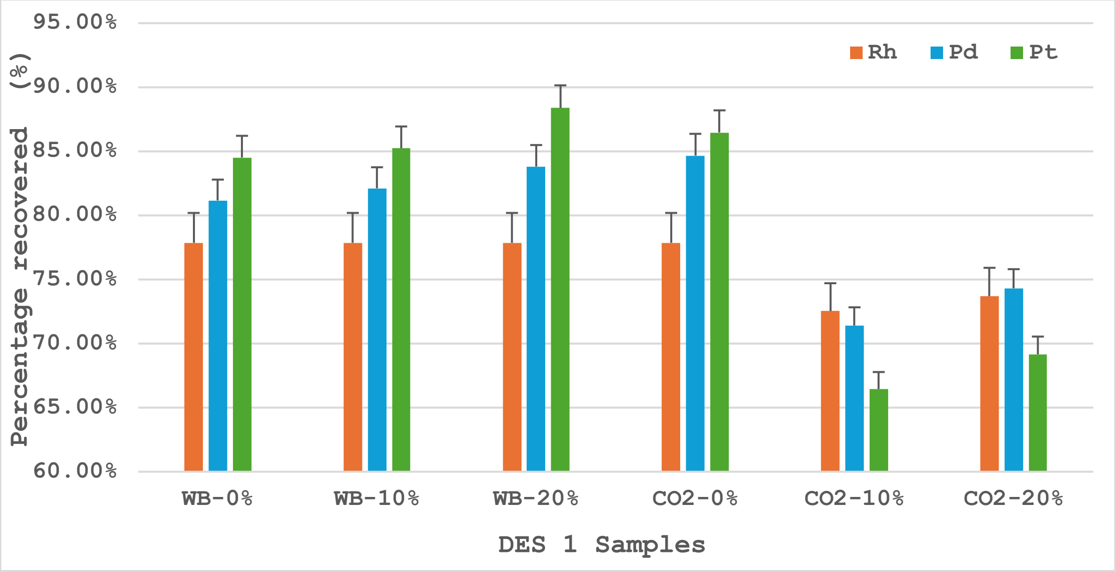


Figure 32 Comparison of percentage of PGM recovered on the residue for DES 1 after the WB and CO_2 experiments

For palladium (Pd):

i. In the WB experiments, the increase of water produced a marginal increase from 81.17% for the 0wt% sample to 82.11% for the 10wt% sample, and then it increased once more to 83.81% for the 20wt% sample. The trend suggests that the increase of water content increased the yield for the recovery of palladium for DES 1.

ii. In the compressed CO_2 experiments, the increase of water content decreased the yield from 86.47% for the 0wt% sample to 71.4% for the 10wt% sample but improving to 74.32% for the 20wt% sample.

iii. Once more, the 0wt% sample in CO_2 showed a better yield than the same sample in the WB conditions and all other samples performed worse when subjected to CO_2.

For rhodium (Rh):

For the rhodium results, the machine used could not guarantee the amount lower that a value of 14.44 µg/kg, which meant that all values below that were not shown or labelled as <LOQ. When converted to a yield %, the value was 77.86%, which was for samples WB-0%, WB-10%, WB-20% and CO-0%. Therefore, the trends for rhodium could not be fully determined.

i. For the WB, it shows that DES 1 can recover rhodium above a 77.86% for all samples.

ii. For compressed CO_2, it follows a similar trend shown for platinum and palladium, the sample with no water content performed the best, then the 10wt% sample performed the worst with a yield of 64.84% and the 20wt% was able to recover 73.7%.

The trends for platinum and palladium suggest that the addition of water increases the yield for the two metals, and in compressed CO_2, it is the opposite effect with the increase of water decreasing the yield for the 10wt% sample and then an increase in the yield is seen for the 20wt% samples.

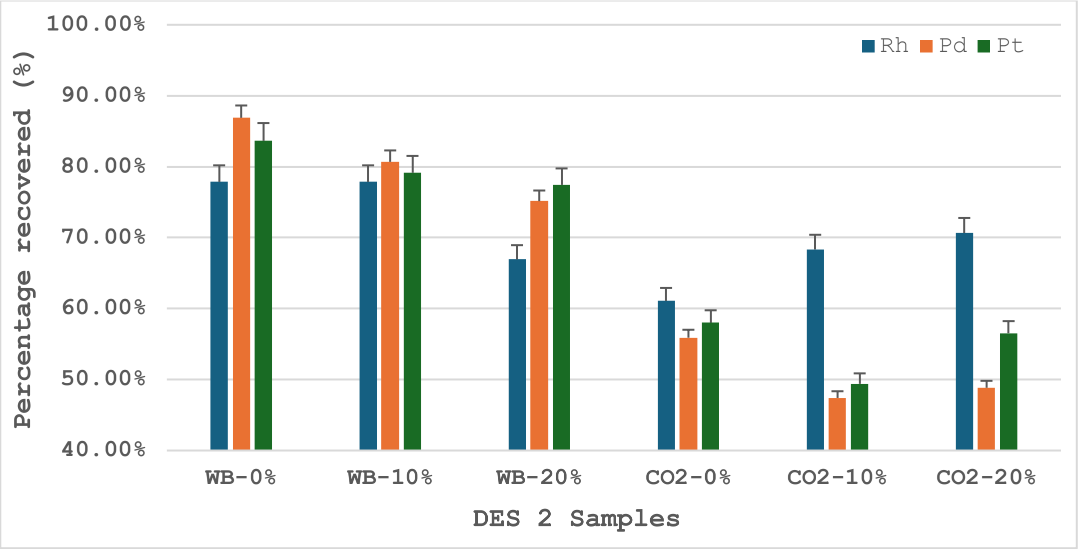


Figure 33 Comparison of percentage of PGM recovered on the residue for DES 2 after the WB and CO_2 experiments

Figure 33 highlights the recovery yields for PGMs using DES 2 for both experiments in the WB and compressed CO_2. The results looked at each metal separately in any given environment. The results looked at each metal separately in any given environment.

For platinum (Pt) the following was determined:

i. The sample with 0wt% had a recovery yield of 83.6%, with the 10wt% sample decreasing to 79.2% and the 20wt% sample further decreasing 77.4%. The results suggest that for the WB experiment, adding water to the DES, decreased the recovery rate.
ii. For the compressed CO_2 experiment, the 0wt% sample had a recovery rate of 58%, with the 10wt% sample recovering 49.4% and the 20wt% had a recovery rate of 56.5%. The trend seems to follow a similar one to DES 1 when it comes to the compressed CO_2 experiments, with the 20wt% sample performed better than the 10wt% sample.

For palladium recovery, the following was observed:

i. The sample with 0wt% had a recovery yield of 86.9%, with the 10wt% sample decreasing to 71.4% and the 20wt% sample further increasing to 73.1%. The results suggest that for the WB experiment, adding water to the DES, decreased the recovery rate.
ii. For the compressed CO_2 experiment, the 0wt% sample had a recovery rate of 56%, with the 10wt% sample recovering 47.4% and the 20wt% had a recovery rate of 48.9%. The trend seems to follow a similar one to DES 1 when it comes to the compressed CO_2 experiments, with the 20wt% sample performed better than the 10wt% sample.

For rhodium, the following was observed:

i. Unfortunately, a trend could not be determined for the WB samples, however the 20wt% sample does perform worse than the others, with a recovery of only 66.9%.

ii. The compressed CO_2 offer a complete change than seen in all other results. The addition of water improved the yield. The 0wt% sample recovered 61.1% and with the addition of water, 10wt%, the recovery yield improved to 68.4%. A further increase of water content, 20wt%, increased the recovery to 70.7%. It was the only sample that increased the recovery yield when subjected to compressed CO_2.

4.3.3 PGM results – DES phase results

While the data for the residue remaining on the catalyst was positive, the absorption into the DES phase was not as positive. The PGM content analysis of the DES phase was shown in Figure 34.

The data showed the only one sample, WB 0% for rhodium, yielded a 20% recovery with every other sample recovering less than that. In addition to that, rhodium recovery was the highest among the 3 metals for all samples. The data suggests that with the increase in water content, the yield decreased, with the 20wt% samples for both water bath and compressed CO_2. This was for all three metals.

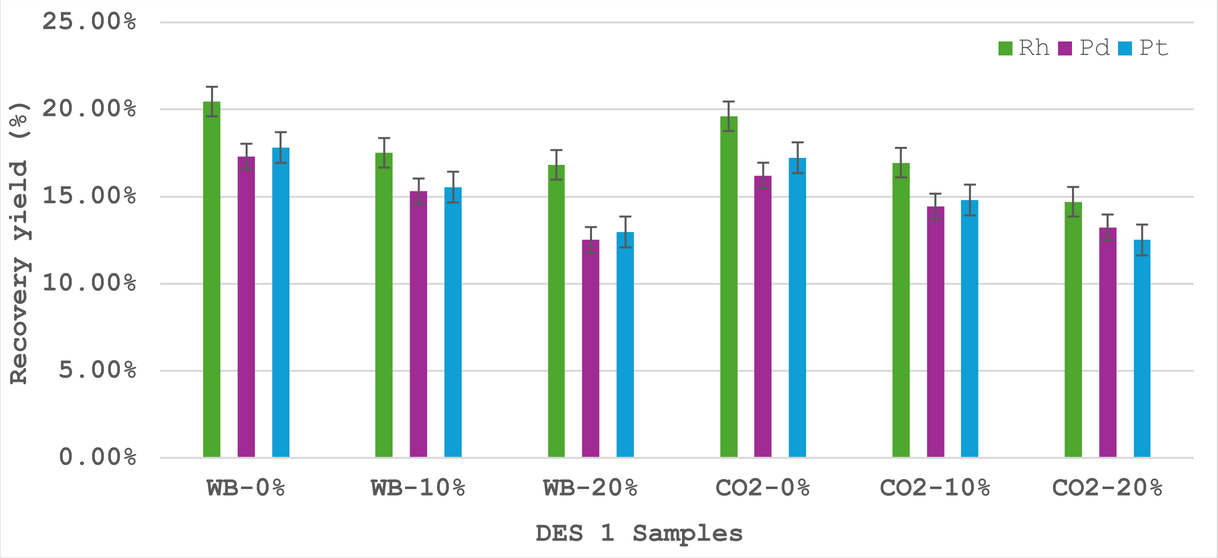


Figure 34 Comparison of recovery yield of PGM in the DES phase for DES 1 after the WB and CO_2 experiments

For Figure 35, the data suggests that for DES 2, rhodium is not as easily absorbed into the DES phase as platinum and palladium compared to DES 1. The increase in water content increases the recovery for platinum and rhodium but not for palladium. With the WB-20% sample, the yields for all metals decreased. For the CO2-0% sample, palladium was the highest followed by platinum and rhodium. The CO2-10% sample did not improve on the yield for any of the samples, with all decreasing in terms of its yield. The CO2-20% sample showed an increase for platinum and rhodium but not for palladium.

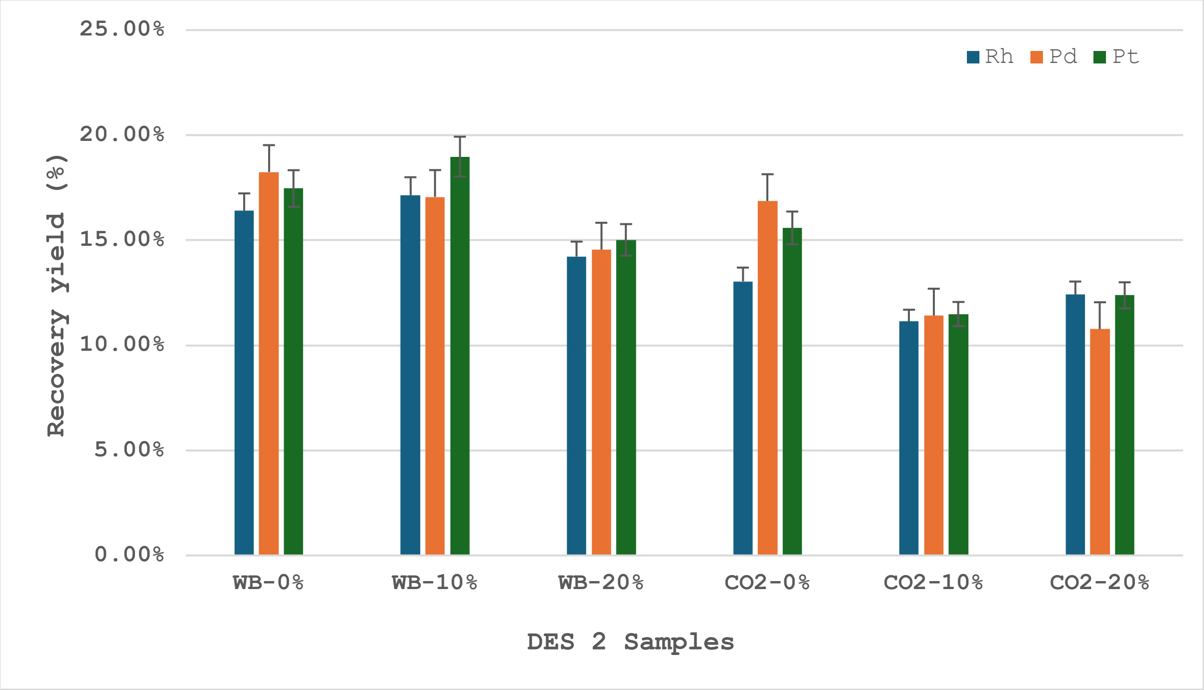


Figure 35 Comparison of recovery yield of PGM in the DES phase for DES 2 after the WB and CO2 experiments

4.4 Chapter outcomes

In this chapter, the results obtained during the experimental work and analysis were obtained. For the first objective, the screening of the best suited HBA and HBD was determined. The results showed that choline chloride was the best HBA, and oxalic acid was the best option for HBD. For the 2nd objective, validation of the experiment using a sample of catalytic converter was carried out and the results discussed in Chapter 5. In addition, the effect of viscosity was analysed and was found that compressed CO_2 has an effect. The analysis data from objective 3 was used to determine the effect of compressed CO_2 on the recovery of PGMs using DES.

Chapter 5: Discussion of results

This chapter provides an in-depth discussion of the results obtained in Chapter 4. The data discussed includes the COSMO-RS screening, extraction kinetics and material balances. From this discussion, conclusions can be drawn relating outcome of the screening tool (objective one), the validity of the analysis (objective two), and the comparison to conventional methods (objective 3). The overall conclusion for this work will be presented in the final chapter.

5.1 Introduction

The use of compressed CO_2 in combination with an IL is not a completely new method of extraction, although only van Dyk *et al.*, (2022) has explored this. The combining of a DES and sCO_2 is a new proposition with no literature found investigating this. The effects on the viscosity of a DES using compressed CO_2 are a new proposition as well.

Lanaridi *et al.*, (2022) explored the use of DES to recover PGMs from a spent catalyst. The aim of this work was not the optimization of the extraction method. However, the results indicate that varying the molar ratio of the DES does yield a higher extraction yield of rhodium.

5.2 COSMO-RS Screening

From the data in the results section, each of the compounds were investigated in terms of their capabilities as an HBA and HBD.

While citric acid showed to be the most effective as both an HBA and HBD, in terms of the sigma profile, it is not an optimal choice. The reasons are as follows:

i. Although citric acid demonstrates favourable sigma profiles and can function as both a hydrogen bond donor and acceptor, its practical application in DES systems is limited by its high viscosity. Peeters *et al.*, (2020) reported that a citric acid-based DES achieved 99% cobalt recovery at a 1:1 molar ratio, but noted that viscosity posed challenges to mass transfer. Adjustments to molar ratio and water content mitigated these effects without compromising yield. Similarly, Troter *et al.*, (2016) observed that citric acid-based DESs were particularly problematic at lower temperatures due to viscosity-related inefficiencies. While viscosity was not directly measured in this study, these findings were considered in the discussion to contextualize the limitations of citric acid as a solvent component.
ii. Citric acid’s acidic nature can pose challenges in the formation of DES. Citric acid has three carboxylic acid groups, each capable of donating protons and because of this, it can lead to competitive interactions with other components in the DES, that could disrupt the stability of hydrogen bond network. Martínez *et al.*, (2016) highlighted that DESs with a high viscosity and complex interactions can result in a less effective reaction media.

iii. Citric acid's ability to perform as an HBA also presents challenges. While the carboxyl groups can accept hydrogen bonds, its overall performance is often inferior when compared to more effective HBAs, such as quaternary ammonium salts. DESs that utilize choline chloride as an HBA often exhibit superior physical properties and lower melting points than those compared to citric acid (Paiva *et al.*, 2014; Zhao *et al.*, 2015)

iv. The solubility and extraction efficiency of citric acid-based DES can be lower than those exhibited in more effective HBDs. Zhao *et al.*, (2015) showed the extraction capabilities of a solvent is significantly influenced by the interaction dynamics between an HBA and HBD, and that citric acid may not provide an optimum environment for that process.

Thus, while citric acid exhibits excellent potential as either an HBA or HBD, according to Figure 14, its high viscosity, complex interaction dynamics, inferior performance other options limit its effectiveness. Oxalic acid showed strong capabilities to being an effective HBA, literature has suggested the following:

i. This is due to its molecular structure, in which it contains two carboxyl groups which can engage in hydrogen bonding interactions.

ii. As an HBD, Stare and Hadži, (2014) showed that oxalic acid has strong intermolecular bonding capabilities by donating its hydrogen bonds. The presence of multiple carboxyl groups in oxalic acid enhances the stability of the resulting DES. However, as seen with citric acid, too many carboxyl groups can negatively affect the DES.

iii. As an HBA, the carboxyl groups donate the proton and forms carboxylate groups. These carboxylate group can accept hydrogen bonds from other molecules. However, no supporting data for the use of oxalic acid as an HBA has been found

Therefore, oxalic acid could be an HBA and HBD, due to its strong hydrogen bonding abilities. However, its use an HBA is not yet proven in open literature but remains an effective option for an HBD.

The results indicate that p-TSA would be a good HBA and HBD. The following was determined:

i. In the study by Sert and Atalay, (2017), utilized a p-TSA based DES that served as a dual solvent catalyst for the esterification of benzoic acid with different alcohols. The p-TSA based DES allowed for reaction temperature for the experiment and maintaining yields of above 65%. Its application in DESs has been explored in numerous studies, demonstrating its effectiveness in catalysing chemical reactions and enhancing solvent properties

ii. Taysun *et al.*, (2017) investigated the properties of DESs formed with benzyl triethyl ammonium chloride (BTEAC) with various HBDs, including p-TSA, and found that the choice of HBD is significantly influenced by the physical properties. In addition, the DES that had p-TSA as an HBD showed high reaction rates and low activation energy and maintained a catalytic activity of above 80% when temperature was decreased. The ability of p-TSA to interact favourably with quaternary ammonium salts, such as BTEAC, underscores its potential as an effective HBD in DES formulations.

In conclusion, toluene sulfonic acid is a highly suitable HBD for the formation of DESs, particularly when paired with appropriate HBAs like quaternary ammonium salts. Its ability to enhance catalytic activity, lower freezing points, and improve solvent properties makes it an attractive option for various chemical processes, aligning with the principles of green chemistry.

Choline chloride showed to be either an effective HBD or HBA, yet literature suggests that it would be more suited for an HBA. The following was found:

i. Choline chloride is widely recognized as the most suitable HBA. This effectiveness is due to its ability to form strong hydrogen bonds and, in the formation of a DES, facilitate a low melting point eutectic (Smith *et al.*, 2014). The combination with different HBDs, such as glycerol or urea, showed its effectiveness in forming DESs with desirable chemical and physical properties (Adeyemi *et al.*, 2022)
ii. The quaternary ammonium structure, within choline chloride, allows it to stabilize the resulting DES through the hydrogen bonding. The DES comprised of choline chloride and urea, showed a significant melting point depression which highlights the strong interactions between the compounds (Zhao *et al.*, 2013; Yadav *et al.*, 2014).

In summary, while citric acid demonstrates potential as both a hydrogen bond acceptor (HBA) and donor (HBD), its effectiveness in forming deep eutectic solvents (DESs) is limited by high viscosity and complex interaction dynamics that can hinder mass transfer and overall solvent efficiency. Oxalic acid shows promise as a strong HBD due to its ability to engage in effective hydrogen bonding through its carboxyl groups; however, its role as an HBA remains unproven in the literature.

Toluene sulfonic acid (p-TSA) emerges as a highly suitable option for both HBA and HBD roles within DESs, demonstrating enhanced catalytic activity and favourable physical properties when paired with quaternary ammonium salts. Its effectiveness in facilitating chemical reactions at lower temperatures further underscores its potential in green chemistry applications. Choline chloride stands out as an optimal HBA due to its capacity to form strong hydrogen bonds and create low melting point eutectics when combined with various HBDs. The quaternary ammonium structure of choline chloride contributes to the stability and desirable properties of the resulting DESs, making it a preferred choice in solvent formulations.

Overall, the comparative analysis of these compounds highlights the importance of selecting appropriate HBA and HBD combinations to optimize the performance of deep eutectic solvents for various applications in chemical processes. In addition, while the sigma profiles did provide valuable guidance, practical factors such as viscosity and stability must be considered to ensure efficient extraction. The chosen DESs were choline chloride and toluene sulfonic acid (DES 1), and oxalic acid and choline chloride (DES 2).

5.3 Effect of water on viscosity

For WB4, Figure 29, strong hydrogen bonds are formed and with the addition of water, these bonds are disrupted which significantly reduces the viscosity by weakening the hydrogen bonding interactions (Dai *et al.*, 2015; Seyf and Zarei, 2022). Additionally, the viscosity of DESs is heavily affected by the balance of HBDs and HBAs and with the introduction of water, this balance is modified, making it more of a fluid system (Smink *et al.*, 2019). The balance can be modified because DESs rely on a specific hydrogen bond network to maintain its eutectic structure, and adding water to that structure means that it competes for hydrogen bonding sites (Contreras *et al.*, 2021).

According to Gygli, Xu and Pleiss, (2020) and Peng *et al.*, (2024), a low water concentration does not affect the Newtonian behaviour, however a higher concentration can lead to a non-Newtonian behaviour. This was seen in Figure 23.

The addition of water, even in small concentrations, disrupts the extensive hydrogen bonds network that characterizes these solvents. Both Vuksanovic *et al.*, (2017) and Fetisov *et al.*, (2018) highlighted that the addition of water leads to the reduction in the number of hydrogen bonds among the DES components, which weaken the overall intermolecular interactions, thus resulting in a lower viscosity. It should be noted that effect of water on the viscosity of DES is not uniform (seen in Figure 23 toFigure 30; it can vary depending on the specific composition of the DES and the concentration of water added. Lomba *et al.*, (2023) and Töpfer *et al.*, (2022) highlighted that while low concentrations of water can lead to a marked decrease in viscosity, higher concentrations may lead to phase separation or alterations in the DES structure, potentially increasing viscosity again or causing the DES to lose its characteristic properties (shown in Figure 30). This indicates a delicate balance in the formulation of DESs with water, where the concentration must be carefully controlled to optimize performance.

Both Morais *et al.*, (2019) and Lopes *et al.*, (2016) highlighted the viscosity of both IL and DES decreased with increasing pressure due to the enhanced molecular mobility and reduced interactions among the solvent molecules. However, with a decrease in temperature, results in a decrease in kinetic energy of the molecules, which can lead to increased viscosity as the solvent molecules become less mobile and more structured (Ciriaco, Ledoux and Estel, 2023). This phenomenon is particularly relevant in systems where the solubility of CO_2 decreases with temperature, potentially leading to phase separation or changes in the solvent's microstructure that can increase viscosity (Huang *et al.*, 2022).

As shown in Section 4.1.2.2, introduction of water leads to a reduction in the viscosity of the DES. This is primarily due to the disruption of the hydrogen bonding network that characterizes DESs, as water molecules interfere with the interactions between the solute and the solvent components (Valverde, Green and Roy, 2017). Parmentier *et al.*, (2015) showed that the reduction in viscosity enhanced the mobility of the solvent, which is beneficial for mass transfer during extraction processes.

Vahidi *et al.*, (2023) demonstrated that CO_2 can permeate into the ionic liquid phase, indicating that the effect could occur in the DES phase as well. The molecular dynamics simulations suggest that the incorporation of CO_2 into the DES can alter its properties, potentially enhancing its utility as a solvent in various applications, including extraction and catalysis (Vahidi *et al.*, 2023)

5.4 Preliminary experiment

The recovery of cobalt using DES is influenced by several factors, including solvent composition, temperature, length of the experiment and the application of compressed CO_2. Each of these factors plays a role in determining the efficiency and selectivity of cobalt extraction.

5.4.1 Solvent to feed ratio

As illustrated in the previous chapter (specifically Figure 31), the highest extraction yield was found to be 68,3% recovery using a DES made up of oxalic acid and choline chloride in a ratio of 1:1 with no water content added, with a S:F ratio of 5:1. Peeters, Binnemans and Riaño, (2020) used a solvent to feed (S: F) ratio of 20:1 and for DES 2, and recovered 19.6% of cobalt from a spent Li-ion battery. Therefore, a similar value was expected for this experiment. However, there were factors that differed which may have impacted on the yield for this work. The first difference was the composition of the solvent used, whereby Peeters, Binnemans and Riaño, (2020) used S:F ratio of 20:1 compared to this work of 5:1. A greater S:F ratio could improve the extraction efficiency of the targeted compound by providing a greater volume of the solvent to solvate, if the targeted compound is in small quantities within the solute (Huang *et al.*, 2015). However, this is not always the case. Lanaridi *et al.*, (2022) highlighted that after a S:F ratio of :1, there was no increase in the yield for the recovery of PGMs.

In summary, while a high S:F ratio could enhance the efficiency by increasing solvent volume, it could lead to a dilution effect. However, even though varying an S:F could improve the yield, for the PGM experiments a constant S:F was maintained.

5.4.2 Temperature

Another factor affecting cobalt recovery is temperature. Higher temperatures may increase the cobalt solubility in the DES and enhance the kinetics of the leaching process. According to Ma *et al.*, (2023) found that microwave-assisted leaching at higher temperatures may reduce the time required for cobalt extraction while increasing the concentration of the recovered cobalt. Additionally, (Djoudi, Le

Page Mostefa and Muhr, (2021) illustrated that temperature influences the precipitation kinetics of cobalt hydroxide from leachates, indicating that optimal temperature conditions are essential for maximizing recovery.

The temperature of the experiment could also influence the yield. The temperature influences the viscosity of the DES, which could limit the mass transfer. (Tsvetov, Korovkina and Paukshta, (2021) determined that the viscosity of DESs decreases with increasing temperature, which can lead to improved extraction rates. Peeters, Binnemans and Riaño, (2020) not only showed the increase in yield with an increase in temperature but also showed that the recovery was faster with an increase in temperature. At 60°C the recovery of cobalt reached ± 99% after 100 minutes, yet at 80°C it reached the same value much faster.

However, it is essential to consider that excessively high temperatures can lead to the degradation of the DES or the target compounds, which may negatively impact extraction efficiency. Yin *et al.*, (2022) highlighted that while moderate increases in temperature can enhance extraction, extreme temperatures may cause thermal degradation of the solvent components, or the solutes being extracted. Therefore, optimizing the temperature in a key step to balancing the benefits of increased solubility and reduced viscosity against the risks of degradation.

In conclusion, temperature is an important factor to consider in the performance of DESs for metals. While temperature was not varied experimentally, it compares the results of the preliminary experiment with findings from relevant literature to contextualize how temperature may influence the system.

5.4.3 Effect of adding water to a DES

Figure 31 shows the water bath and compressed CO_2 experiments. One of the primary benefits of adding water is the reduction in viscosity. Which is highlighted in Figure 23 and Figure 24. However, the reduction in viscosity did not improve the yield for DES 2 in the water bath experiments, when considering the data shown in Figure 31. In the compressed CO_2 experiments, the addition of water had an effect, especially for the DES with not water content (DES 1 – 0 and DES 2 – 0) compared to the samples with water content (DES 1 – 10, DES 1 – 20 and DES 2 – 20). A possible deduction that can be made is that the interaction is not only limited to the reduction in viscosity, but also waters ability to act as a co-solvent or as an anti-solvent (Vilková, Płotka-Wasylka and Andruch, 2020). In addition affecting the viscosity, water enhances the mass transfer, improves the extraction efficiency, can change the DES polarity and could lead to weakening of the interactions between DES components (Vilková, Płotka-Wasylka and Andruch, 2020). Figure 31 highlights some of these changes. The addition of water improved the yield when comparing DES 2 – 0 to DES 2 – 20 in compressed CO_2, suggesting an improvement on mass transfer.

It is possible that for DES 2, its interaction with cobalt is so favourable that the high viscosity in the WB experiment was not a limiting factor (Peeters, Binnemans and Riaño, 2020). Conversely, in the CO_2 system, the presence of water might have created a more favourable environment for extraction, perhaps by influencing the polarity of the DES (Vilková, Płotka-Wasylka and Andruch, 2020) or stabilizing the cobalt-DES complex in the presence of dissolved CO_2. This highlights that the effect of water is not universal but is highly dependent on both the DES composition and the experimental environment (WB vs. CO_2).

5.4.3.1 Water bath vs Compressed CO_2 viscosity comparison

Suriyanarayanan *et al.*, (2023) demonstrated that the addition of water to a non-ionic DES improved the extraction yield of cobalt from spent Lithium-ion batteries (LiBs), which could indicate that water helps facilitate the dissolution of cobalt compounds in the solvent system. This is key when working with cobalt oxide or other less soluble forms, where water can aid in the breakdown of these compounds and increase the availability of cobalt ions.

Hammond *et al.* (2017) reported that a DES made of choline chloride and urea could still maintain its DES structure with 42wt% of water added. This reduction in viscosity, while still maintaining achieving mass transfer, is a key factor. In addition, the presence of water reduces the viscosity of the DES, which could enhance mass transfer during the extraction process.

Ola et al., (2022) demonstrated that in some DES systems, if the water content exceeds a certain threshold, it can form of two distinct liquid phases, which may complicate the extraction process. In addition, Yang *et al.*, (2017) highlighted that the solubility of the DES components in water can also affect the overall extraction efficiency, whereby certain metal ions may leach into the aqueous phase rather than remaining in the DES phase. Thus, although the addition of water does reduce viscosity, an excessive showed to have an opposite effect.

In conclusion, adding water to a deep eutectic solvent can improve its extraction abilities for cobalt by enhancing solubility, reducing viscosity, and stabilizing cobalt complexes. However, careful optimization of the water content is necessary to maximize extraction efficiency and avoid dilution effects.

5.4.4 Effect of compressed CO_2

While not specifically referring to cobalt, the study by van Dyk *et al.*, (2022) showed the impact of subjecting an IL to compressed CO_2. The results showed that when compared to ambient pressure experiments using the same IL and other experimental conditions, on all accounts the compressed CO_2 experiments performed better. Therefore, on can conclude that the effect of pressure could increase the yield. In this work, this effect is not seen however one should consider the time factor of the application of compressed CO_2 and WB experiments. In the same work by van Dyk *et al.*, (2022), it showed that when the length of the application of CO_2 was less than the ambient pressure experiments, the yield was lower on three occasions.

5.5 Validation

A Students t-test was performed using Excel. The outcome of the test was highlighted in Table 10

Table 10 Paired t-test Analysis of Extraction Yield Differences Between Compressed CO_2 and Atmospheric Pressure Conditions

	Variable 1	*Variable 2*
Mean	1,72E+05	2,55E+01
Variance	6,86E+09	7,20E+02
Observations	6,00E+00	6,00E+00
Pearson Correlation	6,86E-01	
Hypothesized Mean Difference	0,00E+00	
df	5,00E+00	
t-Stat	5,09E+00	
P(T<=t) one-tail	1,90E-03	
t Critical one-tail	2,02E+00	
P(T<=t) two-tail	3,79E-03	
t Critical two-tail	2,57E+00	

The test was conducted to confirm the statistical significance of adding compressed CO_2 to the extraction system. The data from Figure 32 Comparison of percentage of PGM recovered on the residue for DES 1 after the WB and CO_2 experiments split into two groups, group 1 WB, and group 2 CO2. The t-test was then conducted on the two groups and from Table 10 it can be statistically concluded that compressed CO_2 enhances the extraction process because the P-value < 0.05. In addition, given that t-Stat > t-critical confirms that the null hypothesis can be rejected. Thus, the validation results showed that the experimental setup is capable of detecting variations in yield caused by a variation of solvents.

5.6 PGM experiment comparison to other methods

Faisal *et al.*, (2008) was the only study to investigate the recovery of PGMs using compressed CO_2. The recovery yield for platinum, palladium and rhodium were found to be ± 5%, 96% and less than 1%, respectively. The experimental conditions were 60 minutes at 200 bar and 60°C, and the chelating agent used was tributyl phosphate (TBP) with nitric acid. For this work, the yields recovery for platinum, palladium and rhodium were 86.5%, 84.7% and higher that 77%, respectively. However, the DES phase data was a more crucial analysis. Table 11 shows the comparison of the remaining residue on the catalytic converter, the absorption of PGMs into the DES phase and the yield of PGMs in the study by Faisal *et al.*, (2008).

Table 11 Comparison of this work and Faisal et al.*, (2008)*

Metal	***This work (CO_2) Cat. Converter residue***	***This work (CO_2) DES phase***	***Faisal et al., (2008)***

Platinum	86.5%	17.2%	Less than 5%
Palladium	84.7	16.2%	96%
Rhodium	Above 77%	19.6%	Less than 5%

The data shows that while recovery from PGM from the catalytic converter is high, above 75% for all metals, its absorption into the DES phase is poor. Compared to other work, the recovery of both platinum and rhodium increased by at least three times compared to Faisal *et al.*, (2008). However, the recovery of palladium was poor, which was 16.2% compared to 96%. Faisal *et al.*, (2008) does show that at 100 bar, the recovery yield for palladium was closer to 75%, and at 300 bar it was ± 100% recovery. Thus, the impact of pressure played a significant role.

Lanaridi *et al.*, (2022) used the same DESs for the recovery of PGMs from a spent catalytic converter, with the following extraction conditions, 80°C, an extraction time of 4 hours, the use of nitric acid as an oxidizing agent, molar ratio of 1:1.8 (choline chloride: p-TSA), and a S:F ratio of 5:1. The achieved recovery rates of 100% for both palladium and platinum, and rhodium had a recovery of less than 50%. In comparison, this work was recovered 86.5% for platinum, 84.7% for palladium and above 77% for rhodium for the recovery from the catalytic converter. For this work, as mentioned in 3.4.8.3, the experimental conditions were 80°C for both water-bath and compressed CO_2, ambient temperature and 100 bar, and 4 hours for the water bath and 2 hours with compressed CO_2. The DES phase data suggests a poor absorption. These results are summarized in Table 12.

Table 12 Comparison of PGM recovery yields

Metal	***This work (CO_2) cat. converter residue***	***This work (CO_2) DES phase***	***No oxidizing agent (Lanaridi et al., 2022)***	***Oxidizing agent (Lanaridi et al., 2022)***
Platinum	86.5%	17.2%	Less than 40%	Above 90%
Palladium	84.7%	16.2%	± 90%	100%
Rhodium	Above 77%	19.6%	Less than 40%	Above 40%

The differences in the two works were the molar ratios used and in the compressed CO_2 conditions, the length of the experiment was shorter, 2 hours compared to 4 hours. The use of compressed CO_2 was positive in terms of the recovery of PGMs from the catalytic converter, however, its absorption into the DES phase was poor. When compared to Lanaridi *et al.*, (2022), it showed a decrease of absorption into the DES phase of palladium by almost five times, platinum, and rhodium twice as less. This was specifically less that the DES phase with no oxidizing agent. One possible mechanism is that the oxidizing agent alters the coordination environment or modifies the solubility equilibrium, thereby affecting partitioning into the DES phase. Similar inhibitory behaviour of oxidizing components has been reported by López et al. (2021) in halide-rich DES systems, where excessive redox potential suppressed metal ion solubilization. Addressing this may involve screening alternative oxidants with milder reactivity or optimizing the DES composition to counterbalance competitive interactions.

A factor that could increase the yield for PGMs using compressed CO_2 is contact time of the experiment. According to van Dyk *et al.*, (2022), who investigated the recovery of gold using sCO_2 and an IL, the longer the exposure to CO_2, the higher the yield for gold. In their work, experiments were conducted at 6 hours and 24 hours in a sCO_2 system. The results show that for all experiments, when the length of the experiment was 24 hours, the yield improved compared to the six-hour experiment.

An additional factor could be the molar ratio. Peeters et al., (2020) demonstrated that the changing the molar ratio for a DES made up of citric acid and choline chloride from 1:1 to 1:2 and this improved the time taken without compromising the recovery yield.

The effect of the compressed CO_2 shows an impact on the DESs with no water content. The results are shown in Table 13.

Table 13 Comparison of WB and CO_2 experiments for DES 1 with no water content

Metal	***This work (WB)***	***This work (CO_2)***
Platinum	84.5%	86.5%
Palladium	81.2%	84.7
Rhodium	Above 77%	Above 77%

For DES 1, the results show an increase in yield for the samples that were subjected to compressed CO_2. This increase can be possible due to factors such as increased solubility of metals, enhanced mass transfer and changes in physical properties of the solvent system.

Compressed CO_2 may enhance metal extraction through its ability to increase the solubility of PGMs within the DES. Tuan *et al.*, (2021) determined that the solubility of certain metal complexes can increase when Co is dissolved within the solvent, there enhancing extraction.

The presence of compressed CO_2 can enhance the mass transfer rates during the extraction process. Uquiche *et al.*, (2016) showed that increased pressure improved the kinetics of the extraction process by reducing viscosity and increasing mobility of the solute. As a result, the extraction process may become more efficient and potentially leading to higher yields.

The application of compressed CO_2 can induce changes in the properties of the DES, namely viscosity and density, which can further enhance the process.

In summary, the application of compressed CO_2 in the extraction of PGMs using DESs can increase the yield by enhancing the solubility of the metals, improving mass transfer rates, and altering the physical properties of the solvent system. These factors collectively contribute to a more efficient extraction process.

Table 14 Comparison of DES 1 and 2 in WB experiments

DES – H_2O%	***Platinum***	***Palladium***	***Rhodium***
DES 1 - 0	84.5%	81.2%	Above 77%
DES 1 - 10	85.2%	82.1%	Above 77%
DES 1 - 20	88.4%	83.8%	Above 77%
DES 2 - 0	83.6%	86.9%	Above 77%
DES 2 - 10	79.2%	80.7%	Above 77%
DES 2 - 20	77.4%	75.1%	66.9%

The performance of two DESs in the extraction of PGMs was assessed and the results tabulated in Table 14. Several factors influenced the recovery yields for each DES system.

For DES 1, reduced viscosity correlated with improved recovery of platinum and palladium. This aligns with findings by Panda and Mishra, (2023) who reported that lower viscosity enhances metal diffusion and mass transfer in DES-mediated extractions. In contrast, DES 2 displayed an inverse trend, suggesting that viscosity alone does not dictate yield, and instead, solvent–metal coordination dynamics play a critical role, as suggested by Abbott *et al.*, (2014).

The addition of water had divergent effects on the two systems: for DES 1, water appeared to facilitate metal solvation, consistent with the view that trace hydration can disrupt HBD–HBA networks and enhance ionic mobility (Kivelä *et al.*, 2022). Conversely, in DES 2, water likely destabilized the extraction matrix or hindered active site formation. These differences may be attributed to factors such as solubility profiles, hydrogen bonding strength, and the chemical nature of DES components, which have been shown to significantly influence recovery mechanisms (Gholami *et al.*, 2025).

The presence of water could have impacted on the solubility of PGMs, which could either enhance the solubility of the metal ions or not. In addition, if a DES is formulated with an HBD that interacts favourable with water, then it may solubilize the PGM complexes more effectively. The opposite is also true, in if it interacts poorly, then it may dilute the concentration, which lowers the yield. This phenomenon was highlighted by Sefako, Sibanda and Sekgarametso, (2019), who indicated that efficiency of metal extraction could vary based on the specific interactions between solvent components and targeted metals. This phenomenon is seen on both accounts for the DESs in this work.

This improved mass transfer can lead to higher extraction yields. However, if the DES is already low in viscosity, the addition of water may not provide significant benefits and could even hinder the extraction process by creating a less optimal environment for the solvation of metal ions. The study by Mao *et al.*, (2022) supports this by showing that the viscosity of solvent systems can significantly impact extraction efficiency.

The effect of water addition is not linear; whereby, there may be an optimal range of water content that maximizes extraction yield. Beyond this optimal point, any further addition of water could lead to dilution effects that reduce the concentration of the target metal.

In conclusion, the differing effects of water addition on the extraction yield of PGMs using different DESs can be attributed to variations in solubility, viscosity, chemical interactions, and the presence of an optimal water content. Understanding these factors is essential for optimizing extraction processes and achieving high yields of PGMs.

5.7 Chapter outcomes

This chapter focused on interpreting and discussing the results obtained during the experimental work and analysis. The experimental conditions were determined through theoretical estimations and literature data.

For objective 1, it was determined that the best suited HBA was choline chloride and the best suited HBD was oxalic acid. The data showed that citric acid would be a good HBD, however literature data suggested that citric acid-based DES are known to be more viscous than compared to those without citric acid as an HBD.

For objective 2, the preliminary experiments using cobalt-doped zeolite was validated using the Students t-test. The validation showed that the experimental setup was capable of detecting variations in yield caused by a variation of solvents.

For objective 3, the data showed the pressure assisted system of sCO_2 and DES was able to recover PGMs from a catalytic converter. There was a high percentage recovery (above 75%) from the solid sample (residue). However, there was an overall low recovery yield (less than 20%), which looked at the DES phase. When compared other sCO_2 methods, the recovery of rhodium and platinum increased by ±15% but palladium recovery decreased by ±80%. When compared to studies that used DESs, all the recovery yields were lower.

With the addition of water, the viscosity was lowered and the percentage recovered from the catalytic improved. However, within the DES phase (liquid sample), the addition of water showed a decrease in the recovery yield of PGMs.

Chapter 6: Conclusion and recommendations

This project aimed to develop a system that uses pressure-assisted extraction with CO_2 to recover platinum group metals (PGMs) from catalytic converters. Currently there are no known processes for extraction of PGMs using DES, in a pressure assisted system. This work aimed to determine whether a pressure-assisted extraction can enhance the recovery of PGM from secondary sources. The objectives included screening for the best combination of a DES, estimating pressure conditions for the compressed CO_2 and validating the measuring system, and evaluating the yields and comparing to conventional methods.

6.1 Summary

For this work to be completed, it was important to establish what was achieved in literature and find the gap for PGM recovery. The initial data indicated that the recovery of PGMs from a secondary source was feasible and had been attempted by Faisal *et al.*, (2008) and Lanaridi *et al.*, (2022). Although, where Faisal *et al.*, (2008) highlighted the difficulty in recovery all PGMs using sCO_2, Lanaridi *et al.*, (2022) showed that the complete recovery of platinum and palladium was possible by using a DES. Thus, with this work, it investigated combining both sCO_2 with DES to determine with the yield could be enhanced. To achieve this, the conditions were of utmost importance. The pressure conditions were determined through literature, by utilizing those set out in van Dyk *et al.*, (2022), 100 bar. The conditions of 80°C was determined by Lanaridi *et al.*, (2022) and the time of 60 minutes by Faisal *et al.*, (2008).

The experimental work consisted of 4 experiments, which included a preliminary run using a cheaper metal and the catalytic converter. With the preliminary run, it was important to evaluate the effect of the compressed CO_2 on the DES. Experiments 1 and 2 consisted of comparing the effect of a water bath experiment and pressure assisted experiment on a cobalt doped ZSM-5 zeolite carrier. The analysis of this data showed that the effect on the yield is visible. Experiments 3 and 4 were carried out in the same manner as 1 and 2 but changing the feed source to the catalytic converter. The process was validated using a t-test. The extracts were sent for ICP-OES analysis, in which the samples were analysed for remaining PPM content on the feed.

6.2 Conclusion

The aim of the work was to determine whether a pressure assisted system of sCO_2, and DES could enhance the yield for palladium. There was a marginal gain for palladium when comparing the water bath sample, with no water content, to the sample same in the pressure assisted system (Figure 32), however even with that the enhancement was not seen.

For objective one, the screening for the HBA and HBD was complete. The screening tool suggested that citric acid is the best option as an HBD and/or HBA, with the best system being a DES made up of CA – CC (DES 1). Although literature suggested that due to its high viscosity in forming a DES, it is not the best option.

Objective two was completed and the validation results showed that the experimental setup was statistically capable of detecting variations in yield caused by a variation of solvents.

For objective three, the following was determined:

- recovery from the feed using a pressure assisted system was above 75% for all metals using the DES with no water content. This compares favourably to existing literature,
- However, in the DES phase, extraction data was less than 20% recovered. Worse than that reported in Lanaridi *et al.*, (2022), but better than compared the results in Faisal *et al.*, (2008).

6.3 Project outcomes

Conversion of current processes to greener versions using more benign solvents is a major contributor to a cleaner environment. The data sets of data produced in this work are an important addition to the scarce literature data on the extraction. The data produced in the current project has confirmed that deep eutectic solvents have the potential to achieve the same yields as those achieved using much harsher reagents, such as strong oxidising agents and strong acids. On the other hand, the data equally shows that, at least for the catalytic converters, pressure assisted extraction may improve the process only marginally.

6.4 Recommendations

This study demonstrated the recovery of PGMs from a secondary source using DESs, validating the potential of compressed CO_2-assisted extraction. For future work, several areas merit investigation:

- **DES–PGM interactions**: A deeper understanding of the poor absorption into the DES phase is needed. Exploring molecular dynamics simulations or conducting NMR studies could help elucidate the solvation behaviour and coordination mechanisms of PGMs in various DES systems.
- **Process optimization**: Suriyanarayanan *et al.*, (2023) demonstrated that temperature could enhance the recovery of cobalt. Further work should assess the influence of elevated temperature.
- **DES formulation tuning**: One of the differences in this work and Lanaridi *et al.*, (2022) was the molar ratio of the HBA and HBD. Modifying the molar ratio between the HBD and HBA may enhance the physicochemical properties and extraction performance. Additionally, the

inclusion of co-solvents or additives like water should be evaluated for their ability to reduce viscosity and improve phase separation.

- **Selectivity and metal profiling**: Examining the selectivity of the DESs for different PGMs and other transition metals would support the development of targeted recovery strategies. ICP-MS or XPS analysis could be used to quantify extraction specificity.
- **Scalability and economic feasibility**: Future research should explore the scalability of the compressed CO_2 process. A cost-benefit analysis, factoring in energy consumption, CO_2 recycling, and DES reuse, would provide insights into industrial applicability.
- **Environmental and lifecycle assessment**: Evaluating the environmental impact of the process through LCA (Life Cycle Assessment) could inform greener solvent design and recovery pathways.

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Chapter 7: Appendices

7.1 Appendix 1

Molar weight of Choline Chloride and oxalic acid calculation:

$$molar\ mass\ (choline\ chloride\ ): 139.6\ {}^{g}/_{mol}$$

$$molar\ mass\ (oxalic\ acid): 90\ {}^{g}/_{mol}$$

Ratio of choline chloride: oxalic acid is 1: 1

Thereafter,

$$Percentage\ of\ choline\ chloride = \frac{139.6}{90 + 139.6} = 60.8\%$$

$$Percentage\ of\ oxalic\ acid = \frac{90}{90 + 139.6} = 39.2\%$$

Calculate final amount based on feed:

Amount of DES desired:	500 ml
Density of DES:	1.24 g/ml
Amount of DES needed:	$500\ ml\ \times 1.24 \frac{g}{ml} = 620\ g$
Thus, Sucrose:	$0.608\ \times 620 = \mathbf{377\ g}$
Citric acid:	$0.392\ \times 620 = \mathbf{243\ g}$