

Optimization of Methyl Lactate from Calcium Lactate & Methanol In The Presence Of Supercritical Carbon Dioxide

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ABSTRACT: The esterification reactions of calcium lactate with methanol and carbon dioxide have been studied in the present article. Additions of a co-solvent, supercritical carbon dioxide (critical point at 31⁰C and 73 bar) for obtain high conversion of methyl lactate at mild temperature, pressure conditions.

A detailed study on the esterification of calcium lactate using methanol and carbon dioxide was carried out to record the effects of various operating parameters (like CO₂ pressure, reaction temperature, reaction time) on the esterification reaction. In the overall reaction calcium lactate reacted with methanol and carbon dioxide for formation of methyl lactate esters and calcium carbonate as by-product. Thus, the recovery and recycle of alkali metal is possible providing a pollution free process for formation of methyl lactate.

KEYWORDS: Esterification; Methyl Lactate; Methanol, CO₂, Calcium Lactate, Calcium Carbonate.

LINTRODUCTION

Supercritical mixtures of methanol in carbon dioxide with methanol mole fractions in the range 0.0939–0.1173 at 323.15 K and pressure from 9.952 to 16.96 MPa. It is well known that the properties of supercritical fluids depend sensitively on pressure and temperature. This makes SCFs attractive as solvents for a variety of chemical, analytical and material processes such as fluid extraction, chromatography, as well as synthesis and analysis. The efficiency, for instance, of some SCFs for replacing toxic industrial solvents is one of the most important reasons for the current scientific interest in such substances. Among several types of solvents, supercritical carbon dioxide appears to be an extremely interesting molecular system, because it satisfies a significant number of requirements for the above-mentioned applications. For this reason supercritical carbon dioxide find a wide range of use as a solvent in the liquid and supercritical state for chemical technologies. As it becomes apparent from earlier studies, the solubility of organic compounds in supercritical carbon dioxide decreases dramatically when their polarity increases. It is worthwhile to note here, that among many polar organic compounds used widely for this purpose are certainly methanol, ethanol, and 2-propanol^[12].

Carbon dioxide is the most commonly used fluid for supercritical fluid chromatography and extraction in part due to its low critical temperature and pressure of 31.06°C and 72.86 atm, respectively^[12]. However, Carbon dioxide often fails to solvate or efficiently extracts large or polar molecules [13]. Methanol are commonly added to CO₂ as solvents to increase the polarity of the resulting mobile phase or extraction fluid. Concentrations of < 1 to 10 mole % of these co solvents are often used in separations methods. Furthermore, SFC systems capable of composition gradients have shown promise when as high as 60% co solvent is used^[13]. Supercritical carbon dioxide is a convenient solvent because it has an easily accessible critical point ($T_c=31.5$ °C, $P_c=74$ bar) and it is non-toxic and non-flammable. There are, however, means that maybe employed to effect increased conductivity in supercritical carbon dioxide for example;

- (i) Addition of small amounts of polar fluids as a co-solvent methanol.
- (ii) Use of a salt with a large hydrophobic cation and anion.
- (iii) Use of a fluorinated ion for increased solubility (e.g. tetra (*p*-fluoro phenyl) borate

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- (iv) A combination of the above. In addition, for electro analytical applications a microelectrode can be coated with an ion-conducting polymer (e.g. poly (ethylene oxide) containing a salt) and, thereby, the polymer phase becomes the electrolyte.

The esters of bio based organic acids like lactic acid, citric acid, etc. fall into the category of benign or green solvents and are promising replacements for halogenated petroleum-based solvents in wide variety of applications. Alkyl esters can be used as additives in a variety of products, including paints, grease removers, packaging, and cleansers. Low-cost salt esters can potentially be used to produce other chemicals such as copolymers of biodegradable plastics, acrylates, glycol, and other specialty chemicals.

In recent years, it has been widely used as a solvent, anti-solvent and plasticizer for synthesis, modification and purification of both synthetic and natural polymers^[1,4]. The solvent properties of SC CO₂, i.e. the solubility of polymers in SC CO₂ and the solubility of CO₂ in the polymers, are two key fundamental subjects in this field. Most pharmaceutical compounds and polymers have demonstrated low solubility in SC CO₂. The advantages of supercritical carbon dioxide have been widely used at the industrial scale for processes like selective extraction, material synthesis and waste destruction.

The chemical process industries, all over the world have been facing the challenges of developing innovative products and processes in the wake of eroding profit margins amidst highly globalized trade competition and fast growing environmental constraint^[1]. Methyl lactate has considerable prospects of industries development in the field of production of biodegradable polymer which are useful for the medical, sanitary fields^[2].

Methyl lactate is one of the important esters of bio based organic acid product having interesting applications at an industrial level. Bio based chemicals typically are environmentally friendly; possess low toxicity, and have favourable biodegradability, making them prime candidates for replacements of petroleum based products. The esters of bio based organic acids like lactic acid fall into the category of benign or green solvents and are promising replacements for halogenated petroleum-based solvents in a wide variety of applications^[3]. Alkyl esters can be used as additives in a variety of products, including paints, grease removers; packaging and cleansers. Low-cost salt esters can potentially be used to produce other chemicals such as copolymers of biodegradable plastics, acrylates, glycol and other specialty chemicals^[4].

Methyl lactate is esters of methanol and lactic acid. Methyl lactates have a variety of application in industries such as cosmetic and pharmaceutical. Methyl esters are water soluble and also fall in the category of green solvents. They are also used in preservative in food processing. Methyl lactate is the most widely existing carboxylic acid has a prime position due to its versatile applications in food, pharmaceutical, textile, leather, and other chemical industries^[5].

II. RELATED WORK

Methyl lactates has molecular formula is CH₃CH(OH)COOCH₃. It is transparent, clear liquid having a characteristic odour with 144.8^oC boiling point. Basically four methods are used for formation of lactates. They are classified as:

- 1) Direct esterification of lactic acid and alcohol.
- 2) Trans- esterification of one ester into another by reaction with alcohol.
- 3) Conversion of a metal lactate or ammonium lactates into an ester by treatment with alcohol.
- 4) Reaction of a metal lactate with an alkyl halide.

In present work we are followed the direct esterification of lactic acid and alcohol for production of methyl esters. Esters are most commonly prepared by the reaction of a carboxylic acid and an alcohol

Reaction of the Direct Esterification:

- 1) In the overall reaction calcium lactate reacted with methanol and carbon dioxide for formation of methyl lactate esters and calcium carbonate as by-product.
- 2) In first step, carbon dioxide reacted with water to form the carbonic acid. This is followed by dissociation of carbonic acid to give protons.
- 3) Second step, carbonic acid reacts with calcium lactate to formation of lactic acid and calcium carbonate as by-product. This reaction proceeds with abstraction of proton by lone pair electron of oxygen of calcium lactate

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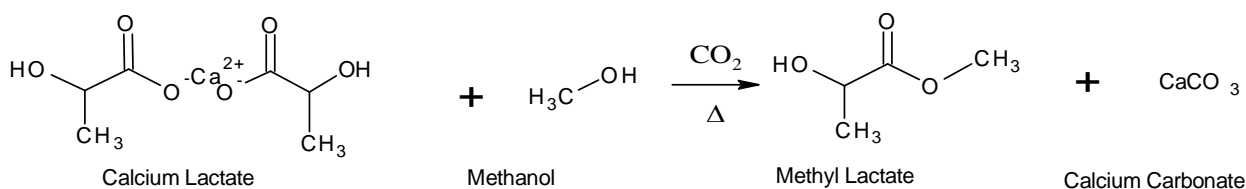
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and creates carbocation which is neutralized by releasing a calcium atom. These calcium ions then combine with carbon dioxide giving calcium carbonate and lactic acid. This reaction appears to be instantaneous.

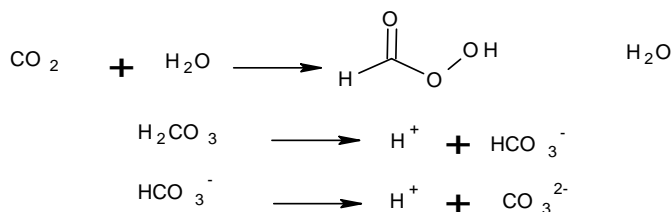
- 4) Third step, methanol reacted with lactic acid to formation of methyl lactates and calcium carbonate. The reaction is autocatalytic because the lactic acid itself acts as reactant and product. From the reaction calcium carbonate gets as a by-product, which environmentally friendly and no any disposal problems.

Overall Reaction and Mechanism of Methyl Lactate

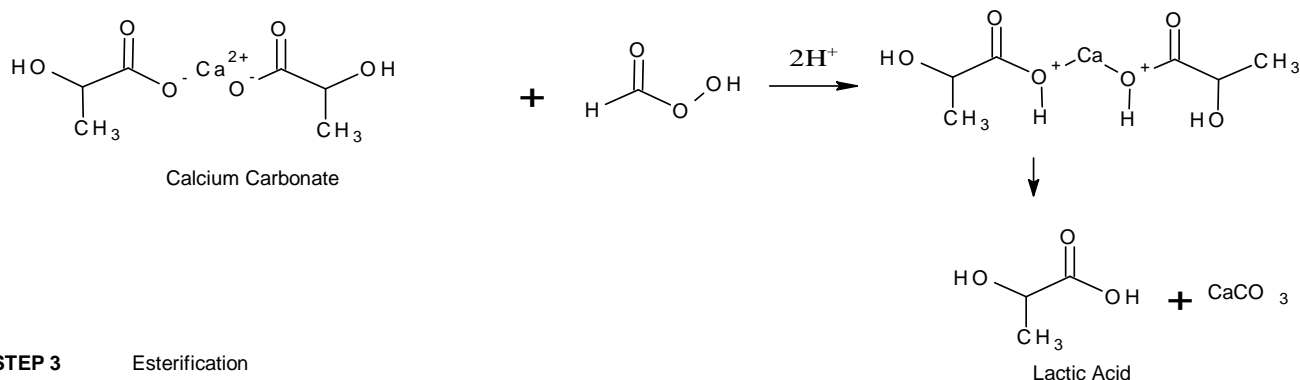
REACTION



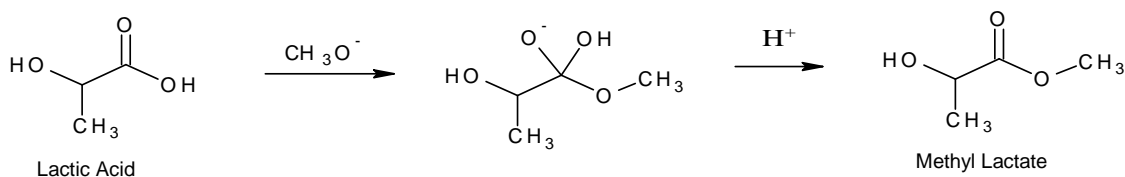
STEP 1 Formation of carbonic acid



STEP 2 Formation of lactic acid



STEP 3 Esterification



III. EXPERIMENTAL PROCEDURE /METHODS

Material: Calcium lactate (purity >99%) was obtained from V. P. Chemicals, Pune, India. Methanol of analytical grade was procured from E. Merck India Ltd., Mumbai. CO₂ Carbon dioxide gas (purity >99.9%) was procured from Deluxe Gas Limited, Pune, India.

Experimental procedure:Dehydration of Calcium Lactate Powder: Calcium lactate powder was dried under vacuum (50 mbar) and at temperature 90-95⁰C using vacuum dryer for 24 hour. The moisture in the calcium lactate was reduced from 23% to 10%, 6% and 1.5%. The dry calcium lactate powder was used in the subsequent experiments.

Direct esterification of calcium lactate using methanol and carbon dioxide: A known quantity of dry alkali metal salt of carboxylic acid and pure methanol was taken in the 83 ml stainless steel reactor fitted with pressure regulator up to 400 bar into the furnaces (Ilesil Innovative Systems, Thane).Then a known amount of carbon dioxide gas at the desired pressure was taken into the reactor through carbon dioxide gas cylinder via CO₂ regulator. Reactor was pressurized with carbon dioxide for 2-3 times and cooled in chillier at -10⁰C for 30 min to *attain thermal equilibrium* condition for condensation of carbon dioxide.

After that reactor was kept at room temperature for attained supercritical state (CO₂ Pressure at 71 bar). Then the reaction mixture was heated in order to reach the desired temperature. Than reactor was heated in furnace with respective temperature, time and different molar ratio. After completion of reaction reactor was cooled for 30 min at room temperature. Than sample was taken from reactor for further analysis.

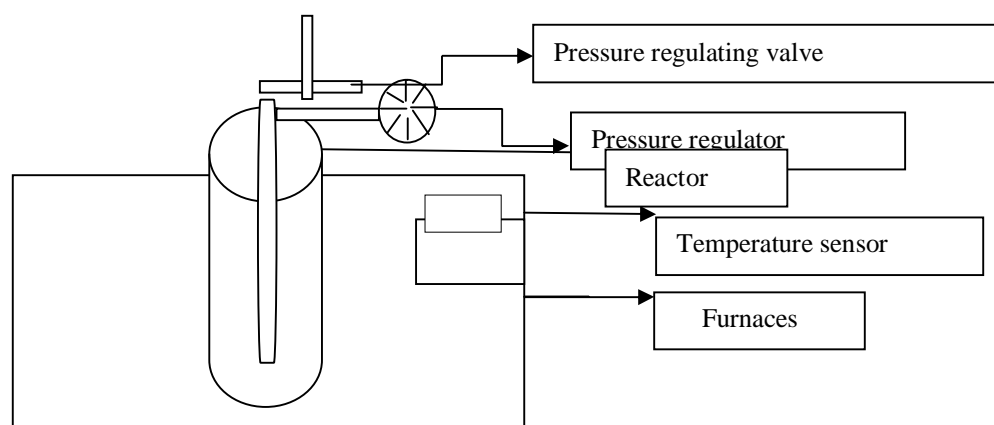


Fig 1: Experimental setup for esterification of alkali metal salts of carboxylic acid

The above figure is experimental setup for esterification of alkali metal salts of carboxylic acid. The reactor was fitted with furnace which made of stainless steel with capacity 83 ml. Pressure regulator was fitted to Stainless steel reactor of 400 bar and one regulating pressure valve. Pressure regulator was used for known pressure level of carbon dioxide and reaction mixture of reactant and products.

IV. EXPERIMENTAL RESULTS

In the design of experiments, eight runs were carried out by two factorial methods for optimization of methyl esters. The three variables were considered for optimization. A positive and negative sign indicates maximum and

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minimum condition. The Design of Experiments (DOE) is a useful tool for identification of operating parameters that affect the reaction and it also helps in reducing the number of experiments to be carried out to achieve optimization.

Where, A: Molar ratio (Calcium lactate: Methanol) B: Reaction temperature (°C) C: Time (hour)

Two Factorial Method:

Operating Parameters	High	Low
Molar Ratio (A)	1:6	1:2
Temperature(B)	120	90
Time(C)	5	2

Table No: 1 Two Factorial Method

Eight batch experiments were carried out to study the effects of various operating parameters like reaction temperature, molar ratio, moisture content in the calcium lactate, reaction time.

Effect of Temperature:For finding the effect of reaction temperature $EE < SV$ so $EE=0.416$ (I) and $SV=120$ (Table 2) Therefore, error value is small than SV so reaction temperature affected on the yield of methyl lactate.

Effect of Molar ratio:For finding the effect of reaction temperature $EE < SV$ so $EE=0.416$ (I) and $SV= -1.36$ (Table 2) Therefore, error value is larger than SV so molar ratio not very much affected on the yield of methyl lactate.

Effect of Reaction Time: For finding the effect of reaction temperature $EE < SV$ so $EE=0.416$ (I) and $SV= -12$ (Table 2) Therefore, error value is larger than SV so molar ratio not very much affected on the yield of methyl lactate.

Effect of Moisture Content in the Calcium Lactate: Initial moisture contain in calcium lactate was 50-55 % after dehydrating it reduces up to 5-6 % with an increase in the initial moisture content, the formation of methyl lactate decreases.

Expt No.	Molar Ratio	Calcium Lactate (gm)	Methanol (gm)	Initial Pressure of CO ₂ (bar)	Final Pressure of CO ₂ (bar)	Temp (°C)	Time (hour)	% Formation
1	1:2	0.09	0.02	80	160	90	5	88.95
2	1:2	0.09	0.02	110	270	90	2	67.75
3	1:2	0.09	0.02	80	110	120	5	81.12
4	1:2	0.09	0.02	80	110	120	2	75.56
5	1:6	0.05	0.06	80	260	90	5	77.77
6	1:6	0.05	0.06	110	270	90	2	77.79
7	1:6	0.05	0.06	110	270	120	5	67.79
8	1:6	0.05	0.06	110	270	120	2	77.72

Table No: 2 Formation of methyl lactates from different molar ratio, reaction temperature and reaction time

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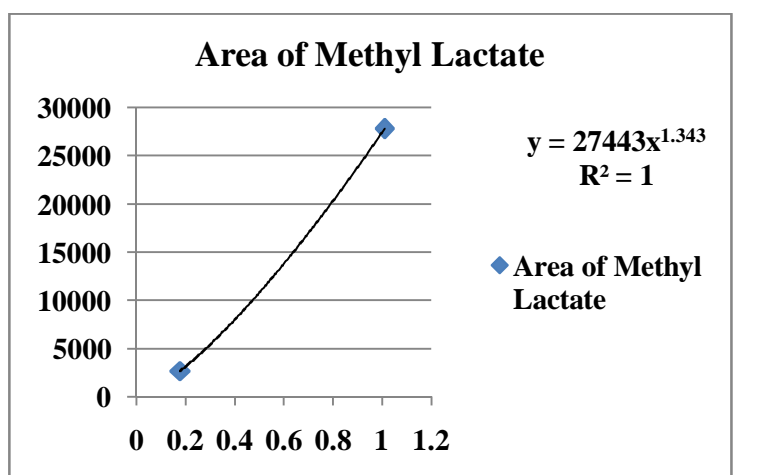
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Sample Analysis: After completion of reaction, the resultant mass was allowed to cool till 30 oC for and the reaction mixture was filtered by filter paper. The moisture content in the calcium lactate and reaction samples were analysed by Karl fisher titration method using automatic Karl-Fischer instrument supplied by M/s Lab India Ltd, Mumbai.

Cont. of Methyl lactate	Cont. of Isopropanol	Cont. of methyl lactate (%)	Area of methyl lactate
0.0177	9.9016	0.17844	2710.7
0.1022	9.9914	1.01	27812

Table No: 3 Calibration of Methyl lactate



Graph No 1 Calibration Curves for Methyl Lactate

From ideal gas law, at low pressure, real gasses behave like ideal gases $PV = NRT$

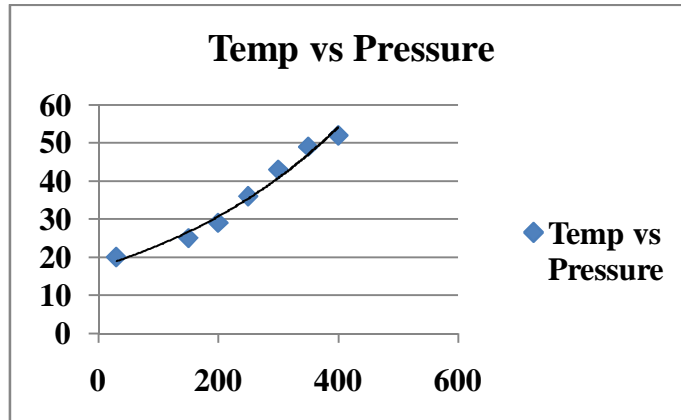
Temperature (°C)	Pressure (bar)
30	20
150	25
200	29
250	36
300	43
350	49
400	52

Table 4 Temperature vs. pressure profile of CO₂ at 20 bar

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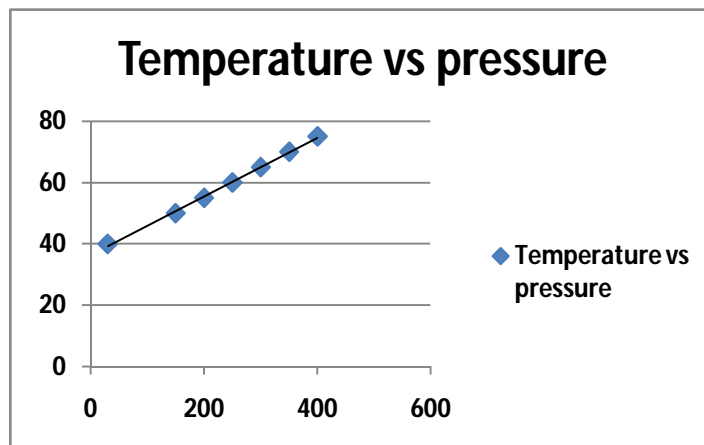
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Graph No 2 Temperature vs. pressure profile of CO₂ at 20 bar

Temperature (°C)	Pressure (bar)
30	40
150	50
200	55
250	60
300	65
350	70
400	75

Table No 5 Temperature vs. pressure profile of CO₂ at 40 bar



Graph No 3 Temperature vs. pressure profile of CO₂ at 40 bar

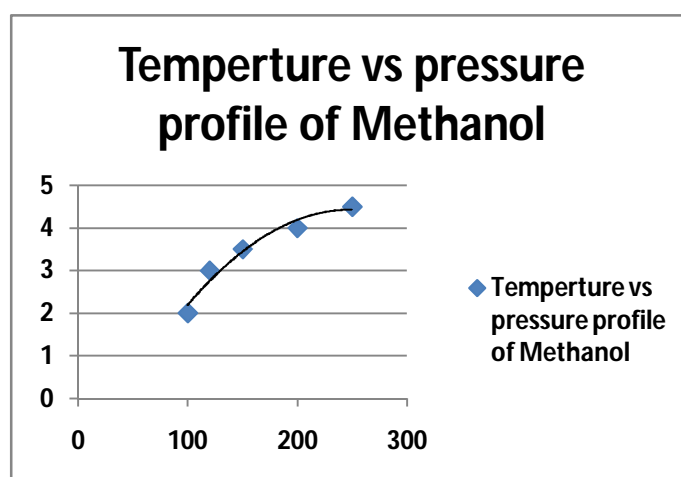
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Temperature (°C)	Pressure (bar)
100	2
120	3
150	3.5
200	4
250	4.5

Table No 6 Temperature vs. pressure profile of Methanol at 4 ml



Graph No 4 Temperature vs. pressure profile of Methanol at 4 ml

V.CONCLUSION

In this process produces methyl lactate by direct esterification of calcium lactate with calcium carbonate as by product. In this processes novel eco-friendly route for the preparation of pure alkyl esters has been presented using alkali metal salts of carboxylic acid, supercritical carbon dioxide, and methanol. The experimental results it was observed that, with an increase in the CO₂ pressure and temperature, the formation of methyl lactate increases. However, with an increase in moisture content in the calcium lactate in methanol, the formation of methyl lactate decreases.

The process route has the advantage that the synthesized by product can be recycled make the corresponding alkali metal lactate or the finely precipitated calcium carbonate can be used for various other applications. Thus, the recovery and recycle of alkali metal is possible providing a pollution free process for pure methyl lactate.

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