Methods of Extracting TiO$_2$ and Other Related Compounds from Ilmenite

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Abstract: Although ilmenite and rutile are extensively used to extract TiO$_2$ at the industrial level, through the sulphate and chloride processes, they can also be recognized to possess the potential to be employed as the raw material to synthesize other titanium compounds as well. The Pulmoddai mineral sand deposit in Sri Lanka is considered as a valuable resource containing pure ilmenite and can be used as a very good source of both titanium and iron. Because of the lower TiO$_2$ content compared to rutile, processes, such as the Becher process, Laporte process and Kataoka process, have been developed to upgrade ilmenite into higher grade synthetic rutile. Additionally, research studies have been carried out to develop methods, such as the hydrochloride process, H$_3$PO$_4$/NH$_3$ process, alkaline roasting process, aluminothermic reduction method, alkaline decomposition method, molten salt electroreduction method and magnesiothermic reduction method, to synthesize TiO$_2$ and other related titanium compounds, such as titanium and iron oxides, composites and alloys, from naturally occurring ilmenite where these methods possess both rewards as well as drawbacks over the others.

Keywords: synthetic rutile; lower-grade ilmenite; batch process; continuous process; calcination; alloys; composites

1. Introduction

Among a diverse range of dense mineral reserves found across the world, only ilmenite and rutile ores are capable of yielding titanium compounds, specifically titanium dioxide, through industrial processes. Since titanium containing compounds possess the capability to be applied in numerous applications, such as environmental remediation, energy technologies, the pharmaceutical industry, paint industry and textile industry, exploration of the ability of these ore materials to yield titanium species is highly significant in the field of research as well as the industrial sector [1–13]. Ilmenite and rutile exhibit a major contrast in their chemical compositions, where ilmenite comprises a significant fraction of both titanium dioxide and ferrous oxide, represented as FeTiO$_3$ or FeO.TiO$_2$, and rutile primarily consists of TiO$_2$ [1,2]. Being more abundant and less expensive, ilmenite has gained higher merits as a superior raw material compared to rutile for the aforementioned purpose [3,14].

The global deposits of commercial ilmenite can be widely categorized into three groups: large-scale hard-rock deposits, deposits linked with alluvial tin and those associated with beach sand. Sri Lanka does not possess massive hard-rock deposits, which typically contain ilmenite, magnetite and hematite. However, such deposits exist in other locations worldwide, including the Allard Lake deposit in Canada, Sanford Lake deposits in the United States of America and the Tellanes deposit in Norway [15,16]. Similarly, Nigeria and Malaysia are two countries where ilmenite deposits associated with tin have mostly been discovered [17]. Particularly, ilmenite beach sand deposits (black sand) are found in numerous countries, such as Sri Lanka, India, South Africa, Australia and Brazil [18].

In brief, the main purpose of this article is to provide a comprehensive review on already well-established processes and novel approaches to extract mainly TiO_2 as well as other related compounds from ilmenite. The availability of ilmenite deposits in Sri Lanka is initially discussed. Furthermore, conventional industrial processes of extracting TiO_2 are thoroughly discussed with a particular attention on their advantages and disadvantages. Importantly, lower-grade ilmenite ores having low contents of TiO_2 cannot be directly utilized as the starting material of some of the TiO_2 extraction methods, eventually diminishing the maximum utilization of the ore. Therefore, in order to facilitate the beneficiation of such lower-grade ilmenite ores, methods of converting them into higher-grade synthetic rutile are emphasized [19,20]. Eventually, several promising approaches of processing ilmenite to synthesize a wide spectrum of titanium and iron species are broadly elaborated.

Pulmoddai Mineral Sand Deposit in Sri Lanka

Pulmoddai ilmenite ore, which contains a higher purity of ilmenite, has been extensively mined for many years among the commercially valuable coastal mineral sand deposits in Sri Lanka. The ore is situated on the north-east coast of Sri Lanka, specifically north of Trincomalee, where the deposit extends approximately 7.4 km in length, has a width of 250 m and a depth of around 2 m [1,21]. The huge quantity of ilmenite present in the Pulmoddai deposit makes it highly exploitable, thereby exerting a significant impact on the economy of the country. Ilmenite can be obtained from the black sand through various techniques utilized during the ore processing, including magnetic separation, floating separation and electrostatic separation [18,22], where the ore material is majorly composed of 75% ilmenite, 10% rutile, 8% zircon and trace amounts of other minerals [21,23]. The composition of Pulmoddai ilmenite and rutile is revealed in Tables 1 and 2, respectively.

Table 1. Composition of Pulmoddai ilmenite [1,24].

Compound	Percentage (%)
TiO_2	53.21
FeO	20.50
Fe_2O_3	22.07
Al_2O_3	0.32
MnO	0.90
MgO	0.72
CaO	0.10
Cr_2O_3	0.10
V_2O_5	0.20
SiO_2	0.89

Table 2. Composition of Pulmoddai rutile [1,24].

Compound	Percentage (%)
TiO_2	97.20
Fe_2O_3	1.29
MnO	Not analysed
MgO	Not analysed
CaO	Not analysed
Al_2O_3	0.11
Cr_2O_3	0.14
V_2O_5	0.03
Nb_2O_3	Not analysed
ZrO_2	0.52
SiO_2	0.65
P_2O_5	Trace

Although the Pulmoddai mineral sand deposit is well-known as an industrially viable natural reserve of ilmenite (75% of the ore), which is a very good resource for titanium

and iron compounds containing 53.21% TiO_2 and 42.57% iron oxides [1,24], Sri Lanka is not entirely benefited from the ore due to the lack of a proper ilmenite processing plant to extract TiO_2 and other related compounds in the country itself.

In general, ilmenite is globally recognized as a vital resource of both titanium and iron. Therefore, it is important to study and discuss both well-established and novel techniques, which are used to process ilmenite to produce titanium compounds, iron compounds as well as titanium-iron composites, so that their plusses and minuses can also be identified.

2. Synthesis of TiO_2 at the Industrial Level

Among the global TiO_2 manufacturing countries, the United States, the United Kingdom, China, Japan, Canada and Slovenia possess the leading TiO_2 companies in the world. Based on its crystalline structure, TiO_2 can be categorized into three forms, i.e., anatase, rutile and brookite [25,26]. Amidst the different crystalline forms of the compound, rutile and anatase can be readily prepared and the brookite form is harder to form under laboratory conditions. The anatase phase of the compound is preferably resulted through solution-phase preparation methods [25].

Numerous TiO_2-based commercial products are available worldwide, where TiO_2 Degussa P25, which consists of 25% rutile and 75% anatase, is well-known due to the superior photocatalytic activity of the composite [27]. However, anatase TiO_2 is found to possess the highest photocatalytic performance compared to the other two pure forms, i.e., rutile and brookite. Moreover, TiO_2 Hombikat and TiO_2 Wackherr are pure anatase forms having different TiO_2 particle sizes, thereby exhibiting photocatalytic activity to different extents [25,27].

Over the past few decades, as a whole, TiO_2 has been renowned in a vast range of photocatalytic applications including water purification [4], air purification [5], plastic degradation [6] and soil sterilization [7]. Furthermore, TiO_2 can also be considered as a promising approach in energy applications such as solar cell applications [8], photocatalytic solar-to-hydrogen energy conversion [28] and biodiesel production [29], where this compound has obtained superiority as it is environmentally friendly, stable under a variety of conditions and inexpensive. Significantly, titanium dioxide plays a crucial role as a primary component in numerous industries such as paint [9], textile [10], rubber [11], cosmetics [12] and pharmaceuticals [13].

Although it is beyond the scope of this review, previous studies have reported that, apart from utilizing ilmenite as the raw material to extract Ti and Fe compounds, the ilmenite itself can also be used in advanced applications. One such study proved the catalytic activity of ilmenite sands in the photo-Fenton-like degradation of textile dyes [30]. Another study reported the capability of ilmenite as a solid oxygen carrier in chemical-looping combustion in power plants [31]. Additionally, a natural ilmenite-based composite has been developed and investigated in neutrons and gamma ray attenuation [32].

However, the greater demand for TiO_2 in a vast range of environmental, pharmaceutical, industrial and energy related applications has resulted in the development of production processes at the industrial level. Industrially, titanium dioxide is extracted from mineral sands found in nature, consisting of titanium salts. Ilmenite is commonly used as the raw material for extracting TiO_2 due its higher abundance in nature. However, in certain cases, although it is rare, higher-grade rutile is also utilized as the raw material to produce TiO_2 and Ti metal in the manufacturing industry. In the industrial production of TiO_2, the sulphate process and chloride process are the two common methods utilized for extracting TiO_2 from ilmenite and rutile, respectively.

2.1. Sulphate Process

Statistical data reveal that 98% of manufacturers in China use the sulphate process for the production of TiO_2 [33]. The process can be categorized into four main stages, namely, acid digestion, hydrolysis, calcination and post-treatment, which are illustrated in Figure 1. In short, the initial step of the process involves converting the raw material, ilmenite, into

titanium-sulphate through acid digestion. The resulting compound is then hydrolysed to yield hydrous titania, $TiO_2 \cdot H_2O$. Finally, the hydrated form is subjected to calcination to form TiO_2 [34–36].
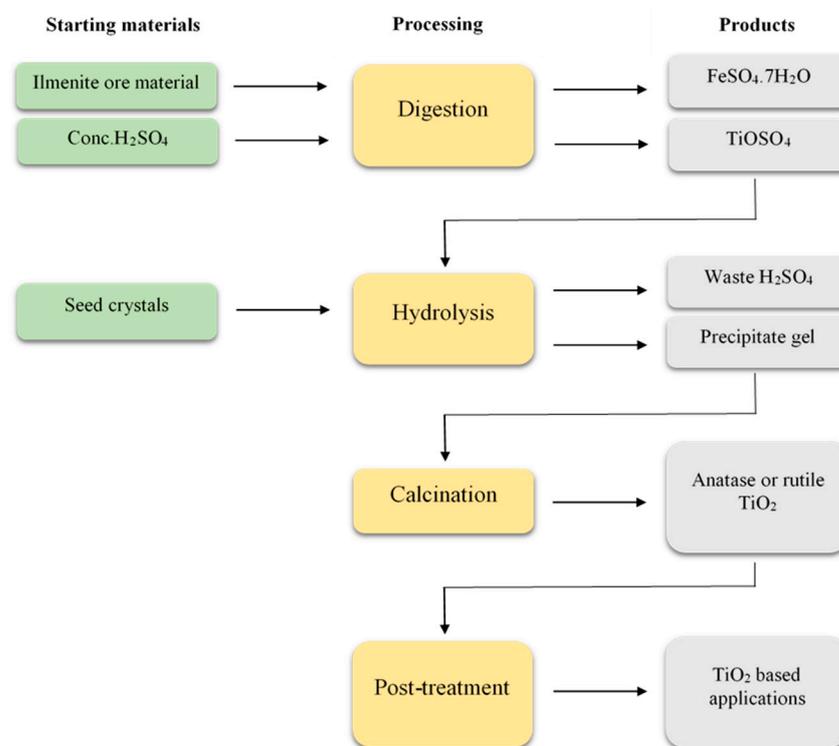

Figure 1. Illustration showing the key stages of the sulphate process.

1.   Acid digestion

To ensure a 94% efficiency in this step, a 60% excess of 96% concentrated sulphuric acid (H_2SO_4) relative to the TiO_2 content in the raw material is required. The excess acid is added to purified ilmenite, which is then digested at 150 °C [34]. The reaction occurring during the digestion of ilmenite, i.e., $FeTiO_3$, is revealed below.

$$2H_2SO_4 \text{ (aq)} + FeTiO_3 \text{ (s)} \rightarrow TiOSO_4 \text{ (aq)} + 2H_2O \text{ (l)} + FeSO_4 \text{ (aq)} \tag{1}$$
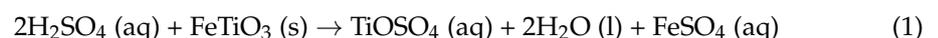
Due to the high temperature used in the digestion step, the ferrous content in ilmenite, which is considered to be an impurity for the final product, undergoes oxidation into the ferric form. Hence, by incorporating scrap iron (Fe) into the mixture, it is possible to convert all of the Fe^{3+} ions into Fe^{2+} that can be conveniently separated as crystalline iron(II) sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) at a relatively low temperature of approximately 15 °C [34].

$$Fe^{3+} \text{ (aq)} + Fe \text{ (s)} \rightarrow 2\,Fe^{2+} \text{ (aq)} \tag{2}$$
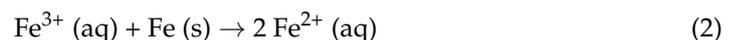
2.   Hydrolysis

Hydrolysis of the titanium salt ($TiOSO_4$) occurs upon heating the digestion yield at 109 °C, resulting in the formation of a gelatinous precipitate and a significant amount of residual sulphuric acid. To eliminate any residual acid, the gelatinous precipitate is subjected to multiple washes during the purification process. Adding different types of seeds during the process allows the formation of the final product (TiO_2) in different phases, i.e., anatase or rutile crystalline phases [34,37].

$$TiOSO_4 \text{ (aq)} + (n + 1)\,H_2O \text{ (l)} \rightarrow H_2SO_4 \text{ (aq)} + TiO_2 \cdot nH_2O \text{ (s)} \tag{3}$$

3. Calcination

The hydrolysis product ($TiO_2 \cdot nH_2O$, hydrous titania) is subjected to calcination in rotary kilns, where the reaction temperature plays a crucial role in determining the final outcome. At temperatures around 200–300 °C the hydrolysed material undergoes dehydration, followed by the formation of crystalline TiO_2 at approximately 480 °C. Moreover, heating up to 750–850 °C results in the production of anatase TiO_2, while the rutile phase is yielded at temperatures ranging from 900–930 °C [34].

$$TiO_2 \cdot nH_2O \text{ (s)} \rightarrow nH_2O \text{ (l)} + TiO_2 \text{ (s)} \qquad (4)$$

It is important to avoid raising the temperature unnecessarily in order to preserve the appropriate structural and chemical propertied of TiO_2 that are advantageous for industrial applications.

4. Post-treatment

The calcined product (either anatase or rutile TiO_2), is subjected to suitable surface modifications in preparation for further applications [38,39].

2.1.1. Advantages of the Sulphate Process

The main advantage of the sulphate process is the feasibility of isolating TiO_2 either in the anatase or rutile crystalline phase, depending on the calcination temperature. The capital investment required for the sulphate process is comparatively lower than that of the chloride process. In the same way, since the energy demand and starting materials are cheaper, operating costs are also lower for the sulphate process compared to the chloride process. In terms of waste generation, the remaining portion of dilute sulphuric acid can be reconcentrated and reused for the ilmenite digestion, enhancing the productivity of the sulphate process. Additionally, waste sulphuric acid can be reacted with limestone ($CaCO_3$), as shown below, in order to produce gypsum ($CaSO_4 \cdot 2H_2O$) [33].

$$H_2SO_4 \text{ (aq)} + CaCO_3 \text{ (s)} \rightarrow CaSO_4 \cdot 2H_2O \text{ (s)} + CO_2 \text{ (g)} \qquad (5)$$
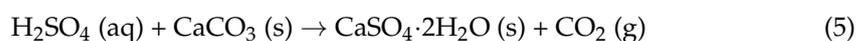
Moreover, the by-product, $FeSO_4 \cdot 7H_2O$, can be used either in the exact form or in an altered form for any other industries. For instance, $FeSO_4 \cdot 7H_2O$ can be oxidized into the ferric form and can then be used for water purification [40,41].

2.1.2. Disadvantages of the Sulphate Process

The main drawback is the environmental damage caused by the waste of the sulphate process. For instance, highly concentrated (98%) sulphuric acid is used to collapse the ore material. Furthermore, the use of water in the hydrolysis step consequently generates a huge amount diluted sulphuric acid with a lower concentration of approximately 20%. According to the reports, the production of one ton of titania using this process generates approximately 25,000 m^3 of exhaust gas, 200 tons of acidic water and 7–11 tons of spent acid [33]. Therefore, environmental pollution control becomes more expensive in the sulphate process. Furthermore, being a batch process, the sulphate process can be utilized to extract only small amounts of TiO_2, where the reactants are allowed to react in the reaction chamber and once the reaction is completed the products are removed and proceeded to the next step [34].

2.2. Chloride Process

Based on statistical data from the industry, the chloride process accounts for 60% of worldwide TiO_2 production [33]. Figure 2 provides a depiction of the major steps involved in the chloride process, which is a continuous process and utilizes higher-grade rutile as the starting material to produce TiO_2. These stages include chlorination, purification (condensation), oxidation and post-treatment. The basic steps of the process involve reacting the ore material with chlorine gas to form $TiCl_4$ in the gaseous state, followed

by a reaction with oxygen to produce TiO_2 [34,36,42]. Because of the high sensitivity of $TiCl_4$ vapour to moisture, it is crucial to maintain an extremely dry environment in the reaction chamber.
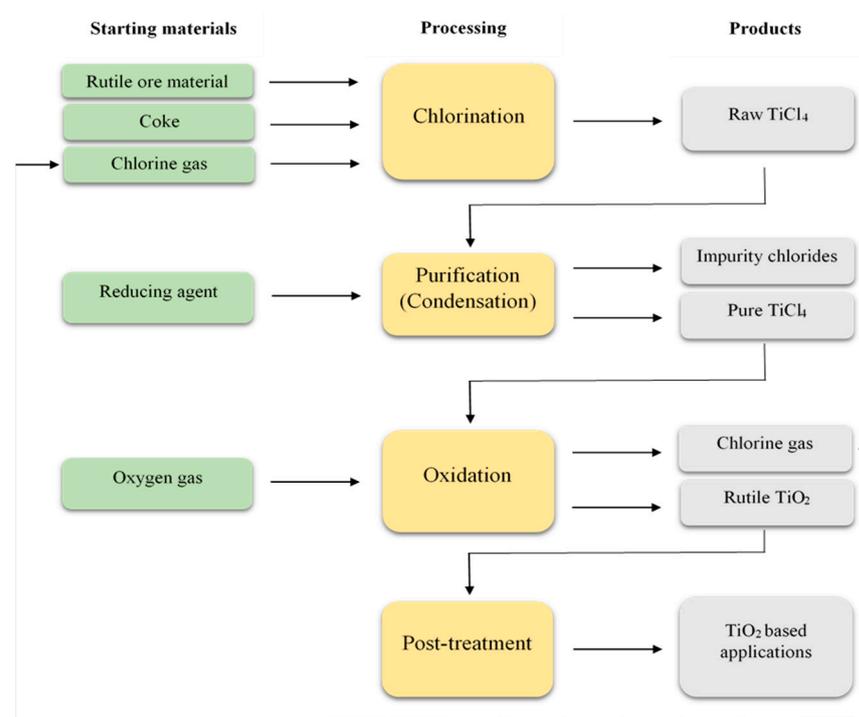

Figure 2. Illustration showing the key stages of the chloride process.

5. Chlorination

During this step, the dry titanium ore material is heated to a temperature of 950 °C while providing Cl_2 vapour to the reaction chamber, where a coke-assisted exothermic reaction is driven to yield $TiCl_4$ vapour along with CO, CO_2 and other impurity chlorides [34].

$$2Cl_2 \text{ (g)} + TiO_2 \text{ (s)} + C \text{ (s)} \rightarrow CO_2 \text{ (g)} + TiCl_4 \text{ (g)} \tag{6}$$
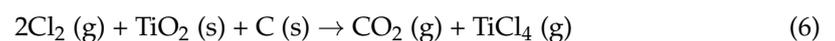
6. Purification (condensation)

With the purpose of removing volatile impurity chlorides with higher molecular masses from the reaction mixture, the gaseous mixture generated during chlorination is cooled, allowing for their efficient condensation [42]. Moreover, it should be noted that vanadium chloride, because it has a similar boiling point to titanium tetrachloride, cannot be eliminated through condensation like other impurity chlorides [19,43].

7. Oxidation

When purified $TiCl_4$ is burned with molecular oxygen, it produces only the rutile phase of TiO_2, and the anatase phase does not form. In order to obtain the highest possible yield in this step, the oxidation reaction should be carried out at a temperature around 1000 °C [34,42].

$$O_2 \text{ (g)} + TiCl_4 \text{ (g)} \rightarrow 2Cl_2 \text{ (g)} + TiO_2 \text{ (s)} \tag{7}$$

8. Post-treatment

After obtaining pure rutile TiO_2, it can be subjected to proper surface modifications using appropriate functionalization techniques to make it suitable for particular applications [38,39].

2.2.1. Advantages of the Chloride Process

Titanium dioxide can be obtained through the chloride process with a higher purity only in the rutile phase without anatase contaminants. Moreover, when compared to the sulphate process, the waste generation is also lower in the chloride process, where the by-product, chlorine gas, can be reused to feed the chlorinator at the beginning of the process [34]. Being a continuous process, the chloride process is endowed with a higher production capability over the sulphate process.

2.2.2. Disadvantages of the Chloride Process

Since the chloride process is able to produce only the rutile form of TiO_2, the industries which require the pure anatase form will not be benefited from this extraction process. Furthermore, the raw material of this process should be higher grade natural or synthetic rutile, with low contents of MgO and CaO, which is more expensive and rarely available compared to ilmenite [33]. Thus, the capital investment required to establish a chloride process plant is 1.7 times higher than that of a sulphate process plant [36]. Since extremely dry conditions and very high temperatures are essential requirements, the operating cost is also greater for the chloride process. Because of the use of very high temperatures, around 1000 °C, impurity chlorides, such as $MnCl_2$ (melting point: 650 °C), $CaCl_2$ (melting point: 782 °C) and $MgCl_2$ (melting point: 714 °C), can accumulate in the chlorinator in their liquid state, eventually retarding the process [42]. Although the waste generation is relatively lower compared to the sulphate process, a number of environmental challenges are associated with the chloride process as well. Most significantly, $TiCl_4$ is highly corrosive and its leakage should be necessarily avoided. Moreover, in accordance with the chlorination reaction, 550 kg of CO_2 is produced along with the production of one ton of TiO_2. It has been further estimated that around 2 million tons of CO_2 are generated annually through this chlorination reaction alone regarding the chloride process [33].

3. Upgrading Ilmenite into Synthetic Rutile

Being a higher grade titanium ore material, rutile has gained merits over ilmenite in the TiO_2 manufacturing sector. Due to the lower availability and the excessive mining of natural rutile ores in the world, researchers have focused their attention on effective processes of converting naturally occurring ilmenite into synthetic rutile. Previous studies have reported several methods of converting low grade ilmenite (40%–65% of TiO_2) to synthetic rutile or titanium slag (90% < TiO_2), which can be used to feed the chloride process as the raw material. These processes are assembled with a variety of operations such as roasting, leaching and physical separation [19].

Among the existing protocols, the Becher process is considered as a key method of synthesizing rutile from ilmenite, which possesses 40%–65% TiO_2 and the majority of the rest as iron oxides. The process yields synthetic rutile with more than 90% TiO_2, leaving the iron content [44,45]. Key processing steps of this approach includes oxidation, reduction, aeration and acid leaching as represented in Figure 3.
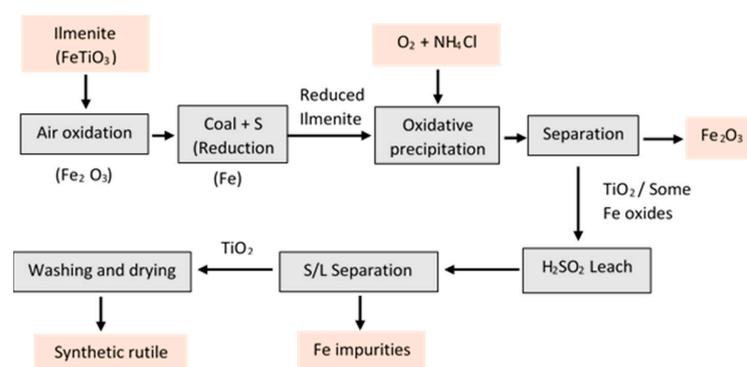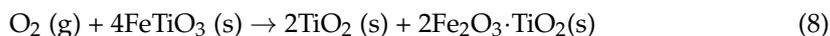

Figure 3. A schematic illustration of the key stages involved in the Becher process.

The iron content in ilmenite is converted to the ferric form through oxidation, where the ilmenite is heated in a rotary kiln with air, as revealed by the following reaction.

$$O_2 \text{ (g)} + 4FeTiO_3 \text{ (s)} \rightarrow 2TiO_2 \text{ (s)} + 2Fe_2O_3 \cdot TiO_2 \text{(s)} \tag{8}$$

The Fe(III) ions in $Fe_2O_3 \cdot TiO_2$ (pseudobrookite) can be reduced to result in metallic iron by heating in a rotary kiln at a temperature greater than 1200 °C in the presence of coal and sulphur [19].

$$3CO \text{ (g)} + Fe_2O_3 \cdot TiO_2 \text{ (s)} \rightarrow TiO_2 \text{ (s)} + 2Fe \text{ (s)} + 3CO_2 \text{ (g)} \tag{9}$$
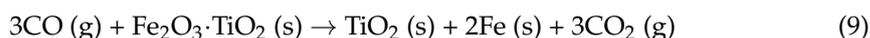
The metallic form is oxidized in the aeration process at 80 °C in the presence of 1% NH_4Cl, where Fe_2O_3 is precipitated from the solution as fine particles and the majority of the precipitate can be separated from synthetic rutile.

$$3O_2 \text{ (g)} + 4Fe \text{ (s)} \rightarrow 2Fe_2O_3 \text{ (s)} \tag{10}$$
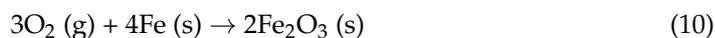
The remaining portion of Fe_2O_3 can be separated from the ultimate product, i.e., synthetic rutile, by leaching with a 0.5 M sulphuric acid solution. Likewise, the Becher process enables the isolation of different important iron species, i.e., Fe and Fe_2O_3, as by-products of the upgrading lower grade ilmenite into higher grade synthetic rutile route. However, the major drawbacks of the process include substantial emission of CO_2 and high energy consumption.

The Laporte process is another approach which is used for the same purpose, where the lower grade ilmenite is pre-oxidized at about 950 °C and subsequently subjected to a reductive roasting at 900 °C in a rotary kiln, where coal is used as the reductant, forming ferrous oxide from the ferric content in ilmenite. However, the complete reduction of ferric into the metallic state is prevented due to the action of CO_2, which is liberated in a sufficient amount while the coal is oxidized, yielding FeO as the only iron containing by-product of the Laporte process.

$$Fe \text{ (s)} + CO_2 \text{ (g)} \rightarrow FeO \text{ (s)} + CO \text{ (g)} \tag{11}$$

Since the roasted ilmenite is chemically more unstable and reactive compared to the initial state, a single stage leaching with an 18% HCl solution for 3.5 h under atmospheric pressure is sufficient to eliminate the ion content, yielding synthetic rutile with a greater purity of TiO_2. It has been reported that the product possesses the same particle size distribution as the starting ore material, i.e., low grade ilmenite, and the solid effluent is free of TiO_2 particles [19]. The requirement of relatively low temperature is an advantage of the Laporte process over the Becher process. However, the high energy requirement and the emission of CO_2 are still challenging drawbacks of the Laporte process.

As another approach, namely, the Kataoka process, the reductive roasting of low-grade ilmenite, where the trivalent iron content is converted into ferrous forms, is followed by leaching with sulphuric acid in order to obtain higher grade rutile. This process is deviated from the other methods of producing synthetic rutile, as the acid leaching solution is fed with hydrous titania ($TiO_2 \cdot H_2O$) seeds, aiming at acceleration the sedimentation of titanium salts and improving the elimination of iron species. Most significantly, the Kataoka process is able to separate the iron content from ilmenite at a lower temperature and with the use of sulphuric acid in a low concentration, thus, making the process greener and economically more viable. It is reported that more than 95% of the entire available content of TiO_2 can be recovered from the ilmenite [46].

4. Other Methods of Processing Ilmenite to Extract Titanium Compounds

Although sulphate and chloride processes are the two well established methods in the industrial sector, there is still a demand to seek for novel approaches mainly because of several major drawbacks associated with these conventional protocols for extracting TiO_2. According to the literature, studies have mainly been performed aiming at modifications of

the existing methods so that the yield can be increased while the drawbacks are eliminated. Furthermore, investigations have been conducted to examine the ability of producing other titanium and iron compounds as well, such as oxides, composites and alloys, from natural ilmenite. Likewise, several such novel approaches are discussed through this article.

4.1. Hydrochloride Process

The key feature which differentiates the hydrochloride process from the sulphate process is the use of concentrated hydrochloric acid to digest the ilmenite raw material where it has been estimated that 80% of titanium and iron in ilmenite can be dissolved [47]. It is also reported that HCl is more advantageous than other acids for the digestion process because it can be retrieved from liquid effluent through pyro-hydrolysis. Nevertheless, the HCl solution recovered by pyro-hydrolysis is at a low concentration, i.e., 20%, which is not sufficient for recycling it in the digestion step [33]. Furthermore, the use of HCl becomes more complex as the concentrated acid is corrosive and highly volatile.

The basic concept of the hydrochloride process has been further modified to devise a more economic approach, where titanium has been extracted and purified as $TiOCl_2$ from low grade ilmenite with a large fraction of iron. It is revealed that TiO_2 can be obtained in a preferred crystalline phase, i.e., anatase ore rutile, by hydrolysing the obtained $TiOCl_2$ solution under different conditions. As a whole, the process consists of a novel combination of several key steps, namely, HCl leaching, solvent extraction of iron and hydrolysis, for the extraction of TiO_2 with a high purity [48]. The major steps of this process are depicted in Figure 4.
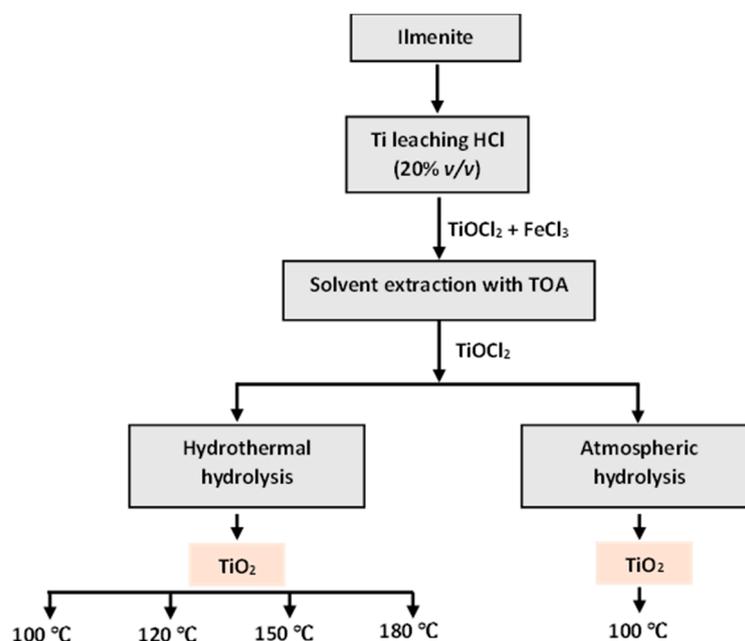

Figure 4. A schematic illustration of the major steps of the modified hydrochloride process.

First, the finely ground ore material is collapsed with a 20% (v/v) HCl solution at 70 °C, where 94.6% of the entire titanium content in ilmenite has been successfully extracted into the leachant after a 3 h extraction. The composition of the ilmenite leachant has been found to be 36.4 g/L and 23.0 g/L for iron and titanium, respectively. The decomposition of the titanium and iron content in ilmenite by concentrated hydrochloric acid during the leaching step can be described as follows [49]:

$$FeTiO_3 \text{ (s)} + 4HCl \text{ (aq)} \rightarrow TiOCl_2 \text{ (aq)} + FeCl_2 \text{ (aq)} + 2H_2O \text{ (l)} \tag{12}$$
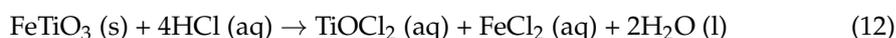
The obtained ilmenite leachant was diluted and fed with nitric acid, where the resultant solution was boiled for 15 min, confirming the complete oxidation of all the ferrous

species in the leachant into their ferric forms. The iron content can be separated from the titanium species ($TiOCl_2$) through a solvent extraction using 30% (*v/v*) trioctylamine (TOA) in kerosene at room temperature. Likewise, it is reported that the ilmenite leachant is composed majorly of titanium (12 g/L), and only a trace amount of iron (0.02 g/L) [48]; thus, it is clear that the solvent extraction process has been highly successful in removing nearly all of the iron content.

The purified $TiOCl_2$ solution can be subjected to either hydrothermal hydrolysis or atmospheric hydrolysis, expecting the ultimate product, i.e., TiO_2, with different physio-chemical properties. In the hydrothermal approach, $TiOCl_2$ is heated at different temperatures (100 °C, 120 °C, 150 °C and 180 °C) for 6 h in a closed vessel. On the other hand, atmospheric hydrolysis involves adding the pure leachant into boiling water and stirring the mixture for 6 h under boiling conditions. The reaction below can be used to explain the hydrolysis of acidic $TiOCl_2$ solution to produce TiO_2 [49].

$$H_2O \text{ (l)} + TiOCl_2 \text{ (aq)} \rightarrow 2HCl \text{ (aq)} + TiO_2 \text{ (s)} \tag{13}$$
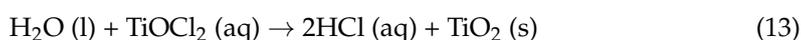
With reference to the hydrothermal hydrolysis of the titanyl chloride solution, the polymorphic form of the ultimate product, TiO_2, is determined by the reaction temperature. Titanium dioxide was obtained in pure rutile phase, without forming any anatase products, when the $TiOCl_2$ solution was hydrolysed at 100 °C and 120 °C, where it has been noticed that both the hydrolysis yield and the crystallinity of the product is elevated along with the increment of the reaction temperature from 100 to 120 °C. However, a mixture of both anatase and rutile TiO_2 has been obtained at 150 °C and the anatase becomes the most abundant form at 180 °C with only a minute amount of rutile TiO_2. However, the efficiency of the hydrothermal hydrolysis at all the studied temperatures was greater than 80%. SEM and TEM studies of the products reveal that nanometre scaled TiO_2 particles with a rod-like morphology can be yielded through hydrothermal hydrolysis at 150 °C and 180 °C. At a temperature of 100 °C and under an open atmosphere, hydrolysis produces an exceptionally stable titania nanocrystal suspension with a leaf-like morphology. However, anatase TiO_2 has been superior over the rutile phase in the hydrolysed product, where the yield of hydrolysis has been lower (75%) when compared to the hydrothermal hydrolysis method [48].

As a whole, the modified hydrochloride process exhibits superiority due to its ability to synthesize extremely pure TiO_2 with a very low content of impurities, i.e., iron compounds. Furthermore, because of the requirement of lower temperature, the process can be considered as greener compared to both the sulphate and chloride processes. However, the use of concentrated acid is still problematic as in the sulphate process. As the other major drawback, the nitric acid oxidation and TOA solvent extraction steps make the overall process more complex.

4.2. H_3PO_4/NH_3 Process

The method devises a simple and novel hydrothermal route for the synthesis of both anatase and rutile TiO_2, where the digestion of natural ilmenite with concentrated phosphoric acid (H_3PO_4) is followed by reacting the resultant solid, i.e., titanium bismonohydrogen orthophosphate monohydrate (TOP/$Ti(HPO_4)_2 \cdot H_2O$), with an aqueous ammonia solution in order to obtain $Ti(OH)_4$, which is eventually calcined into TiO_2 [50]. Figure 5 depicts the steps of the H_3PO_4/NH_3 process.
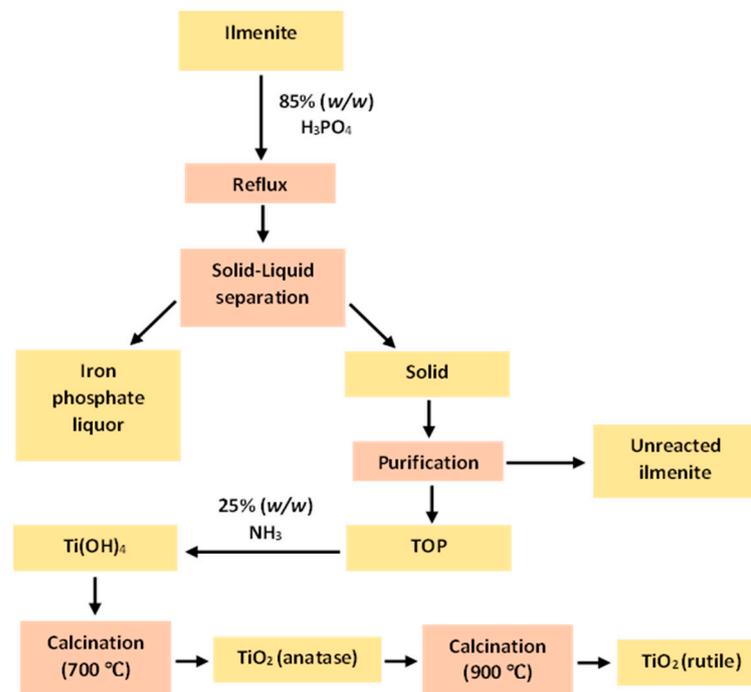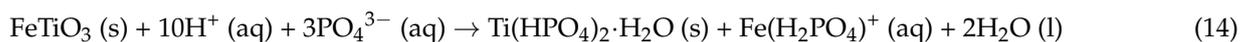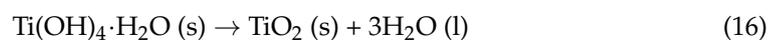
Figure 5. Representation of the major steps of the H_3PO_4/NH_3 process.

As the first step, TOP is synthesized by refluxing the ilmenite with 85% (*w/w*) H_3PO_4 for 5 h, where the ore material is collapsed to release titanium and iron species as the major constituents. Most importantly, it is reported that almost all the titanium content can be precipitated as iron-free TOP. The ferrous content in ilmenite is leached into the acid solution during the acid digestion process through the formation of a soluble phosphate complex, $Fe(H_2PO_4)^+$, as $H_2PO_4^{2-}$ becomes the predominant anionic form of H_3PO_4 under acidic conditions (pH < 3) [51]. The formation of TOP and $Fe(H_2PO_4)^+$ during the acid digestion can be described in accordance with the following reaction [50].

$$FeTiO_3 \text{ (s)} + 10H^+ \text{ (aq)} + 3PO_4^{3-} \text{ (aq)} \rightarrow Ti(HPO_4)_2 \cdot H_2O \text{ (s)} + Fe(H_2PO_4)^+ \text{ (aq)} + 2H_2O \text{ (l)} \qquad (14)$$

Moreover, Fe(II) in ilmenite can be oxidized into Fe(III) while refluxing the digestion mixture at high temperatures. The resultant ferric ions can also form soluble complexes with phosphoric acid. Therefore, as a whole, the removal of iron from solid TOP has been achieved by leaching into the acidic liquid phase through the formation of highly soluble Fe(II)/Fe(III) complexes, such as $FeH_5(PO_4)_2^{2+}$, $FeH_7(PO_4)_3^{3+}$, $Fe(H_2PO_4)^+$ and $Fe(H_2PO_4)^{2+}$ [51–53]. These phosphate complexes of iron can be used for the industrial manufacturing of a variety of products such as paints, fertilizers and pesticides.

As the second step of the process, the obtained pure TOP is treated with 25% (*w/w*) NH_3 and the resultant mixture should be heated at 40 °C for 2 h, leading to the formation of $Ti(OH)_4$, which can be subsequently calcined at a suitable temperature to yield TiO_2 in either rutile or anatase phase [50].

$$Ti(HPO_4)_2 \cdot H_2O \text{ (s)} + 4NH_4OH \text{ (aq)} \rightarrow Ti(OH)_4 \cdot H_2O \text{ (s)} + 2(NH_4)_2HPO_4 \text{ (aq)} \qquad (15)$$

$$Ti(OH)_4 \cdot H_2O \text{ (s)} \rightarrow TiO_2 \text{ (s)} + 3H_2O \text{ (l)} \qquad (16)$$
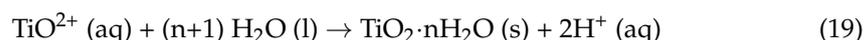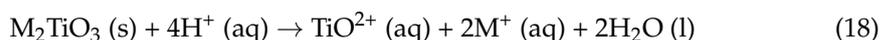
Results of the study reveal that nano-sized pure anatase TiO_2 particles could be obtained when $Ti(OH)_4$ was calcined at 700 °C, whereas the product was in pure rutile phase at a calcination temperature of 900 °C.

Most significantly, the H_3PO_4/NH_3 process enables the synthesis of a variety of economically valuable titanium and iron phosphate species from natural ilmenite. However,

the process cannot be deliberated as an ecofriendly approach owing to the requirement of concentrated phosphoric acid, eventually leading to the generation of huge amounts of acidic effluents.

4.3. Alkaline Roasting Process

The main purpose of this approach is to eliminate the necessity for concentrated acids to collapse the ore material, which is one of the major drawbacks related to many TiO_2 extraction processes. The key strategy used in this process is diminishing the stability of the ore material through an alkaline roasting pretreatment, so that the conditions required for the digestion can be moderated [54,55]. The titania slag, which is the raw material, is subjected to roasting with a molten strong base (KOH or NaOH) at 500 °C for 1 h, where an amorphous phase of titanate salts (K_2TiO_3 or Na_2TiO_3) is formed from the original crystalline phase. The titanate salts can easily dissolve in acidic solutions having a pH of about 0.2, where the reactions regarding the formation of TiO^{2+} can be stated as shown below (M stands for K and Na) [33]. However, TiO^{2+} can be subsequently hydrolysed and calcined to obtain TiO_2, consistent with the sulphate process.

$$TiO_2 \text{ (ore material)} + 2MOH \text{ (l)} \rightarrow M_2TiO_3 \text{ (s)} + H_2O \text{ (l)} \qquad (17)$$

$$M_2TiO_3 \text{ (s)} + 4H^+ \text{ (aq)} \rightarrow TiO^{2+} \text{ (aq)} + 2M^+ \text{ (aq)} + 2H_2O \text{ (l)} \qquad (18)$$

$$TiO^{2+} \text{ (aq)} + (n+1) \, H_2O \text{ (l)} \rightarrow TiO_2 \cdot nH_2O \text{ (s)} + 2H^+ \text{ (aq)} \qquad (19)$$

$$TiO_2 \cdot nH_2O \text{ (s)} \rightarrow nH_2O \text{ (l)} + TiO_2 \text{ (s)} \qquad (20)$$

The sufficiency of a mild acid digestion is a plus point of the alkaline roasting process, eventually nullifying the issues related to the generation of large amounts of acid wastes. Therefore, this approach can be considered to be more eco-friendly compared to the well-known sulphate method. However, since the partial loss and the recycling of the alkaline solution are costly, the overall procedure is economically less favourable due to the higher operating cost.

4.4. Aluminothermic Reduction Method

With the purpose of balancing energy consumption as well as waste generation, another method has been introduced for the extraction of TiO_2 from ilmenite or titania slag, where the primary unit operations comprise phase transformation of the raw material, carrying out mild acid digestion and implementing regulated hydrolysis (Figure 6) [33].
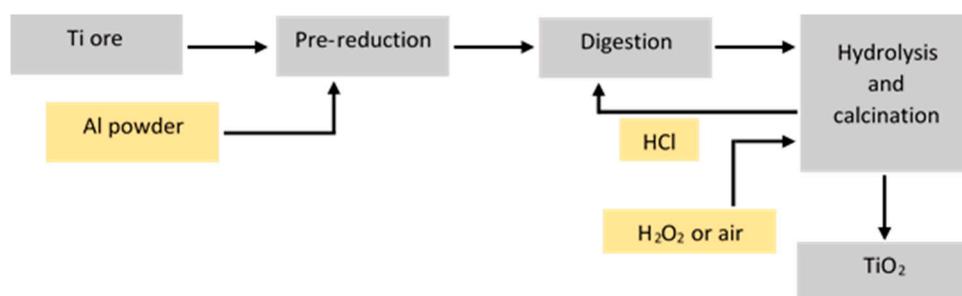
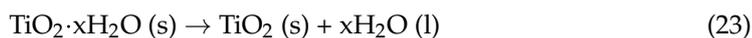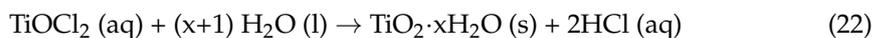**Figure 6.** Representation of key steps of the aluminothermic reduction process.

Initially the stable crystalline phase of the raw material is reformed by forming titanium suboxides, where TiO_2 is partially converted into TiO_x ($x \leq 1.5$) through aluminothermic reduction. Magnesium and calcium can also be used as the reductant, instead of aluminium, for the lattice deformation purpose. However, the use of Mg and Ca is not

favoured as $MgTiO_3$ and $CaTiO_3$, which are formed during the reduction process and co-exist with the suboxides, are slightly soluble in mild acidic media at low temperatures, retarding the extraction of titanium [33,56]. Therefore, Al gains higher merits over Mg and Ca in this regard. However, low grade ilmenite with a higher content of Fe is not preferred as the raw material due to the excessive consumption of Al reductant by the iron oxides in ilmenite.

The formed titanium suboxides, i.e., Ti_2O_3 and TiO, which possess trivalent titanium ions, can be easily digested with the assistance of a HCl solution having a proton concentration of 6 M, in order to obtain a solution containing Ti^{3+}.

$$TiO_x \ (1 \leq x \leq 1.5) + 3HCl \ (aq) \rightarrow 2TiCl_3 \ (aq) + xH_2O \ (l) + (1.5 - x)H_2 \ (g) \tag{21}$$
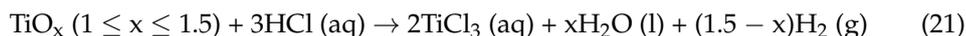
The obtained $TiCl_3$ solution can be treated with H_2O_2 so that the trivalent state is oxidized into the tetravalent state resulting in $TiOCl_2$ having TiO^{2+} ions. Then, $TiOCl_2$ undergoes hydrolysis in the same HCl medium resulting in hydrous titania, i.e., $TiO_2 \cdot H_2O$, as shown below [33], which can eventually be converted into TiO_2 through calcination as in the sulphate process.

$$TiOCl_2 \ (aq) + (x+1) \ H_2O \ (l) \rightarrow TiO_2 \cdot xH_2O \ (s) + 2HCl \ (aq) \tag{22}$$

$$TiO_2 \cdot xH_2O \ (s) \rightarrow TiO_2 \ (s) + xH_2O \ (l) \tag{23}$$

The aluminothermic reduction method partially eliminates the necessity of highly concentrated acids to digest the ore material as the moderately collapsed ilmenite should be treated with hydrochloric acid with an elevated concentration to achieve complete digestion. The other main drawbacks of this technique include the requirement of high-grade ilmenite as the starting material and the complexity of the process.

4.5. Alkaline Decomposition Method

Recently, a novel method was proposed to extract TiO_2 from ilmenite, which is initially decomposed in a highly concentrated sodium hydroxide or potassium hydroxide solution under atmospheric pressure, where a titanate intermediate ($M_4Ti_3O_8$) is obtained in addition to iron oxide as follows (M stands for K or Na) [57,58]:

$$3FeTiO_3 \ (s) + 4MOH \ (aq) \rightarrow M_4Ti_3O_8 \ (s) + 3FeO \ (s) + 2H_2O \ (l) \tag{24}$$
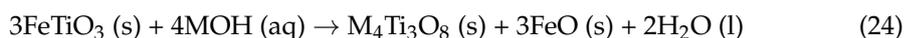
The resultant mixture can be enriched with the titanate intermediate and iron oxide through water treatment, where the concentrated NaOH or KOH liquor is separated and purified with the purpose of reusing it for the decomposition of ilmenite.

Potassium titanate ($K_4Ti_3O_8$), which is obtained when KOH is used to collapse the ore material, can be converted into hydrous titania ($TiO_2 \cdot H_2O$) through a phase transformation, where the titanate intermediate is hydrolysed by refluxing with an acid solution of pH = 2.0 at 25 °C for 1 h. Moreover, the iron forms are excluded from the hydrolysed product by treatment with acid. The hydrous titania is then calcined at 400 °C in order to obtain anatase-TiO_2 with a perfect crystalline structure. Likewise, 98% of the Ti in ilmenite has been successfully extracted with this approach and the TiO_2 purity in the ultimate product was greater than 99%. The basic steps of the alkaline decomposition method are revealed in Figure 7 [19].
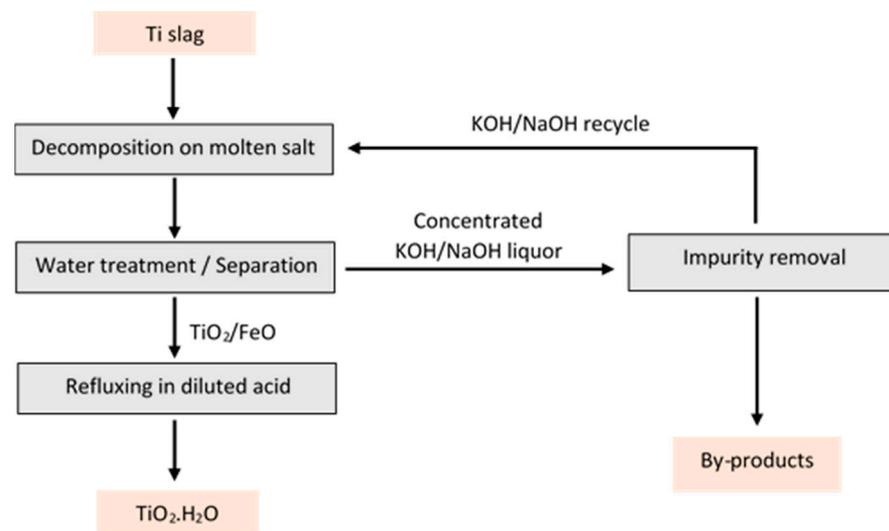
Figure 7. A schematic illustration of the major steps of the alkaline decomposition method.

The same procedure has been performed in order to obtain rutile-TiO_2, where finely ground ilmenite, with micrometre-scaled particles, has been reacted with 10 M NaOH solution at 220 °C for 4 h [59]. It is reported that $Na_4Ti_3O_8$ is yielded as the hydrothermal product when the alkali to TiO_2 ratio was 4. The hydrothermal product is hydrolysed at 100 °C by an acid solution with a pH range of <1.2. It is also reported that rutile-TiO_2 can be obtained with a purity of >99% when HCl is used for the hydrolysis of $Na_4Ti_3O_8$.

The process gains merits as it does not require the presence of concentrated acids for the digestion of the ore material, consequently reducing the issues related to the generation of acidic wastes. However, the higher operating cost related to the recycling of the alkaline solution has depreciated the overall process as a high-cost method. Moreover, since the titanate intermediate should be hydrolysed by a concentrated acid, the acid waste generation is still a challenging drawback of the process.

4.6. Molten Salt Electroreduction Process

This is a promising approach to producing titanium alloys and composites directly from different titanium-containing ore materials, such as natural ilmenite, high titanium slag (HTS) and Ti-bearing blast-furnace slag (TBFS), through a molten salt electroreduction process [60]. TBFS is mainly composed of $CaTiO_3$ and $CaMgSi_2O_6$, whereas the major constituents in HTS are Ti_3O_5, Fe_3O_5, TiO_2 and $CaTiSiO_5$. Natural ilmenite mainly consists of $FeTiO_3$ and Fe_3O_4.

Recent studies reveal that the process is capable of synthesizing a wide spectrum of industrially valuable alloys/composites, including Ti_5Si_3, $TiAl_3$, Fe/TiC, Ti_5Si_3/TiC and Ti_5Si_3/Ti_3SiC_2 [61–64], from natural titanium containing ores. Basically, the direct synthesis of these alloys and composites is accomplished through an electroreduction of the ore constituents in molten calcium chloride ($CaCl_2$) at 950–100 °C, where a consumable graphite-based anode is used with the provision of a voltage of 3.8 V [60].

The crucial step of this method is the preparation of the cathode material, where the initial titanium ore material, i.e., TBFS, HTS or natural ilmenite, should be mixed with other necessary compounds, such as TiO_2, Al_2O_3 and carbon powder, in accordance with the stoichiometric ratios of elements in the anticipated alloys/composites. These substances should be mixed thoroughly with a proper binder and pressed under high pressure so that the cathode pellet material can be obtained. The cathodic reaction, eventually leading to the formation of the alloys and composites, can be generalized as follows, where x and y can be integers:

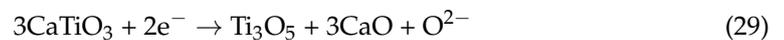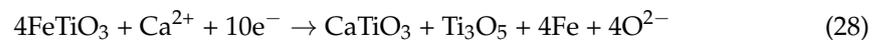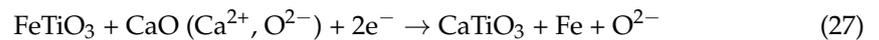$$M_xO_y + 2ye^- \rightarrow xM + yO^{2-} \tag{25}$$

The simultaneous anodic process, where carbon is consumed as the reductant to react with oxide ions generated by the cathodic reaction, can be described as follows [64,65]:

$$C + yO^{2-} \rightarrow CO_y + 2ye^- \tag{26}$$

Molten calcium chloride is used as the electrolyte, where the reaction chamber should be continuously provided with ultra-pure argon gas in order to facilitate an inert atmosphere during the intended electrochemical process. In addition to the predesigned alloy or composite, other species, such as $CaTiO_3$, $Ca_{12}Al_{14}O_{33}$, $CaSiO_3$, $CaSi_2O_5$, $MgAl_2O_4$ and Ti_2O_3, can also be yielded, depending on different parameters, i.e., the type of the initial ore material, ratio between cathode constituents and electrochemical reaction conditions [60].

For instance, the electrochemical production of Fe/TiC requires a mixture of natural ilmenite and carbon powder (94% ilmenite and 6% carbon) as the cathode precursors, where $CaTiO_3$ and Fe were obtained as the main phases after 1 h electroreduction in molten $CaCl_2$ at 1000 °C and under a voltage of 3.8 V. Being an electronic conductor, the produced Fe can further trigger the reduction of cathode materials, so that Fe/TiC can be readily produced after only 3 h of the electrochemical process. In addition to the desired product, $CaSiO_3$ is also formed in the cathodic pellet. However, it is supposed that the produced $CaSiO_3$ is dissolved in molten $CaCl_2$ as the Si content in the ultimate Fe/TiC product has been assessed to be even less than 1%.

The mechanism regarding the formation of Fe/TiC through the electrochemical reduction of ilmenite and carbon in liquefied calcium chloride can be described by the following reactions.

$$FeTiO_3 + CaO\,(Ca^{2+}, O^{2-}) + 2e^- \rightarrow CaTiO_3 + Fe + O^{2-} \tag{27}$$

$$4FeTiO_3 + Ca^{2+} + 10e^- \rightarrow CaTiO_3 + Ti_3O_5 + 4Fe + 4O^{2-} \tag{28}$$

$$3CaTiO_3 + 2e^- \rightarrow Ti_3O_5 + 3CaO + O^{2-} \tag{29}$$

$$Ti_3O_5 + 3C + 10e^- \rightarrow 3TiC + 5O^{2-} \tag{30}$$

$$TiFe + C \rightarrow TiC + Fe \tag{31}$$

$$Fe_3C + Ti \rightarrow TiC + 3Fe \tag{32}$$

Likewise, the same electroreduction process can be studied with the use of mixtures of different molten electrolytes, such as $CaCl_2$-NaCl [66,67], LiCl-KCl and LiCl-KCl-$CaCl_2$ [68], where the alloy-production process can be carried out at different temperatures and cell voltages. However, the excessive use of molten salts is the major drawback, which makes the overall electroreduction process more costly and less effective.

4.7. Magnesiothermic Reduction Process

Another recent study reported an optimistic method of converting natural ilmenite into valuable Ti containing alloys, such as TiC, FeTi, TiB_2 and $FeTiSi_2$ [61–63], through a magnesium-assisted reduction pathway. It is claimed that, all the aforementioned titanium alloys could be obtained as fine powders with a purity greater than 95% (*w/w*) [69].

The study has revealed a general combustion strategy for the production of titanium alloys from ilmenite ($FeTiO_3$), where a precursor mixture is initially prepared in accordance with the common formula, $FeTiO_3$-αMg-kNaCl-C (B, Si), where α and k represent the stoichiometric coefficients of Mg and NaCl, respectively. The numerical values of α and k

can be optimized, so that the ultimate product is yielded with different phase compositions and morphological features.

The synthesis process mainly consists of two major stages, i.e., combustion of the precursor mixture at an elevated temperature (900–1000 °C), where titanium and iron compounds are reduced by magnesium, and acid leaching of the combustion products. Therefore, the ignition of the initial reaction mixture in an inert atmosphere provided by argon gas is followed by acid leaching of the combusted sample in a HNO_3 solution, where the combustion by-products are dissolved and only the alloy products remain as a powder. Furthermore, NaCl is added to the precursor mixture so as to decrease the combustion temperature, where the added NaCl does not involve in the magnesiothermic reduction reactions.

It has been revealed that the ultimate yield of the magnesiothermic process is mainly composed of titanium suboxides (TiO, Ti_2O_3 and Ti_4O_7), double metal oxides (Fe_2TiO_4, $MgTiO_3$ and Mg_2TiO_4) and metals (Ti and Fe) at low α ($\alpha < 3.0$), where the phase transition of ilmenite and magnesium can be described as follows;

$$FeTiO_3 \rightarrow Fe_2TiO_4 \rightarrow Ti_4O_7 \rightarrow Ti_2O_3 \rightarrow TiO \rightarrow Ti \tag{33}$$

$$MgTiO_3 \rightarrow Mg_2TiO_4 \rightarrow MgO \tag{34}$$

However, the minimum Mg ratio has been optimized to be $\alpha = 3.5$ in order to obtain metallic forms of Fe and Ti as the major phases. As a whole, it has been perceived that a precursor mixture, with the composition of $FeTiO_3 + 3.5Mg + 2NaCl$, could be combusted to obtain the product, mainly comprising of three phases, i.e., FeTi, MgO and NaCl, in addition to residual magnesium. Subsequently, the combustion product is subjected to acid leaching with nitric acid, in which NaCl, MgO and Mg can be readily dissolved, leading to the isolation of FeTi. It has been revealed that FeTi is obtained as the major phase when the acid leaching is carried out at low temperatures (40 °C), where Fe_3Ti_3O also exists as a minor phase. However, the Fe_3Ti_3O phase becomes more abundant when the acid leaching is accomplished at high temperatures (100 °C), where the oxidation of FeTi into Fe_3Ti_3O by HNO_3 is in accordance with the following reaction.

$$9FeTi + 2HNO_3 \rightarrow 3Fe_3Ti_3O + 2NO + H_2O \tag{35}$$

Likewise, when the precursor mixture consisted of carbon, boron and silicon, the formation of TiC, TiB_2 and $TiFeSi_2$ phases can be achieved, respectively, through the combination with FeTi, as represented by the following reactions [69].

$$FeTi + C \rightarrow TiC + Fe \tag{36}$$

$$FeTi + 2B \rightarrow TiB_2 + Fe \tag{37}$$

$$FeTi + 2Si \rightarrow TiFeSi_2 \tag{38}$$

Likewise, various processes have been developed based on conventional techniques, where the objectives are mainly focused on the elimination of the drawbacks of the previously reported methods as well as to improve the quantity, quality and the diversity of the products. Nullifying the requirement of harsh conditions, such as high temperatures and strong acids and bases for the decomposition of the raw material can be recognized as one of the main purposes of developing a novel technique. On the other hand, reducing the acidic effluent level, so as to minimize the impact on the environment, has been another key feature of a novel method. Furthermore, strategies have been used to improve the yield of the final product having desired chemical and physical properties. Most significantly, several novel techniques are endowed with the ability to yield a huge variety of Ti, Fe and

Ti/Fe compounds. All the abovementioned facts regarding the well-established as well as novel methods of processing ilmenite can be summarized as revealed in Table 3, which contains key information, such as the raw material, digestion agent, products, advantages and disadvantages related to particular methods.

Table 3. Summary on ilmenite processing techniques.

	Name of the Process	Raw Material	Digestion Agent	Products	Advantages	Disadvantages
Conventional processes of extracting TiO_2 from ilmenite	Sulphate process	Ilmenite	Conc. H_2SO_4	TiO_2 (anatase or rutile) $FeSO_4 \cdot 7H_2O$ (by-product)	Feasibility of isolating TiO_2 in preferred crystalline phase Raw materials are cheaper and highly available Lower operating cost Acidic effluents can be recycled	Requirement of extremely harsh conditions such as huge excess of concentrated sulphuric acid and very high temperatures. Environmental pollution due to acidic (gaseous and liquid) effluents.
	Chloride process	Higher-grade rutile	Chlorine vapour Coke	TiO_2 (rutile)	Highly pure rutile-TiO_2 can be obtained (without anatase impurities) Chlorine gas can be reused Higher production capability compared to sulphate process	Anatase form of TiO_2 cannot be obtained Raw material is more expensive and rarely available Higher capital and operating cost (due to necessity of extremely dry conditions) Requirement of very high temperatures
Upgrading ilmenite into synthetic rutile	Becher process	Lower-grade ilmenite	Oxygen (Heating in air)	Higher-grade rutile Fe and Fe_2O_3 (by-products)	Higher-grade rutile as well as iron species can be synthesized	Requirement of high temperatures Substantial Emission of CO_2
	Laporte process	Lower-grade ilmenite	Oxygen (Heating in air)	Higher-grade rutile FeO (by-product)	Requirement of lower temperature compared to Becher process FeO can also be isolated without ferric forms	High energy requirement Substantial emission of CO_2
	Kataoka process	Lower-grade ilmenite	Oxygen (Heating in air)	Higher-grade rutile	Acids are required in low concentrations Low temperatures are required	Hydrous titania seeds are required to accelerate the recovery of TiO_2 from ilmenite
Other methods of processing ilmenite to extract TiO_2 and other related compounds	Hydrochloride process	ilmenite	Conc. HCl	TiO_2 (anatase or rutile)	HCl can be retrieved from the liquid effluent through pyro-hydrolysis	Severe health and environmental issues are caused by corrosive and highly volatile HCl
	Modified hydrochloride process	ilmenite	20% HCl	TiO_2 (anatase or rutile)	Preferred crystalline phase of TiO_2 can be yielded based on hydrolysis conditions Ability to synthesize extremely pure TiO_2 Low temperatures are required	Requirement of concentrated acids Greater complexity of the process due to nitric acid oxidation and TOA solvent extraction
	H_3PO_4/ NH3 process	ilmenite	Conc. H_3PO_4	TiO_2 (anatase and rutile) $FeH_5(PO_4)_2^{2+}$ $FeH_7(PO_4)_2^{3+}$ $Fe(H_2PO_4)^+$ $Fe(H_2PO_4)^{2+}$	Preferred crystalline phase of TiO_2 can be yielded Economically valuable iron-phosphate complexes can be obtained as by-products	Requirement of concentrated acids

Table 3. *Cont.*

Name of the Process	Raw Material	Digestion Agent	Products	Advantages	Disadvantages
Alkaline roasting process	Titania slag	Molten KOH or NAOH	TiO_2 M_2TiO_3 (M = Na or K)	Concentrated acids are not required	Use of strong bases Requirement of high temperatures Recycling of the alkaline solution is costly
Aluminothermic reduction method	Titania slag	Al	TiO_2	Requirement of concentrated acids is partially eliminated	Low-grade ilmenite cannot be used as the raw material
Alkaline decomposition method	Titania slag	Conc. NaOH or KOH	TiO_2 $M_4Ti_3O_8$ (M = Na or K)	Concentrated acids are not required	Higher operating cost for the recycling of the alkaline solution
Molten salt electroreduction process	ilmenite Titania slag	Molten chlorides such as $CaCl_2$, NaCl, LiCl and KCl	Numerous alloys and composites containing Ti and other elements	The process is capable of synthesizing a wide spectrum of alloys/composites	Greater complexity of the process Requirement of very high temperatures
Magnesiothermic reduction process	Titania slag	Mg NaCl	Various alloys containing Ti, C, Fe, Si and B, and double metal oxides containing Ti, Fe and Mg	The process is capable of synthesizing a wide spectrum of alloys with a greater purity	Greater complexity of the process Requirement of very high temperatures

5. Conclusions

As a whole, it can be clearly concluded that a vast range of industrially valued compounds, in addition to TiO_2, can be produced using naturally occurring ilmenite as the starting material, with the assistance of various techniques. However, all the aforementioned methods are endowed with advantages as well as disadvantages. Generally, the requirement of harsh conditions, such as excessive use of concentrated acids and bases, and very high temperatures, is the major drawback associated with these processes. Additionally, necessity of huge capital cost, high processing cost, complexity, low purity of products and the liberation of toxic gaseous and liquid effluents into the environment are the other key disadvantages related with aforementioned methods. Therefore, future works are still required, aimed at further modifications of these basic techniques, and to develop novel greener methods to process naturally occurring ilmenite to extract and synthesize TiO_2 and other titanium containing species, so as to eliminate drawbacks of the existing protocols.

Author Contributions: Conceptualization, R.M.d.S. and K.M.N.d.S.; Literature data curation, A.H.J.S. and N.D.W.; writing-original draft preparation, A.H.J.S. and N.D.W.; writing-review and editing, K.M.N.d.S., R.M.d.S. and A.H.J.S.; supervision, R.M.d.S. and K.M.N.d.S. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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