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Nature-inspired Bio-Mineral Refinery for Simultaneous Biofuel Feedstock production and CO_2 mineralization

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ABSTRACT

Inspired by Nature, we propose that synergies between biorefinery and mineral refinery can be exploited so that at least a part of the carbon is captured before being released to the atmosphere. In doing so, carbon is captured not only from CO_2 but also from biomass and developing more such processes may be the cornerstone for controlling CO_2 emissions. A comparison of circular economy in traditional biorefineries and bio-mineral refineries is done by using general chemical formulas and it is shown that the bio-mineral refinery captures carbon. In this work, we have shown that Serpentine may be used to partially neutralise biomass pyrolysis oil. The extracted oil may be used as feedstock to produce downstream chemicals and further studies are required to produce the same.

Keywords: Biofuels, Biomass, Carbon Capture, Carbon Dioxide Sequestration, Environment

INTRODUCTION

Circular economy, a concept that focuses on recycle, is viewed as a potential means of reducing new resource usage, thus limiting CO_2 emissions. Applying the concept of circular economy to the chemical process industries; biomass, fossil resources, all the chemical products and CO_2 can be considered as the intermediates, while energy to the system comes from the Sun. Currently, the rate of CO_2 emissions is greater than the rate of biomass regeneration and this is leading to CO_2 accumulation in the atmosphere, and this is viewed as being linear. Furthermore, CO_2 utilization/mineralization to reduce atmospheric CO_2 accumulation may be viewed as the process of closing the loop in a circular economy; however, doing so is energy intensive and leads to further CO_2 emissions. Biorefineries have been proposed as a panacea since they can potentially substitute fossil sources, and the energy for CO_2 capture and production of biomass is taken directly from the sun. However, biorefineries have had limited success, and most are single product chemical plants.

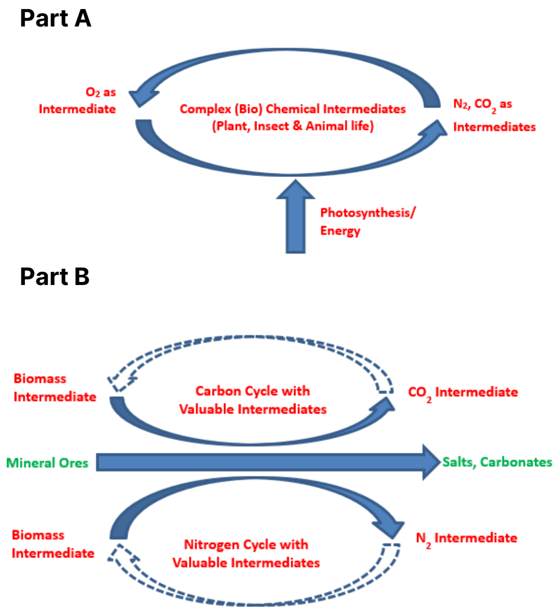
The critical difference between fossil sources such as crude oil, natural gas and biomass is that biomass has about 40% (w/w) oxygen and the same is almost non-existent in the fossil sources. In view of this, one can expect that biomass to chemicals/fuels is going to be expensive especially if oxygen elimination is necessary. Another critical difference is that fossil source is produced by natural interaction of dead biomass with the environment surrounding them and it is unknown how many tonnes of biomass produced one tonne of fossil source. On the contrary, biomass to chemicals process must have high productivity and the mass balance is stacked against bio-refineries. While this is challenging, our efforts must continue to focus on the use of biomass since it replaces fossil sources. Where possible, this skewed mass balance must be turned to our advantage by furthering our research. Further, the effect of the natural environment on biomass is not completely simulated in a biorefinery. In view of this, we try to simulate the interaction of biomass with the environment by combining biorefinery and mineral refinery. This inspiration comes from the fact that animals, which are complex chemical systems, take biomass as feed, produce complex (bio) chemicals within their body and leave mineral carbonates as bones at the end of their life cycle.

The objective of this work is thus to demonstrate that it is possible to combine biorefineries and mineral refineries such that synergies can be explored for the benefit of CO_2 mineralization. In view of this, we present details of two chemical processes where the synergies between biomass refining and mineral refining can be explored, and carbon is captured. They are the production of acetone and acetamide/acetonitrile. While the two processes are based on existing know-how, we also apply the concept to demonstrate that the field of "Biomineral refinery" can be developed to exploit the synergies while using raw biomass source. In view of this, we use biomass pyrolysis oil with Serpentine and the concept of Biomineral refinery is introduced by conducting preliminary experiments. In doing so, a multiproduct biomineral refinery is designed; carbon is captured both from biomass and CO_2 and good productivity achieved.

CIRCULAR CHEMICAL ECONOMY WITH BIO-MINERAL REFINERIES

In the natural world, dead biomass degrades by bacterial action while producing organic acids that dissolve the surrounding mineral ores. The process produces mineral salts that serve as nutrients to plant life and plants support the insect and animal life. At the end of their life, the biomass from the insects, plants and animals degrades and the cycle continues. This entire process can be viewed as a circular (bio) chemical system with several recycle loops where the biomass, insects, animals, O_2 and CO_2 are considered as intermediates and energy is input to the system in the form of sunlight (Fig. 1A). Similarly, the processes in the chemical and allied industries can also be visualized where all the materials move in a loop with several recycles and energy is input to the system in the form of heat and electricity.

On further examination, we can see that the animal life leaves mineral carbonates at the end of their life cycle. Hence, the entire process can be viewed as a circular (bio) chemical system that is supported by a linear process where mineral ores are converted to mineral carbonates. We can see that there are synergies between the circular (bio) chemical system and linear mineral processes, and it is this synergy that we must exploit to develop new chemical processes. The overall process can be viewed as the carbon and nitrogen cycles interacting with the linear mineral processes (Fig. 1B). Here we present two processes in support of the Nature inspired 'linear supported circular (bio) chemical system'. They are theoretically feasible and further research must be carried out to evaluate the productivity, energetics, and the economic feasibility. The first is a bio-mineral refinery based on the carbon cycle and the second is based on carbon and nitrogen cycles. Briefly, mineral ores such as Wollastonite and Serpentine are used as raw materials to produce mineral carbonates and other inorganic products. One of the common products of biomass degradation is acetic acid and we present on the use of palm empty fruit bunch (EFB, C6H10.8O3.72) [1] derived acetic acid as one of the raw materials to produce organic intermediates such as acetonitrile and acetone. The materials thus produced can be treated as intermediates and these chemicals can be used as platform materials to produce downstream chemicals. In the proposed Circular Chemical Economy, we consider carbon capture both from biomass and from CO_2 thus limiting CO_2 emissions to the atmosphere.


Part A

Part B

Figure 1. Part A: A tratitional circular (bio) chemical system. Intermediate materials move in cycles with energy from the sun. Part B: A circular (bio) chemical system that is dependent on a linear mineral process. Dotted arrows represents natural processes.

CO_2 MINERALIZATION POTENTIAL

The reactions that may occur in a circular chemical economy to produce fuels and/or chemicals may be written by assuming a general formula for biomass. Given, 'n' is the number of moles of biomass used to produce the products and capture CO_2, 'i' is the number of moles of CO_2 mineralized, 'm' is the number of moles of biomass combusted in order to provide heat to the process and 'e' is the CO_2 consumed/emitted by the process; where 'i' is a positive integer, 'e', 'm' and 'n' are real numbers; when i=0, the proposed bio-mineral refinery becomes a traditional biorefinery i.e., no carbon is captured. The same is depicted in Fig. 2 with reference to the circular economy. Biorefineries emit CO_2 either by way of energy uses in the process or as a byproduct and a sequestration process is necessary to minimize the CO_2 emissions. On the contrary, a part of the carbon is mineralized in Bio-mineral refineries and over a period of several cycles, the amount of carbon mineralized would be far greater than the carbon emitted as CO_2 and thus, the process turns from being a CO_2 emitting process to carbon sequestration process.

We can see from Fig. 2. that carbon is mineralized in each cycle as mineral carbonates; hence the Bio-Mineral refineries become net CO_2/carbon negative processes after a few cycles. The total CO_2 emissions (tonnes/tonne of CO_2 mineralized) can be calculated to be equal to (mx+e)/i and the number of cycles required for the process to become net carbon negative from being a CO_2 emitting process is also (mx+e)/i. We can conclude that 'e' and 'm' must be as small as possible and 'i' must be as large as possible so that maximum amount of carbon is mineralized while the input energy to the process is low. However, as 'm' and 'n' increases, the amount of valuable products produced per ton of CO_2 increases and this needs to be high to recover the cost of production. In view of this, detailed analysis on individual processes is necessary to understand the trade-off between the opposing objectives of maximizing the amount of CO_2 mineralized (with low chemical production) and maximizing the mass of valuable products produced (with low CO_2 mineralization).

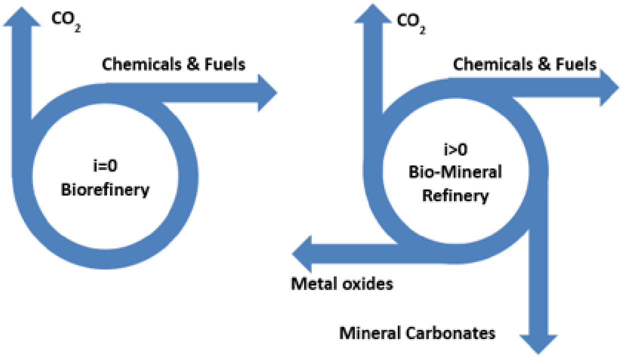


Figure 2. A comparison of circular economy in traditional biorefineries (i=0) and bio-mineral refineries (i>0) is depicted here.

$$iM(OH)_2 + (n+m)C_xH_yO_z + m\left(x+\frac{y}{4}-\frac{z}{2}\right)O_2 \rightarrow$$
$$iMCO_3 + C_pH_{ny}O_q + \left(i+\frac{my}{2}\right)H_2O + (mx+e)CO_2$$

$$where, p = nx - i - e; q = nz - 2i - 2e$$

Bio-Mineral refinery – Carbon Cycle

Acetic acid can be produced from biomass by (bio) chemical action. The chemical process has faster kinetics when compared to the bioprocess and may be suitable for large scale production. First, methanol is produced from biomass derived Syngas, next acetic acid is produced by the carbonylation of methanol (Monsanto and Cativa process) where the carbon monoxide may be produced from biomass derived carbon. Acetic acid can be used for leaching Wollastonite and SiO_2 is precipitated [2] in the process. The salt that is produced, calcium acetate, can be separated and used to produce acetone while calcium carbonate is precipitated [3]. Acetone serves as a platform chemical [4] to produce downstream chemicals such as isopropyl alcohol, propane, solvents (Methyl isobutyl alcohol, methyl isobutyl ketone), Bisphenol-A (Polycarbonates, Polyurethanes, epoxy resins), Methyl methacrylate, among others. Acetone thus produced can potentially reduce the dependence on acetone from the Cumene process and hence some of the crude oil can be used in the production of other petro-chemicals and the overall use of crude oil reduced. Benzene may also be produced in a bio-mineral refinery to offset loss on production via Cumene process. Hydrogen from biomass derived Syngas may be used to meet downstream demand. The schematic of the processes is shown in Fig.3 and the detailed chemical reactions for Fig. 3. are given in Table 1. Briefly, Carbon either from biomass or from CO_2 is converted into mineral form thus removing some of it from the system. While such processes occur in geological time scales in the earth, chemical reactions in chemical plants are targeted to have faster chemical kinetics and it is hoped that the process of mineralization can be fastened.

The carbon and nitrogen cycles-based bio-mineral refinery produces acetamide/acetonitrile by using serpentine. These details, corresponding to Fig. 4., are only shown briefly due to limitation of space.

EFB is used to produce both Syngas which is later used to produce acetic acid. We can see from Table 1 that 1.32 moles of EFB successfully mineralizes 1.9 moles of CO_2 as $CaCO_3$ when Wollastonite is used. This is equivalent to sequestering 0.44 tons of CO_2/tonne of EFB used while producing 0.59 tonnes of acetone and 0.61 tonnes of Silica that can generate income. Like the Wollastonite process, we observed that 1.32 moles of EFB successfully mineralizes 1.9 moles of CO_2 as MgCO3 when Serpentine is used. The same amount of CO_2 is mineralized while producing 1.19 tons of acetamide. The amount of acetamide produced per tonne of EFB is higher compared to the amount of acetone produced. This is obvious because CO_2 is mineralized from biomass when acetone is produced, and flue gas is used as the CO_2 source when acetamide is produced. Here, we have assumed 100% conversion, and the actual values will be much different. In view of this, we take the basis as the amount of valuable product produced as it is straight forward and these values won't be dependent on the conversion, but only on reactions R8 (Fig. 3) or R12 (Fig. 4). When Wollastonite and Serpentine are used, 0.76 tonnes of CO_2/tonne of acetone and 0.37 tonnes of CO_2/tonne of acetamide (or 0.54 tonnes of CO_2/tonne of acetonitrile) is mineralized respectively. We can see that the amount of CO_2 mineralized per tonne of valuable product is large and these processes potentially can be used to produce valuable chemicals while simultaneously capturing CO_2. The CO_2 emissions from the use of energy and the penalty thereof must be estimated separately and this is estimated from the values presented in Table 1. To calculate the energy requirements of the processes, we only consider the endothermic energy of the processes; any gains by heat integration associated with exothermic processes is neglected as these must be subjected to detailed heat integration calculations.

Based on Fig. 4. each cycle 6.95 tonnes or 8.78 tonnes of CO_2 is released into the atmosphere for every tonne of CO_2 mineralized (detailed reactions not shown). Here, the amount of CO_2 released to the atmosphere is large compared to the CO_2 mineralized, and hence the proposed concept of circular chemical economy through bio-mineral refineries holds. In view of this, over a period of 7 and 9 cycles the net CO_2 emitting processes become CO_2 neutral processes since the atmospheric CO_2 is effectively an intermediate that will be taken up in biomass

Table 1: Reactions in a Bio-Mineral refinery that uses palm EFB and Wollastonite as feed. ΔH at a given temperature is calculated using HSC 6.1 software [5]. Calculations for Serpentine (Carbon-Nitrogen cycle) are not shown.

Use of Wollastonite as Feed & Production of Acetone		**Rxn. T (°C)**	**ΔH (kJ)**
Syngas Production (R1)	$C_6H_{10.8}O_{3.72} + 1.14O_2 \rightarrow 6CO + 5.4H_2$	700	2802
Syngas Upgrading (R2)	$6CO + 5.4H_2 + 2.2H_2O \rightarrow 3.8CO + 7.6H_2 + 2.2CO_2$	300	86
Methanol Production (R3)	$3.8CO + 7.6H2 \rightarrow 3.8CH_3OH$	250	373
Carbon production (R4)	$0.32C_6H_{10.8}O_{3.72} + 0.532O_2 \rightarrow 1.9C + 1.71H_2O$	1300	563
CO production (R5)	$1.9C + 1.9CO_2 \rightarrow 3.8CO$	800	-323
Acetic Acid Production (R6)	$3.8CH_3OH + 3.8CO \rightarrow 3.8CH_3COOH$	200	620
Mineral Digestion (R7)	$1.9CaSiO_3 + 3.8CH_3COOH \rightarrow 1.9(CH_3COO)_2Ca + 1.9SiO_2 + 1.9H_2O$	50	209
Mineralisation (R8)	$1.9(CH_3COO)_2Ca + Heat \rightarrow 1.9CH_3COCH_3 + 1.9CaCO_3$	160	-183

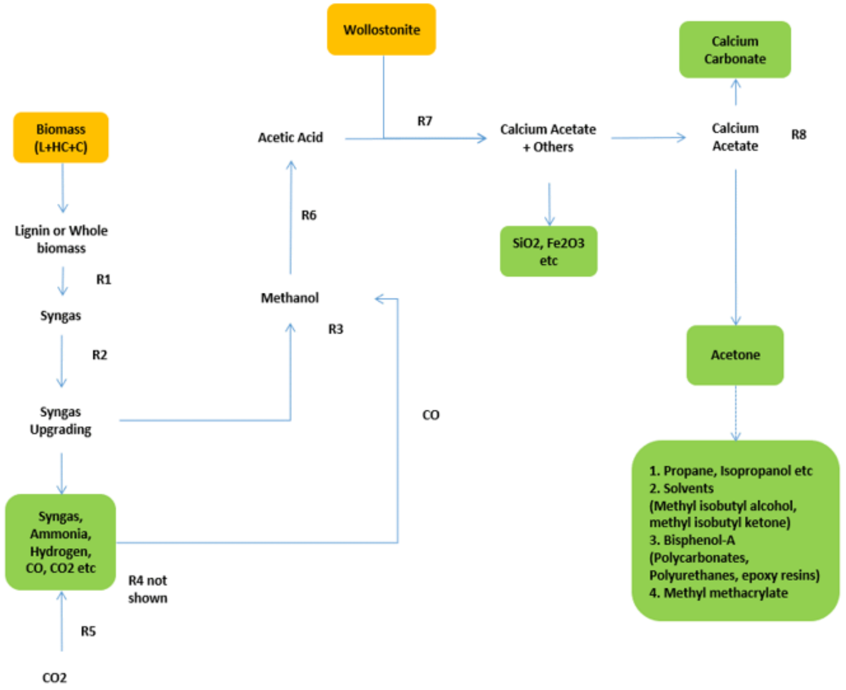


Figure 3: Schematic of the process of producing Acetone from Biomass and Wollastonite. Acetone can be used a precursor to many other chemicals.

regeneration. After the 7 or 9 cycles the processes become purely CO_2 mineralization processes. A cycle is complete when the CO_2 emitted by the process is taken up in biomass regeneration. Hence, biomass doubling time can be considered as time for one cycle i.e., the cycle time is dependent on the biomass growth rate which in turn is dependent on the land area and the type of crop that is cultivated. Clearly, over the long term these processes have the potential to sequester large amounts of CO_2 and effectively de-carbonize the atmosphere. In contrast to the traditional biorefinery where fuels and/or chemicals are produced and no CO_2 is captured, a bio-mineral refinery captures at least some amount of carbon as mineral carbonates and partially prevents atmospheric CO_2 accumulation. This contrast is the key to the successful development of circular chemical economy because the focus is on carbonate accumulation and not on CO_2 accumulation in the atmosphere. EFB is produced at the rate of 18 to 30 tonnes/hectare/year [6]. Considering the lower value of 18 tonnes/hectare/year, each tonne of CO_2 mineralized requires about 0.21 hectares or 0.26 hectares of land for CO_2 recycle and biomass regeneration. However, the land required to produce biomass that is used as feedstock is larger at 0.33 hectares or 0.38 hectares per tonne of CO_2 mineralized since all the carbon in the biomass is not released to the atmosphere, but carbonates and valuable products are produced. Thus, we have demonstrated through two examples that there is scope for developing circular chemical economy with carbon mitigation and the development of other processes to produce valuable products must be explored.

While the proposed routes are interesting, the apparent question is how fast each loop in the circular economy is. To answer such a question, detailed kinetics studies are necessary. While it suffices to say here that since CO_2 of about 10 % (based on less than 10 cycles) is mineralized and that reactions in chemical industries are typically faster in the matter of minutes to hours, we also need to answer this in terms of the amount of mineralization with reference to the mass of products produced. The same was presented earlier as 0.44 tonnes of CO_2/tonne of EFB is mineralized for each of the two processes. While this is theoretical conversion, the efficiency related to energy penalty in such processes are expected to be 50% [7, 8] and may be appropriate to assume that 0.22 tonnes of CO_2 are mineralized per tonne of EFB after scale-up.

Although more such examples exist in literature where biomass derived chemicals can be used for CO_2 mineralization and the production of valuable chemicals in a bio-mineral refinery, the key for successful implementation of the processes in a commercial scale is to use whole biomass so that the number of processing steps and the associated costs are reduced. The possibility that whole biomass, which has a large amount of oxygen, be de-oxygenated by Ketonic decarboxylation must be explored so that valuable hydrocarbons and inorganic products are produced, and carbon is mineralized. Biomass has phenols and other aromatic compounds, and it may (not) be possible to produce higher hydrocarbons which have a high C/O ratio using biomass as feedstock. Considering the variety of compounds in biomass, it would be rather difficult to predict the type of products that can be produced in hydrothermal/thermochemical treatment of biomass & mineral ore mixtures. Further, addition of acid for acid hydrolysis of biomass and/or leaching of the mineral ore and production of salts thereof would lead to increased complexity. In view of this, experiments to study the products and the mechanism of product formation in biomass-mineral interactions are warranted for the development of bio-mineral refinery based circular chemical economy that can at least partially replace fossil fuel based chemical economy. Hence, we have conducted experiments using biomass pyrolysis oil and serpentine mineral and present the same here.

Table 2: CO_2 capture potential of the proposed processes. W-wollastonite; S-serpentine.

	W	S
Endothermic energy required (MJ)	4.65	5.91
Biomass for energy supply (80% energy efficiency, kg)	0.31	0.39
CO_2 emissions from Biomass combustion (kg)	0.57	0.72
Total Biomass required (tons/ton CO_2 mineralized)	5.92	6.91
Total CO_2 emissions (kg)	0.58	0.73
CO_2 emissions (tonnes/tonne CO_2 mineralized)	6.95	8.78
Products produced (tonnes/tonne CO_2 mineralized)	1.32 (acetone)	2.68 (acetamide)
Number of Cycles required for the process to become net CO_2 capture process	7	9
Land area for feedstock biomass production (hectares/tonne of CO_2 mineralized)	0.33	0.38

CAPTURING CARBON FROM BIOMASS

Preliminary Experiments

In this work, we need to first establish if bio-oil would react with Serpentine. In view of this, 20 grams of serpentine were mixed with 260 ml of water-soluble bio-oil (60 ml water soluble component from 100 ml pure bio-oil and 200 ml water) and stirred overnight. Then the solid samples, serpentine that gets disassociated, were collected, and analyzed. We were able to collect 12.8 grams of suspended solids (fine solids), 9.5 grams of settled solids (coarse) and 0.75 grams of magnetic material that sticks to the magnetic bar. The samples were left to air dry for three days inside a fume-hood and weighed again. The measured weights are as follows: 10.1 grams of suspended solids (fine solids), 9.3 grams of settled solids (coarse) and 0.69 grams of magnetic material. It was observed that there was a pH change from 1.0 to 4.3 due to the addition of Serpentine.

Separately, 100 ml of biomass pyrolysis oil is mixed with 200 ml of water. The water-soluble mixture is decanted (260 ml) and 10 g of serpentine is added to it and stirred for 4 hrs. A sample was collected for analysis by GC-MC. This mixture is heated in a Parr reactor at 175°C for 4 hrs. at a maximum CO_2 pressure of 20 barg. The Parr reactor is left to cool over-night before opening. The contents are allowed to settle at RTP for 2 hrs. after opening and before filtration to allow for the dissolved CO_2 to escape. 23 g of cake is collected, and this is allowed to air-dry in a fume hood for two days after which the weight was observed to be 16 g. Elemental Analysis and TGA were conducted on this solid residue. A liquid sample is collected for analysis by GC-MS (results not presented).

Preliminary Results

TGA has shown that there is a 44% weight loss when heated up to 800°C; hence we can conclude that 56% (8.96 g) of the material is inorganic oxides and this is reasonable since serpentine (10 g) is expected to have about 10% water of hydration and this would be lost during calcination at high temperature [9]. The rest of the mass (7.04 g) can be expected to be organic matter. The elemental analysis of the material indicated 41.22% carbon, 0.32% nitrogen, 4.11% hydrogen and 0.21% sulphur, leading to a total weight of 101.8% and this excess can be expected to be due to instrument error.

Alternative uses

One of the uses for the residual water insoluble solids is the production of construction material. With respect to carbon capture, the precipitate so produced can then be compressed into bricks and stored as a material

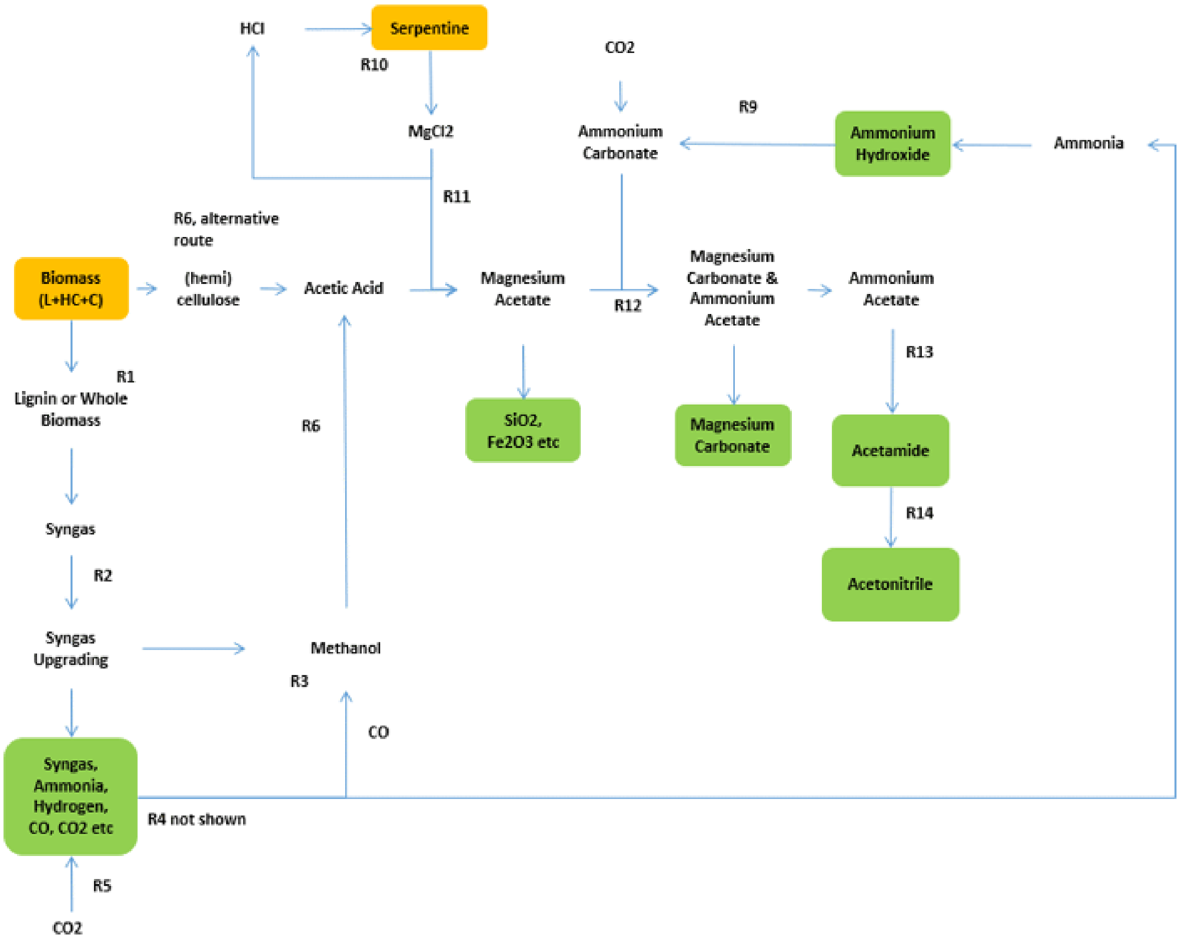


Figure 4: Schematic of the process of producing Acetamide/Acetonitrile from Biomass and Serpentine.

that effectively captured carbon. The solid material was mixed with water and shaken for 15 min and allowed to settle overnight. It was observed that the solid and water separated indicating that the material is largely insoluble in water. The advantage of this process is that the precipitate holds more carbon than if the mineral serpentine were to be reacted with CO_2 and hence this process would require mining of fewer serpentine. In general, a gram of serpentine can hold up to a third of a gram of CO_2 to produce its mineral carbonate [10] and this is equivalent to about a tenth of a gram of carbon. In contrast, the precipitate we produced holds about 0.66 g of carbon per gram of serpentine used. In view of this, it is worthwhile to explore two options; the first is to hydrogenate these residual water-soluble organics to produce a fuel. Preliminary results of hydrogenation of the mixture without the use of an additional catalyst were performed at 10 barg initial H2 pressure and a temperature of 175°C in a Parr reactor. The Parr reactor was allowed to cool overnight, and the hydrogenation is repeated at the same conditions and this process is repeated on 4 consecutive days to test the catalytic effect of the mineral; the resultant liquid samples were analyzed by GC-MS. It was observed that the composition of the product is rather different compared the starting material indicating that serpentine has some catalytic effect, but the process did not produce any fuel or water insoluble materials (results not presented) and it may be necessary to use a commercial catalyst at a higher pressure and/or temperature to produce a fuel. The second option is to use this water-soluble bio-oil as a substrate in a biochemical reactor to produce higher value chemicals in view of the current low crude oil price. Preliminary results have shown that the treated bio-oil is not bactericidal unlike the untreated pyrolysis oil. Notwithstanding the economics, we are of the opinion that this concept must be explored further with a view of developing more Bio-Mineral refineries to mitigate climate change and hence we suggest other possible routes that could be explored.

Other Possible Routes

We present more examples where biomass derived chemicals are used to produce valuable products through decarboxylation. Propionic acid [11], Levulinic acid and Adipic Acid [12], Benzoic Acid [13], Butanol [14] and Butyric Acid [15] can be derived from biomass and used in bio-mineral processes. Briefly, Cyclopentanone and Cyclopentene from Adipic Acid [16], 3-pentanone from Propionic Acid [17], Acetic acid or acetone and a mixture of Cyclopentenones from Levulinic Acid [18], Benzene from Benzoic Acid [19], 5-nonanone from Pentanoic Acid [20, 21] and 4-heptanone from Butanol via Butyric Acid [22] are other examples of bio-mineral processes where different metal oxides are used for decarboxylation. A list of possibilities using two different chemicals in a single Ketonic decarboxylation reaction can be found elsewhere [23]. The ketones so produced can be hydrogenated and dehydrated to produce olefins [24]. Considering that it is possible to capture carbon as a by-product of a chemical process, it may be possible to reengineer the crude oil, biorefinery and mineral refinery supply chains by the development of Bio-Mineral refineries that capture carbon and control climate change. Hence, it may be worthwhile to pursue research in this direction for the betterment of the planet.

CONCLUSIONS

We have proposed a circular chemical economy to produce silica, acetone and acetamide/acetonitrile while capturing carbon as mineral carbonates. The proposed concept relies on the notion that valuable chemicals can be produced in a circular economy while synergies between circular bio-economy and linear mineral economy are exploited. Details of two examples of multi-product bio-mineral refineries are given to demonstrate the concept. Such refineries can capture some of the carbon before it is released into the atmosphere, while also capturing CO_2 from flue gas. We have shown that the proposed processes turn from being net CO_2 emitters to being CO_2 neutral processes in 7 or 9 cycles, after which they can be treated as CO_2 mineralization processes with the production of valuable chemicals as by-products. While the proposed processes are technically feasible, it is of importance to optimize them and identify more such processes, keeping in mind the large number of chemical products that potentially need to be replaced with alternative processes to mitigate climate change. Further, it may be worthwhile to study the use of biomass along with mineral ores and reduce the number of processing steps which have a direct impact on the overall cost of production. Hence, we have conducted experiments using biomass pyrolysis oil and serpentine and these show promise for further studies. In view of this, detailed studies are necessary to further develop this research area.

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