

Application of the TRIZ Contradictory Matrix to Foster Innovation for Sustainable Chemical Engineering

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This work demonstrates how to apply the Theory of Inventive Problem Solving (Russian acronym TRIZ) on two industrial-scale case studies. The first case study addresses processing of mineral metal carbonates, which is characterized by high CO₂ emissions and high energy demand. As solver strategy a novel reductive pathway is suggested. The second case study refers to biobased industrial processes, which discharge aqueous effluents with unexploited carboxylic acid loads. Reactive separations are proposed to isolate the carboxylic acids. In both solver strategies, chemical reactions adopt a central role.

Keywords: Contradictory matrix, Innovation, Ore processing, Reactive separation, TRIZ

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1 Introduction

If we do not take countermeasures, our steadily growing economy, accompanied by pronounced material and energy consumption, will entail environmental devastation. Climate change due to greenhouse gas emissions has become a topic of global concern. Scarcity of fossil resources is an unsolved issue. The chemical industry, source of our material welfare and the majority of products of everyday life, has a leading role to play in tackling these challenges. The improvement and intensification of existing processes towards a more efficient and sustainable production is at present a high priority topic. However, to transform and shape the future of today's chemical industry and to enable sustainable development process innovations are required. The term process innovation refers to changes in a process without changing the final product. The primary goal is to improve the overall productivity, e.g., by saving time and/or costs, and make manufacturing more efficient. Process innovation may also be dedicated to enhance reliability and safety of a process, or to reduce material and energy consumption [1]. In this regard, it addresses environmental constraints and legal aspects that pose current challenges to chemical engineering.

Psychological inertia is said to be the main barrier to innovation. The psychological meaning of the word "inertia" already implies an indisposition to change. It means the inevitability of human beings of behaving in a certain way, the way things have always been done. [2, 3]

The general way of handling tasks is closely linked to experiences from the past. Humans use remembered information to solve problems; they take past issues as a starting basis and remember their solutions to tackle new problems.

Using earlier experiences and adapting them to solve a new, similar problem is the strategy we rely on most in everyday life. [2]

When it comes to inventive problem solving, many people have the impression that this is a psychologically driven activity. They think that innovations arise from chance and if not by chance, from a higher intellect. In western culture, it is assumed that creativity is given by birth and there is no other way to obtain such an exceptional talent. [4]

The contrary opinion is that creativity is a skill that can be learnt and trained, and anybody can improve their ability to generate innovative solutions [5]. According to Bertonecelli [4], being creative is linked to memory structure and the ability to learn. Several methods exist that intend to stimulate innovative ideas and enhance creativity. The most popular ones are trial and error and brainstorming. These methods try to access and reach the whole (existing) knowledge. They are easy to understand and implement, but often do not increase knowledge. [2]

Another popular methodology that is based on storing and retrieving past experiences is the method of case-based reasoning (CBR). This methodology relies on a cycle of four individual steps – retrieve, reuse, revise and retain – and is often referred to as the R⁴ model. [6]

CBR has already proven its efficiency in chemical engineering for a wide range of applications. Its success is

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related to its affinity with human learning. However, some scientists claim that it only gives access to minor or incremental innovations. CBR works on knowledge within one single domain, for instance chemical engineering, and in most cases, it uses only information from one specific part of this technical domain (e.g., one unit operation). Knowledge from related domains is not accessible, which may limit the level of innovation. [2, 3]

Advocates of innovation tools claim that the field of knowledge needs to be enlarged when the intention is to find non-routine solutions. This is often not possible by the use of past experiences only. [2, 3]

Other technical domains than the one in which the problem occurs give access to new pieces of knowledge that may be applicable to the problem domain and allow to come up with a rupture innovation, meaning a solution with a high level of innovation. A methodology that uses information from all domains is TRIZ (Russian acronym for Theory of Inventive Problem Solving) [7]. It is based on the general idea that universal ways exist to solve problems and claims that every engineer can create innovative solutions. It rather proposes directions for research to find innovative solutions, in such a way that the search for solutions is not carried out randomly, while giving space to creativity. [2]

In this work, TRIZ is chosen because it is regarded as the most structured and comprehensive method to enhance creativity in the chemical industry [7]. The methodology is based on the TRIZ contradictory matrix, which is applied on the example of two industrial-scale case studies with significant environmental impacts; one in mineral metal carbonate processing, the other in valorization of carboxylic acid-laden effluents from biorefinery. Solver strategies are developed and their application potential is demonstrated.

2 Method

The Russian scientist and engineer Genrich Altshuller [8] and his colleagues developed their first ideas about TRIZ in the 1940s. They studied several hundred thousand of technology patents and identified certain patterns and regularities that characterize innovative problem-solving concepts and creative new ideas. TRIZ was originally developed for mechanical systems. It has long been suspected that TRIZ cannot be applied in modern chemical industry. [9]

Nowadays it is a globally accepted heuristic approach that aids development of innovative solutions to complex problems in different disciplines. [2, 3, 9] TRIZ follows three core ideas [2, 9]:

- 1) Technical evolution follows patterns. They repeat across industries.
- 2) Problems and solutions repeat across industries.
- 3) It is possible to teach and to learn innovation.

In his analysis of patents from various engineering fields, Altshuller found that different technical processes show similar features in their evolution. In different domains, the

same generic problem is solved with the same generic principle. Hence, many inventions are transferable from one domain to another. The TRIZ problem-solving process follows a general scheme (Fig. 1). [2, 3, 10] First, the initial, specific problem is transferred into a generic problem. Several TRIZ tools aim at this step. Then a search for a generic solution for the generic problem is carried out – this is accomplished with TRIZ resolution tools. The result is not a finished ready-to-use solution, but rather a proposal of research directions. Finally, the theoretical generic solution is transformed into a real solution that addresses the real problem. The TRIZ problem-solving process is intended to overcome psychological inertia. [2, 3]

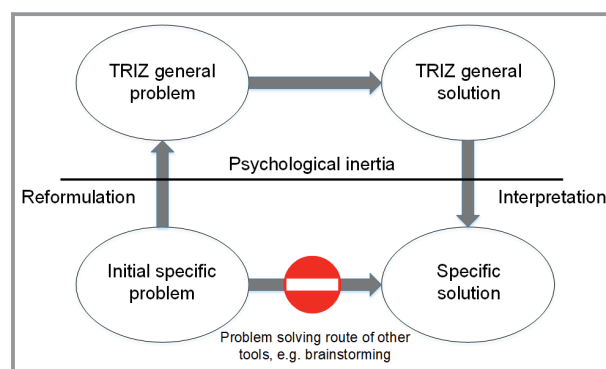


Figure 1. TRIZ problem-solving process [2, 3, 10].

All TRIZ concepts can be classified as belonging to one of the following three categories [2]:

- 1) tools for modeling a problem,
- 2) tools for breaking psychological inertia during problem formulation and problem interpretation and
- 3) tools for solving generic problems.

Abramov et al. [9] illustrated an innovation roadmap of TRIZ, which consists of a series of steps. These are portfolio analysis, selection of innovation targets, problem identification, problem solving, concept substantiation, and verification and implementation. In general, it follows a traditional roadmap for innovation, apart from two differences. Firstly, it places particular emphasis on system analysis to ensure that questions are asked accordingly in order to tackle the right problem. Secondly, there is a range of practical TRIZ tools for ideation and problem solving (e.g., function-oriented search, contraction matrix, ARIZ – Algorithm of Inventive Problem Solving). These tools go well beyond brainstorming. [9]

Three concepts are central to TRIZ. These are the concept of patterns of evolution of systems, the concept of ideality and the concept of contradiction. Each TRIZ problem-solving process applies at least one of these three concepts. [2, 10]

- 1) *Patterns of evolution of systems:* Systems generally follow certain regularities in evolution during their life cycle. Altshuller translated these regularities into laws, which

he called patterns. There are eight generic laws that aid the development of solutions to problems. With their help, the future evolution of a system is anticipated.

- 2) *Ideality*: One of the objectives in TRIZ and life in general is to increase ideality. To achieve ideality is often a utopian goal, but to define the ideal final result (IFR) is helpful as it indicates the direction for the search of a new and better system.
- 3) *Contradiction*: Contradiction stands for a conflict in a system due to incompatible desired features or requirements. Even though the requirements exclude each other, they must be reconciled to achieve the overall objective. Inventive problems contain at least one contradiction, which needs to be overcome at least partially through inventive problem solving. Technical contradictions and physical contradictions represent the two main types of contradictions. A technical contradiction in a system arises when the improvement of the performance of one useful function of a system involves the deterioration of another function's performance. A physical contradiction is the existence of two contradictory, mutually exclusive states of a system (e.g., hot and cold).

From his patent analysis, Altshuller concluded that for the whole technical field only a limited number of research directions (the way problems are solved) give rise to technical innovations. These so-called principles are summed up in the "40 Inventive Principles". The 40 principles are further subdivided into sub-principles. They form the basis of approx. 80 % of all patents. [11]

Principles do not give a straightforward solution to a problem, but they indicate ways to find a solution and thus, limit the solution domain for research. Hipple [12] and Cortes Robles et al. [13] proposed examples of the "40 Inventive Principles" for chemical engineering in order to facilitate implementation of TRIZ in the chemical and process industry. Grierson et al. [14] added chemical illustrations to the 40 principles to show how they may be applied directly to chemical problems. In the evolution of TRIZ, Altshuller and his colleagues developed a series of techniques and tools. Ilevbare et al. [10] highlighted the most prominent ones in his review.

The TRIZ methodology has already been successfully applied to various chemical engineering tasks, e.g., [7, 9, 15–17]. Rahim et al. [15] presented an automotive case study regarding a liquid bumper technology. The main purpose was to solve problems and make forecasts in product development. Abramov et al. [9] performed a statistical analysis of TRIZ projects and found that 60 % were related to chemistry, which they concluded might be an indication for an elevated demand for innovation in this field. They stated that TRIZ is perfectly suited to analyze and solve problems in chemical engineering as well as in adjacent areas such as biochemistry, microbiology, the pharmaceutical and food industry. Kim et al. [16] suggested a modification of TRIZ for its application in chemical process safety.

They reorganized 39 TRIZ parameters into the six categories mechanic, operator, process upset, design, natural hazard and material. This modified version of TRIZ was tested for a jacketed reactor and a polyethylene reactor. Among the TRIZ tools, the contradictory matrix is probably the most utilized one. It is mainly dedicated to solve technical contradictions. Pokhrel et al. [7], for instance, extended the TRIZ contradiction matrix and proposed new characteristics and inventive principles with the aim of expanding its applicability to typical problems encountered in chemical process industries.

Altshuller suggested using technical contradictions to specify a problem: one feature of a system improves while another feature deteriorates. He identified 39 parameters that describe all contradictions and developed the so-called contradiction matrix. This is a matrix of the 39 technical parameters with the improved parameters in the rows and the deteriorated parameters in the column. For a specific contradiction, the principles located at the intersection of the row and the column are to be explored. [2, 3, 8, 11]

The technical contradiction matrix (39 parameters, 40 principles), updated in 2003, can be found on the webpage of the TRIZ Journal [18]. The principles are numbered to indicate the routes that have been most popular for solving that type of problem. They are listed in descending order of priority. It is advisable to start with the suggested principles of the contradiction matrix. However, in some cases, it can be a good idea to examine all 40 principles. With two minutes per principle that would require 80 min. [19]

Application of the contradiction matrix to a specific problem proceeds via five steps [2]:

- 1) formulation of the problem as a conflict between two parameters,
- 2) identification of the two parameters among the 39 parameters,
- 3) application of the matrix,
- 4) identification of the principle(s) to use: the principles in the intersection cell give a statistic recommendation of the order of the principles to use for contradiction resolution,
- 5) expression of creativity: transformation of the principle(s) into operational solution(s).

In a patent study from 2002, Mann [20] argued that only about 50 % comply with the original version of the contradictory matrix. Mann and Dewulf [21] then proposed an extended version of the contradictory matrix with an increased number of parameters of 48. The number of principles was kept at 40. Several works argue about the low popularity of TRIZ and its limited application in industrial settings. The main challenges of using TRIZ are cited as being the complex and diverse methods, the difficult application and acquisition, and the lack of standard. [22, 23] But even in cases when application of TRIZ does not fully comply with its original techniques and tools and it is used in a simplified manner, it provides a powerful base from which to trigger creative thinking and inventive problem solving.

3 Results and Discussion

In this work, the concept of the TRIZ contradictory matrix was applied to two industrially relevant processes. The first considers mineral metal carbonate processing for metal and metal oxide production (case study I). The second deals with the recovery and exploitation of carboxylic acids from dilute, aqueous effluents from, for instance, biorefinery (case study II).

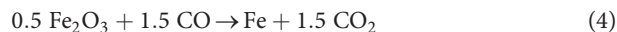
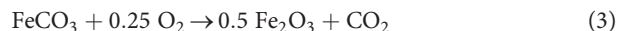
3.1 Case Study I: Mineral Metal Carbonate Processing

3.1.1 Starting Point

The state-of-the-art procedure for processing of mineral metal carbonates (MeCO_3) is largely based on thermal treatment (calcination) under oxidizing conditions to release the carbon dioxide from the carbonaceous ore (Eq. (1) for main-group elements). The reaction pathway for the thermal decomposition of transition metal carbonates is more complex, as redox reactions may occur (Eq. (2)). This type of process inevitably emits high amounts of CO_2 into the atmosphere and consumes a lot of energy.



Processing of mineral metal carbonates is used on a large scale for producing iron from siderite ores (which contain ferrous carbonate, FeCO_3), for producing magnesia (MgO), which is used as a refractory material, from magnesite (which contains magnesium carbonate, MgCO_3), and for producing lime (CaO), a main ingredient of cement, and an alkalinizing agent, from limestone (which contains calcium carbonate, CaCO_3). The method presented in this work is exemplarily shown for the calcination of siderite ore. In Austria, domestic siderite ore is used in addition to imported iron oxide ore for iron and steel production. The state-of-the-art smelting process of siderite ore is based on concentrate preparation by calcination on the sintering plant to release CO_2 and convert the ore into hematite (Fe_2O_3 , Eq. (3)), which is reduced to pig iron in the blast furnace (reducing reactor). The purpose of calcination is to minimize the CO_2 content in the reduction stage and thus, to minimize grain decomposition in the blast furnace. In the blast furnace, hematite is reduced with carbon monoxide (CO) to elemental iron according to Eq. (4). The reaction proceeds via the intermediates magnetite (Fe_3O_4) and wüstite (FeO) releasing 1.5 mol CO_2 per mol Fe due to the stoichiometry of the reaction. A typical blast furnace process is specified by a sophisticated temperature profile with temperatures of about 1500 °C above the pig iron melt at the bottom. [24]



As a sum of the calcination and blast furnace steps, at least 2.5 mol CO_2 are directly emitted for the manufacture of 1 mol elemental iron from iron carbonate using the current state-of-the-art processes. In Austria, more than 2 Mt of siderite ore with an approximate iron carbonate content of 70 wt % is processed per year [25]. Thus, calcination liberates 0.6 Mt CO_2 per year as direct process emissions. Total Austrian production was 5.3 Mt of pig iron and 6.8 Mt of crude steel in 2020 [26]. In order to mitigate CO_2 emissions from mineral metal carbonate processing in general and iron production in specific, an alternative, environmental benign reaction path needs to be developed.

3.1.2 Solver Strategy

Application of the TRIZ contradictory matrix to this specific task looks as follows: In conventional mineral metal carbonate processing, the intention is to increase the amount of substance (product), meaning the metal either in its elemental (e.g., Fe) or oxidic (e.g., MgO) form. Thus, “the amount of substance (10)” is defined as the improving parameter (stated in the row) in the contradictory matrix (Fig. 2). To achieve this goal, harsh process conditions are generally required, entailing high-energy demand. At the same time, higher product yields imply higher CO_2 emissions as CO_2 is inevitably released as by-product. Consequently, the worsening feature (stated in the column) is identified as “other harmful effects generated by (31)”.

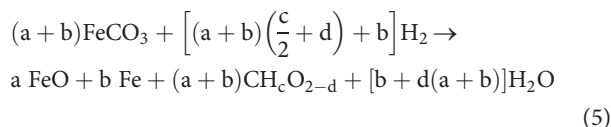
		Worsening feature	
		Amount of substance	Other harmful effects generated by
Improving feature	10	35	40
	Amount of substance	3	12

Figure 2. Contradictory matrix for mineral metal carbonate processing, e.g., mineral iron carbonate processing. The 40 inventive Principles for Chemical Engineering are applied.

The following four principles arise from the intersection of column 10 (amount of substance) and line 31 (other harmful effects generated by) from the contradictory matrix:

- 35 Parameter changes
- 40 Composite materials
- 3 Local quality
- 12 Equipotentiality

Two of those principles are suitable for the problem on hand. First, the highest ranked principle, principle 35, is “parameter changes”. Exemplarily, the TRIZ Journal mentions changing temperature, e.g., when knowledge of the reaction kinetics or decomposition rate helps to control the reactor [12]. In the context of mineral processing such as processing of siderite ore, which is conventionally carried out by roasting of the ore in air in the sinter plant, this could imply an action that allows for reduction of the process temperature. Additionally, the reactor output including desired products and inevitable by-products and the energy demand are controlled through precise adjustment of the process conditions on which the reaction kinetics of CO₂ release depend. In terms of the contradiction, the desired products represent the improving parameter and the by-products and the energy demand embody the deteriorating parameters. In oxidizing atmosphere, optimized process conditions imply high reaction temperatures that cannot be significantly reduced. The reaction kinetics are governed by this specification. Thus, the stated conflict cannot be solved under oxidizing process conditions. However, another type of parameter change could be to change the gas atmosphere and switch from an oxidizing atmosphere to a reducing hydrogen atmosphere (= reductive calcination). Hydrogenation of mineral metal carbonates leads to a highly innovative solution, which gives access to a portfolio of different products (Eq. (5) for iron carbonate, Eq. (6) simplified form when the formation of reduced carbon species is not considered) and significant improvements regarding sustainability. [27]



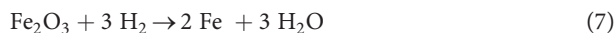
Second, principle 3 refers to “local quality”. One suggestion is to render each part of an object work in its most suitable conditions for operation [12]. In the figurative sense, this principle could be interpreted as using local mineral reserves as raw material base (e.g., siderite ore from the Austrian Erzberg for iron and steel production), regardless of its quality, and exploiting it completely. Again, hydrogenation of mineral metal carbonates provides a promising solver strategy. It opens up a route for more efficient raw material use and allows exploitation of low-grade ores that are currently only deposited.

3.1.3 Reductive Calcination for Alternative Mineral Metal Carbonate Processing

The reduction of iron ores with hydrogen is being propagated as a future key technology that has the potential to decarbonize steelmaking. [28–30] Hydrogen direct reduction is proposed to manufacture so-called directly reduced iron, which is generally converted to steel in an electric arc furnace. [31, 32] However, these approaches focus solely on the reduction of iron oxide-based hematite. Countries with major mineral iron carbonate reserves, such as China [33] and Austria [34], preferably use their domestic siderite ore for iron and steel production. Although this reduces the demand for imported ore and mitigates the risk of iron ore shortage, it brings with it the additional effort of processing siderite.

Very few scientific publications on the chemistry of metal carbonate hydrogenation are available. Initial studies in the 1960s were done in a geological context – aimed at understanding the formation of hydrocarbons from inorganic sources in the earth’s crust [35]. Another focus of interest has been the possibility of synthesizing organic compounds from carbonaceous inorganic rocks, based on the idea that carbonaceous minerals could be a renewable and almost inexhaustible resource [36]. Transformation of transition-metal carbonates in a hydrogen atmosphere has been explored as a new pathway for the synthesis of finely dispersed active catalysts [37]. And finally, reductive mineral calcination has been studied as a novel approach for CCU (carbon capture and utilization) [38]. However, mineral carbonate processing by reductive calcination for industrial application – specifically, direct reduction of iron carbonate for iron production, has not been considered.

In hydrogen atmosphere, iron carbonate is directly reduced to elemental iron. This tackles the problem holistically and opens up a completely new pathway for siderite ore processing. It circumvents the conventional two-step calcination/blast furnace route as elemental iron is directly formed from iron carbonate through hydrogenation. Due to the stoichiometry of reaction direct CO₂ emissions reduce by at least 60 % compared to siderite calcination and subsequent reduction. Hydrogenation of iron carbonate consumes 1 mol H₂ per mol of elemental iron (Eq. (6) without consideration of CO₂ reduction). In comparison, 1.5 mol H₂ are required per mol of elemental iron for the reduction of hematite with hydrogen (Eq. (7)). This reduces the demand of hydrogen as reduction agent by 33 %. [39]



In hydrogen atmosphere, the product gas contains carbon monoxide (CO) and methane (CH₄) in addition to CO₂, resulting in further CO₂ emission savings. This adds value to the overall process. [40] Experimental studies with siderite ore from the Austrian Erzberg confirmed that the siderite ore phase as well as the iron-rich ankerite and the low-iron ankerite ore phase are converted. A final product with

a degree of metallization of >80 % at complete FeCO_3 conversion was obtained. Thus, the use of ore with an iron content below the current cut-off grade is feasible. In addition to that, it can be assumed that the product of direct reduction can be directly used in the steel converter.

This type of hydrogenation process is also applicable to other metal carbonates. Applicability to magnesite [41] and magnesite/dolomite [42] has already been demonstrated.

3.2 Case Study II: Carboxylic Acid Recovery from Aqueous Effluents

3.2.1 Starting Point

Carboxylic acids are an important class of bulk chemicals with a wide range of different applications, either in the form of the free acid, or as their corresponding salts and esters. Their industrial production is still mainly based on chemical synthesis from petroleum-based feedstock and on fermentation of carbohydrates. Novel approaches for production from biobased residues include fermentation of wastewater [43] and solid municipal waste [44], decomposition of lignin [45], and hydrothermal treatment of non-lignin residues [46]. Carboxylic acids also occur as by-products and degradation products in various biobased process streams originating from, e.g., lignocellulose processing such as pulping [47] and pyrolysis [48, 49]. These acidic by-products often exist with numerous other components in low concentrations in an aqueous medium and, thus, disposal of the acidic aqueous effluents poses a severe environmental hazard due to lowering the pH of waterways and groundwater. Exploitation of the carboxylic acids from these effluents would make a valuable contribution to the complete use of biomass. However, there is a major obstacle to overcome before exploitation as their isolation from dilute, aqueous process streams requires energy-intensive downstream processing, causing high costs. Furthermore, separation is often complicated by azeotrope formation. Consequently, in most cases acidic side streams are treated more as a nuisance than as abundant source for bulk chemicals.

3.2.2 Solver Strategy

The specific problem how to isolate carboxylic acids from aqueous effluents is formulated as a conflict between increasing “productivity” (44, improving feature) and deteriorating “manufacturability” (41, worsening feature), meaning higher costs and higher effort (Fig. 3).

From the contradictory matrix for the separation of carboxylic acids from aqueous effluents in general, and azeotrope separation in particular, the proposed principles include:

- 1 Segmentation
- 10 Preliminary action**
- 24 Intermediary**
- 35 Parameter changes**

			Manufacturability	
			41	
44	Productivity		1 10 24 35	

Figure 3. Contradictory matrix for the recovery of carboxylic acids from biobased effluents. The 40 Inventive Principles for Chemical Engineering are used.

Three principles seem to be predestined for the conflict between improved productivity, meaning efficient isolation of valuable constituents from effluents, and poor manufacturability. These are “preliminary action”, “intermediary”, and “parameter changes”. All three take the same line. Principle 10 – preliminary action suggests to take an action beforehand to ease an event, in the respective conflict: to ease constituent isolation [14]. This may be achieved by the changing of an object before it is needed. The change may either be complete or partial. [12]

To use an intermediary object to transfer or carry out an action is addressed by principle 24 – intermediary [14]. The TRIZ Journal lists the use of an intermediary carrier article or intermediary process and merging one object that can be easily removed temporarily with another as examples for principle 24. [12]

Principle 35 – parameter changes proposes, e.g., to change the physical state of an object (e.g., to a gas, liquid or solid). This could mean to extract a constituent of a liquid mixture in the gaseous state. Another example of principle 35 is to change the concentration. [12]

Introducing a chemical reaction to the separation task – reactive separation – meets all three proposed principles and efficiently tackles the conflict of azeotrope separation. Through chemical conversion, the substance properties are modified such that product isolation becomes easier. According to TRIZ, the chemical conversion can be seen as a preliminary action that forms an intermediary and changes the parameters of the constituents that need to be isolated.

3.2.3 Reactive Separation for Exploitation of Carboxylic Acids

Reactive separation of carboxylic acids in the form of their corresponding esters opens up pathways for complete material utilization of the acids from aqueous streams, even when acid concentrations are low (below 10 wt %) [50]. The

basic idea is to esterify the carboxylic acids with aliphatic alcohols, thus changing their substance properties and facilitating removal. There are different options for esterification-enhanced reactive separation for solution, e.g., reactive distillation, reactive extraction and combinations of these. [50]

In reactive distillation with a low boiling alcohol, the carboxylic acids are transferred into their corresponding low-boiling esters. Esterification (Eq. (8)) can be seen as a preliminary action in which an intermediate, the low-boiling ester, is formed. The ester is separated in its vaporous form – via parameter change – with the distillate phase. In reactive extraction with conversion, esterification (= preliminary action) of the carboxylic acid with longer-chain alcohols enhances extraction from the aqueous effluent due to the higher affinity (= change of parameters) of the corresponding esters (= intermediary) to the organic phase. The same principles can be applied for regeneration of the ester-laden solvent and ester isolation. Transesterification with a second, low boiling alcohol via reactive distillation completes this process concept (Eq. (9)).



Depending on the technology to be intensified, different options are conceivable for alcohol admixture. The alcohol can be admixed (i) with the aqueous effluent and/or (regenerated) solvent for reactive extraction supported by esterification, (ii) directly with the laden solvent phase after reactive extraction with, for instance organophosphorus compounds, or (iii) with the aqueous distillate of the solvent regeneration unit. [50]

Reactive Distillation: Esterification of carboxylic acids with short-chain alcohols (e.g., methanol) leads to esters with lower boiling points than the acids. In reactive distillation, the amount of energy required can be reduced because of the low boiling temperatures and the low heat of evaporation of the methyl esters. The water, which is the main component in aqueous process streams, does not have to be evaporated as in the case of carboxylic acid/water separation by conventional distillation. Also, continuous product removal shifts the reaction equilibrium to the side of the products and allows for complete carboxylic acid conversion. This makes the processing of acidic aqueous effluents possible, e.g., the distillate phase from solvent regeneration after reactive extraction. [51, 52] Besides processing of aqueous effluents, reactive distillation with methanol can be successfully applied for combined solvent regeneration and carboxylic acid isolation after reactive extraction. For this purpose, reactive distillation is performed directly in the laden solvent phase (organophosphorus solvent Cyanex[®] 923) after the reactive extraction step. Solvent regeneration via reactive distillation reduces the demand of energy and apparatuses. With the catalyst 4-dodecyl-

benzenesulfonic acid (4-DBSA), catalyst recovery from the solvent phase is not mandatory due to the extractive interaction between the solvent Cyanex[®] 923 and the catalyst at the temperature of the extraction process. During the extraction step the catalyst forms an adduct with the solvent and remains in the solvent phase. Then, during reactive distillation at elevated temperature, the adduct is cleaved. [53]

Reactive Extraction Intensified by Emulsification: In reactive extraction with esterification enhanced by emulsification, three elements of the solvent composition are crucial: the solvent itself, the alcohol as reactant for esterification and the surfactant catalyst. The solvent must feature high solubility for the alcohol and the catalyst while being hardly miscible with water. *n*-Undecane fulfills these requirements. As reactant for esterification, preferably higher aliphatic alcohols like 1-octanol are used. The main benefit of higher aliphatic alcohols is that the corresponding esters are hardly soluble in water. Low solubility of the products in water improves the extraction efficiency and prevents secondary pollution of the aqueous feed. The catalytically active surfactant 4-DBSA works in two ways; its Bronsted acid properties enhance the rate of reaction whereas the surfactant behavior increases the mass transfer through emulsification. It consequently allows for the formation of a quasi-homogeneous state. This measure drastically decreases the mass transfer limitation of the esterification reaction in the aqueous environment [54]. With the concept of emulsion-enhanced reactive extraction, measures for emulsion splitting prior to solvent regeneration are unavoidable. This adds an additional separation step to the overall process. Emulsion control is possible with a metallosurfactant catalyst, Ni(DBSA)₂. The ion-exchange properties of 4-DBSA allow it to be combined with the transition metal nickel. The Ni(DBSA)₂ catalyst is characterized by the surfactant properties of 4-DBSA and the catalytic effect of transition metals. With Ni(DBSA)₂, formation of stable emulsions is suppressed (biphasic reactive extraction). [55]

Transesterification of the octyl ester with the low-boiling alcohol methanol directly in the solvent phase provides a suitable concept for solvent regeneration and completes the overall reactive separation process. Transesterification has the decisive advantage that the higher aliphatic alcohol is regenerated. As the same catalyst is used for esterification and for transesterification, the catalytic, reactive solvent can be recycled. Therefore, the overall process concept with reactive extraction with esterification and reactive distillation with transesterification represents a closed-loop approach. [56]

5 Conclusions

Going back 350 years: a falling apple is said to have inspired the mathematician, physicist and astronomer Isaac Newton (1642–1726) to his monumental law of gravity. This is one of the most famous anecdotes in the history of science.

However, may it be coincidence, higher intellect or through structured innovation methods, it should not matter how an innovative solution comes about. The important thing is that it comes about. A series of innovation tools exist that may act as auxiliary means to enhance creativity and foster innovation. In this work, the methodology of the TRIZ contradictory matrix was applied on the example of two research challenges. A novel reductive calcination technology was developed for sustainable mineral metal carbonate processing. To isolate carboxylic acids from multicomponent aqueous effluents, reactive separation concepts were applied. These examples illustrate the development of solver strategies with the help of TRIZ based on chemical conversions to meet the needs of more sustainable production routes.

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Abbreviations

CBR	case-based reasoning
4-DBSA	4-dodecylbenzenesulfonic acid
MeCO ₃	metal carbonate
TRIZ	Theory of Inventive Problem Solving

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