2. GREEN CHEMISTRY: PART- II

2.1 SELECTION OF SOLVENT

The selection of appropriate solvent is the most important aspect out of 12 principles. The 5th principle of green chemistry promotes the use of safer solvents and auxiliaries. Solvents are the most common auxiliary substances used in the reactions. Generally, solvents don't react with the reagents, but these are necessary to dissolve, mix all the reagents, and control the temperature of the reaction.

Many conventional solvents are petrochemical organic solvents. These are extensively used in synthesis, extraction, recrystallization and dissolution of solids. Many conventional solvents are toxic, flammable, explosive, and corrosive. Most of them are Volatile Organic Compounds (VOCs). The release of VOCs causes environmental pollution and health issues. It is estimated that solvents are responsible for **60% of all industrial emissions** and **30% of all VOC emissions**.

The selection of solvent depends on many factors. The selected solvent should be stable, inexpensive, readily available, easily recyclable, and environmentally friendly.

Green Solvents: The solvents with minimal environmental impact are called as green solvents. These are also called as environmentally friendly solvents or biosolvents. The most common green solvents are:

- Water
- Ionic liquids
- Supercritical fluids (water, carbon dioxide)
- Biosolvents
- Organic carbonates
- Deep Eutectic Solvents (DESs)
- Fluorous biphasic solvents

2.1.1 Aqueous Phase Reactions

The most important and well-known green solvent is water. It is environmentally friendly solvent. It is nonflammable, harmless, cheap and abundant. It can breakdown ionic and polar compounds. The use of water as a solvent improves reactivity and selectivity, simplifies workup procedure and recycling of catalyst, and allows mild reaction conditions in many reactions.

Advantages

- Non-toxic, no effect on environment.
- Naturally occurring and can replace VOCs.
- Inexpensive, readily available.
- Non-flammable.
- High specific heat capacity, exothermic reactions can be effectively controlled.

Disadvantages

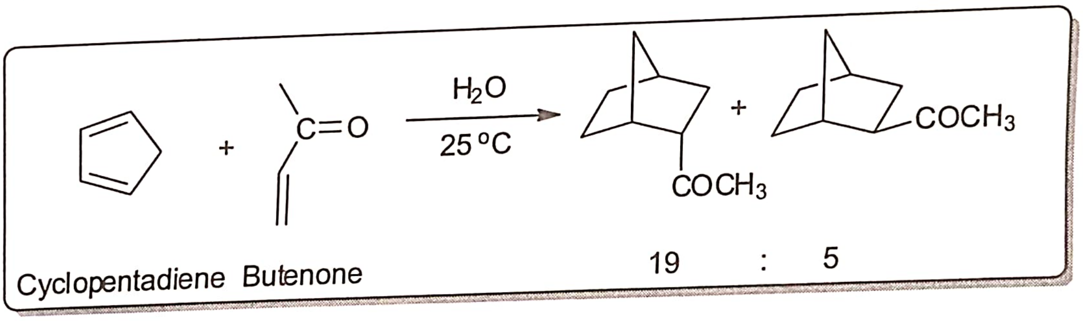
- The separation of solvent requires high energy (distillation is energy intensive).
- Difficult to heat or cool due to high specific heat capacity.

Subcritical Water: The liquid water under pressure at temperatures above boiling point is called as subcritical water. It possesses special properties and functions. It behaves like a polar organic solvent and acts as strong acid and strong base at temperature above 300 °C.

Recently developed important reactions carried out using water as solvent are Diels-Alder reaction, Wurtz reaction, heterogeneous catalytic hydrogenation, addition reactions of carbonyl compounds, pinacol-pinacolone rearrangement, oxidation reactions, reduction reactions, etc.

Diels-Alder Reaction

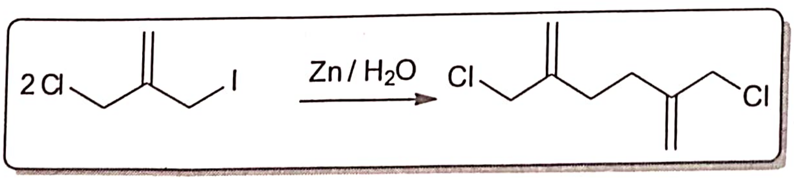
The water mediated Diels-Alder reaction between cyclopentadiene and butenone is about 700 times faster than the same reaction mediated in isooctane (organic solvent) mediated Diels-Alder reaction. It is due to hydrophobic effect of water.



Wurtz Reaction: The conventional Wurtz reaction involves formation of alkanes by coupling of alkyl halides with sodium in dry ether.

$$\underset{\text{Alkyl halide}}{2\ R{-}X} \xrightarrow{\text{Na / dry ether}} \underset{\text{Alkane}}{R{-}R}$$

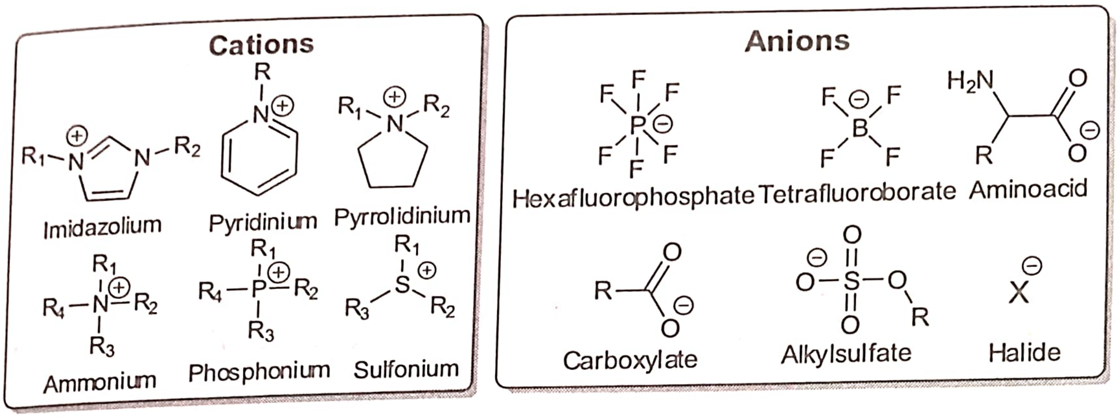
Wurtz coupling reaction can be carried out with zinc in water medium (Zn/H_2O)



2.1.2 Reactions in Ionic Liquids

Ionic liquid (IL) is an organic salt in the liquid state at room temperature with the melting below 100 °C. Even though ionic liquids are ionic salts, these are liquids at room temperature due to poor packing of ions. It is achieved when ions in the ionic liquids are large, non-coordinating, and asymmetric. Ionic liquids are non-volatile and can replace VOCs and reduce or eliminate the environmental hazards of VOCs.

The most commonly used cations anions in ILs are listed below.



The most commonly utilized alkyl chains are methyl, ethyl, butyl, hexyl, octyl, and decyl.

Advantages

- Readily prepared.
- Non-volatile.
- Non-flammable.
- Can act as catalyst.
- High ionic conductivity in molten or solution state.
- Tunable viscosity, acidity, basicity and melting point. By varying cation-anion size ratio, type and length of the alkyl chain, the properties can be changed.
- High thermal stability: Stable at temperatures over 300 °C, can carry out high-temperature reactions at low pressure.
- Highly solvating and non-coordinating.
- Recyclable.

Disadvantages

- Non-biodegradable.
- Concerns over toxicity.
- Synthesis often requires haloalkanes.
- Product isolation often requires distillation or extraction into an organic solvent.

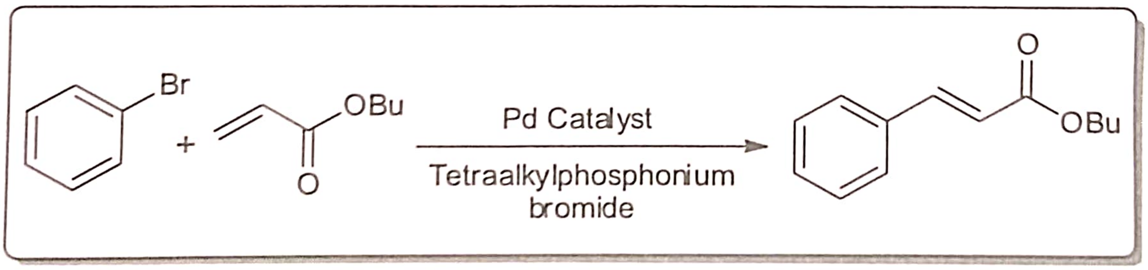
The following reactions are successfully performed in ionic liquids: Diels–Alder, Friedel–Craft alkylation and acylation, Heck and Suzuki coupling reactions, oxidation, epoxidation, cyclization, polymerization, hydroformylation, and hydrogenation of alkenes.

2.1.2.1 Heck Reaction

The palladium-catalyzed coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base is referred as the Heck Reaction.

Heck reaction is one of the best methods to prepare substituted alkenes. However, the conventional Heck reaction has certain limitations such as decomposition of catalyst, low activities and selectivities, difficulty in isolation of products and catalyst. In recent times, ILs such as quaternary ammonium, pyridinium and imidazolium salts have been used as solvent for the Heck reaction of alkenes with aryl halides. The solvent modifications to Heck reaction improved activity of catalyst and regioselectivity of the reaction.

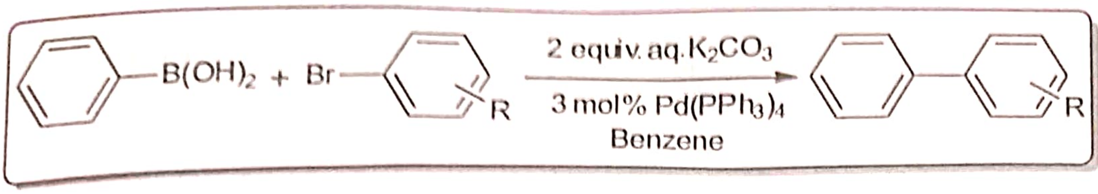
The first example for Heck reaction in ILs is synthesis of trans-cinnamates by the reaction of bromobenzene with butyl acrylate catalyzed by palladium salts. Tetrabutylammonium bromide (TBAB) and tributylhexadecylphosphonium bromide (TBHPB) were used as ILs.



2.1.2.2 Suzuki Reaction

The palladium (0) complex catalyzed coupling reaction of aryl- or vinyl-boronic acid with aryl- or vinyl halide is known as Suzuki coupling. It is extensively used for the synthesis of polyolefins, styrenes, and substituted biphenyls. The cross-coupling reactions have been studied in a range of ionic liquids at ambient temperature. The bromoarenes react very fast in ILs and isolation of product is very easy.

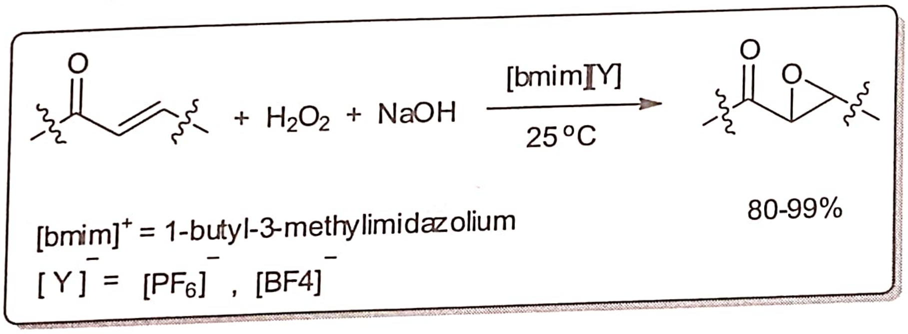
The conventional Suzuki reaction of bromobenzene with phenylboronic acid forms biphenyl with 88% yield in 6 h. The same reaction in ionic liquid [bmim][BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate) formed biphenyl with enhanced yield of 93% in 10 minutes with high turnover number of catalyst.



After the work up of the Suzuki reaction, the ionic liquid/catalyst system was reused for three times without effecting the yields of the products and turn over frequency of the catalyst.

2.1.2.3 Epoxidation

Ionic liquids are useful for conducting the epoxidation of alkenes. Epoxidations of electrophilic alkenes can be carried out using a mixture of an ionic liquid containing the substrate and aqueous hydrogen peroxide in the presence of a simple base catalysts such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$). Epoxidation of electron-deficient α, β-unsaturated carbonyl compounds takes place at room temperature with very high selectivities, high yields and high rate of reactions.



2.1.3 Solid Supported Synthesis

Earlier chemists believed that solvent is necessary for conducting a reaction. Recently, studies have shown that many reactions are possible in solid state without the solvent. In many solid-state reactions, the efficiency and selectivity are more than that of reactions carried out in solvents. Further, the solid-state reactions are simple to handle, cheaper to operate, and ecofriendly.

The most amount of waste generated from the industries is due to using of solvent in chemical reactions. It can be reduced by designing solvent free solid supported organic synthesis or solid supported organic synthesis.

Solid supported organic synthesis involves using of solvents and solid supporters. The most commonly used solvents are water, alcohol, methylene chloride, etc. The most common solid supporters are alumina, silica gel, zeolite, clay, phyllosilicate, polymeric resins, etc.

In solid supported synthesis, the reactants are dissolved in a suitable solvent. The resulting solution is stirred with solid supporter. Later, the solution is dried by removing solvent in vacuum.The obtained solid is used to carry out reaction.

Advantages

- Solid-supported reagents can be removed easily by filtration.
- Recycling of reagents is cheap, environmentally friendly and efficient.
- Tunable chemical properties.
- Toxic, flammable and explosive reagents can be handled easily by solid supporters
- The solid supported reactions are very selective than that of unsupported reactions

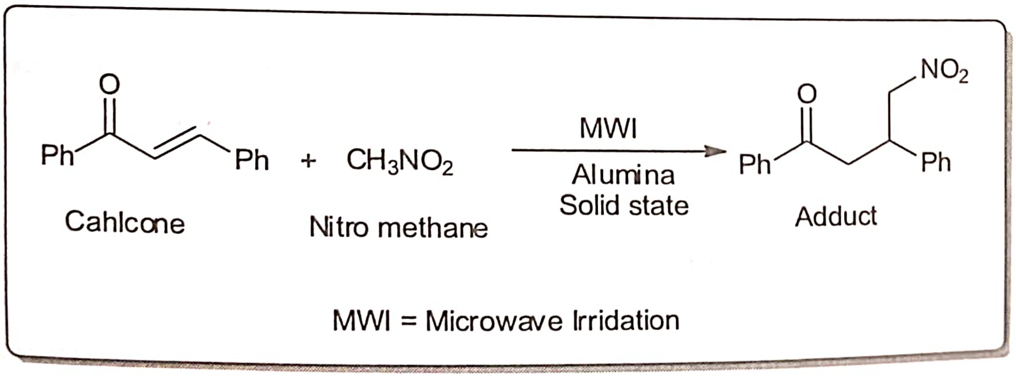
Disadvantages

- The interaction of supporter with some reagents may be poor.
- Recycling of reagents is difficult in some reactions.
- Reactions may be slow due to slow diffusion of reactants.
- Some supporters like polymeric materials are expensive.
- The thermal stability of some supporters is poor.
- Side reactions may be possible in some polymeric supported organic synthesis.

Solid supported synthesis has been used extensively in selective reduction, selective esterification, preparation of many heterocyclic compounds and Michael addition reaction

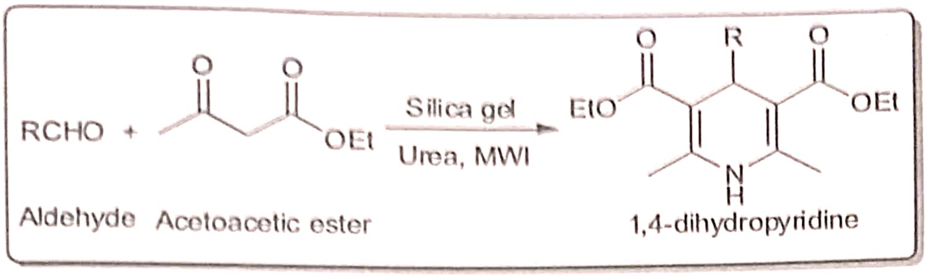
Michael Addition Reaction

The reaction of nitromethane with chalcone in the presence of alumina under microwave irradiation condition forms adduct with 90%.



Synthesis of Pyridines

The reaction of aldehyde with acetoacetic ester and urea in presence of silica gel under microwave irradiation (MWI) forms 1,4-dihyropyridine. The reaction is very rapid and high yielding.



2.2 SUPERCRITICAL CO_2

Supercritical fluid (SCF) is any substance at a temperature above its critical temperature (T_c) and at a pressure above its critical pressure (P_c). Generally, a gas is converted into liquid by increasing pressure on gas. However, above critical temperature, the increase in pressure can't convert gas into liquid but it forms a state in which both liquid and gas coexist, and the boundary between gas and liquid is disappeared. SCF is a homogeneous fluid and exhibits the properties of liquids and gases simultaneously.The properties such as density, diffusivity, and viscosity of SCFs are in between liquids and gases. The most commonly used gases as SCFs are CO_2, C_2H_6, NH_3, H_2O, etc.

Supercritical CO_2 ($scCO_2$) is formed above its critical temperature, T_C (31.1°C) and critical pressure, P_C (72.8 atm). $scCO_2$ is one of the most widely used SCFs due to its special properties.

Advantages

- Chemically inert.
- Non-inflammable.
- Non-toxic.
- Cost-efficient.
- Readily available with high purity.
- High diffusion rates and low viscosity.
- Easily separated from the reaction.
- Potentially recyclable.
- Ease of control over properties.

Disadvantages

- The production of $scCO_2$ involves very expensive and complex high-pressure equipment.
- Low solubility for polar compounds.
- Reactive with powerful nucleophiles.
- Relatively poor solvent.
- High power consumption.

2.2.1 Preparation of $scCO_2$

The phase diagram of CO_2 shows the forms of solid, liquid and gas phases at different temperatures and pressures. The point obtained at critical temperature and critical pressure is called as critical point (CP) ($T_C = 31.1°C$, $P_C = 72.8$ atm). Beyond CP, the increase in temperature can't transform the material from liquid to gas and increase in pressure can't transform gas to liquid. The $scCO_2$ can be prepared in two ways. One is increasing the pressure first above P_C (72.8 atm) at constant temperature and then increasing the temperature above T_C (31.1°C) at the stable pressure. Other way is increasing the temperature above T_C at constant pressure and then increasing the pressure above P_C at the stable temperature.

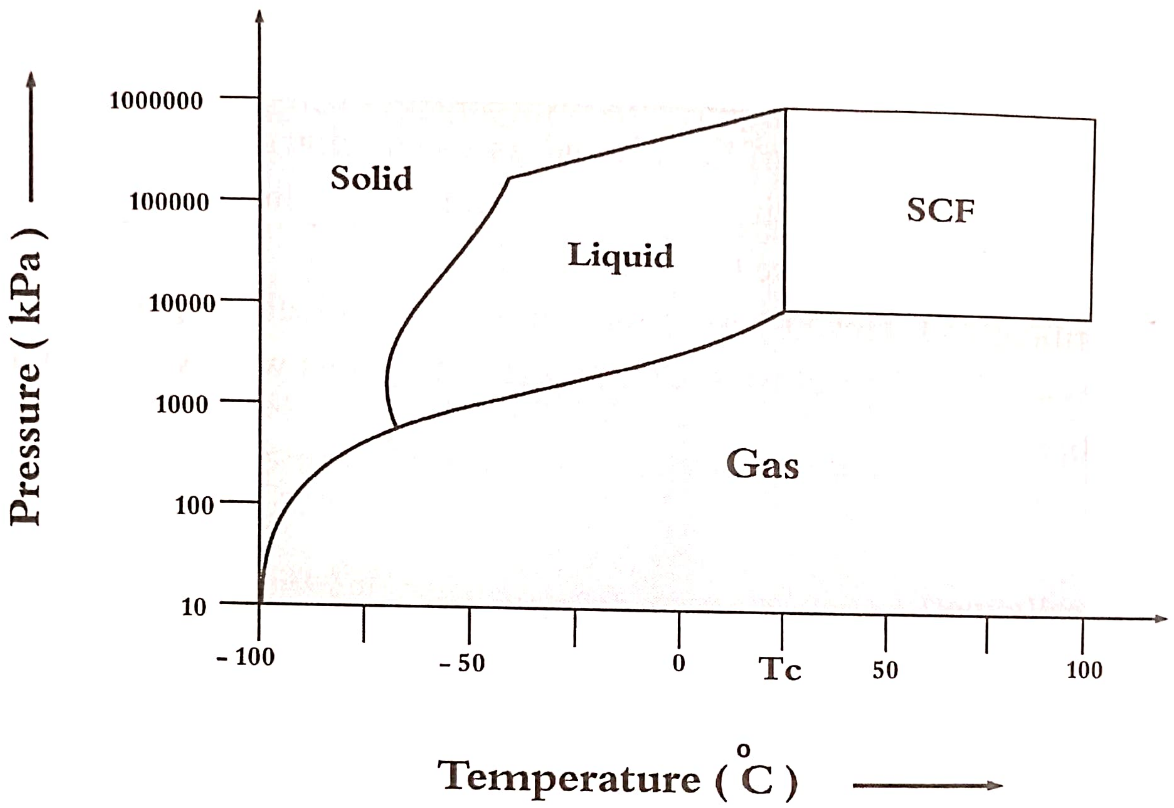


Fig. 2.2.1 Phase diagram of CO_2

2.2.2 Properties of $scCO_2$:

- Dissolves materials like liquid.
- There is no surface tension like gas.
- It has a very good solvent property.
- In supercritical environment, only one phase exists and hence no liquid-gas phase boundary.
- Close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties to be "fine-tuned".

2.2.3 Applications of $scCO_2$

- It is largely used in food & flavoring industry to preserve food.
- It is used for decaffeination of tea & coffee.
- It is used in drycleaning.
- It is used in extraction of essential oils, aroma materials from spices, etc.
- It is used in organic synthesis.

2.2.3.1 Decaffeination

The $scCO_2$ is mostly used in extraction of caffeine from the coffee beans since 1970s. Previously, dichloromethane, ethyl acetate, trichloroethane, etc., solvents were used in decaffeination of coffee beans, but these are volatile and harmful to environment. These volatile solvents are replaced by $scCO_2$.

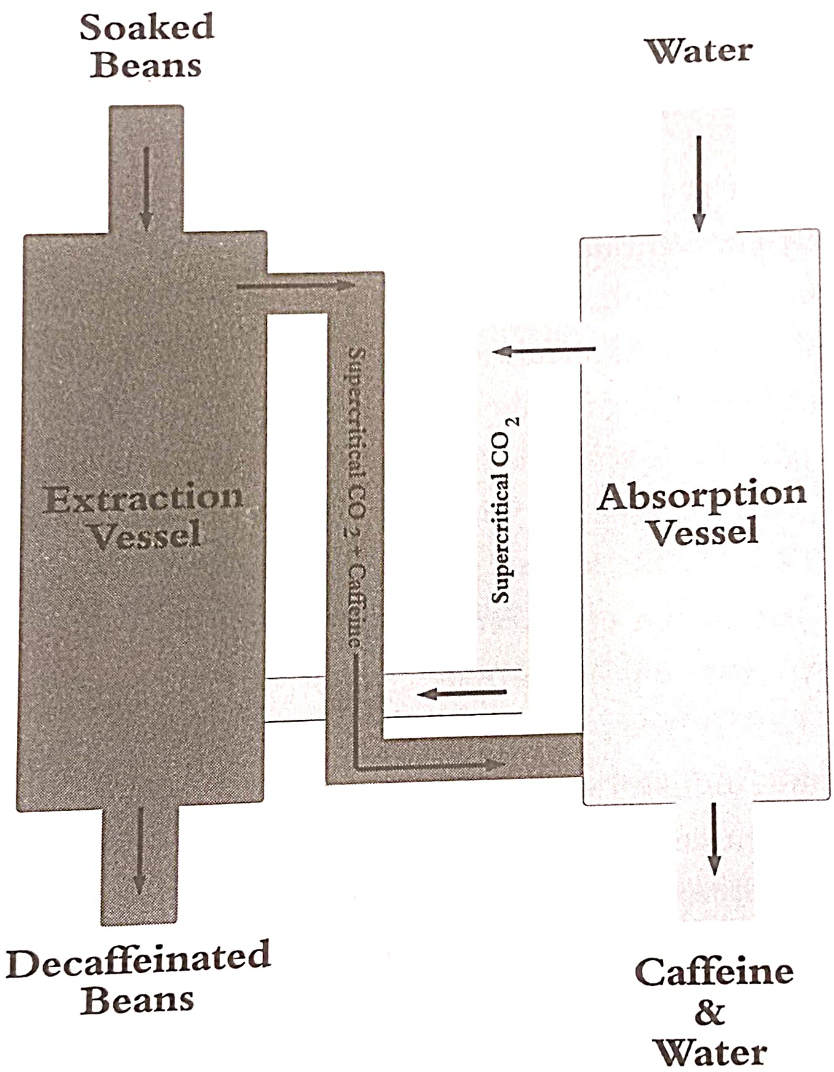


Fig. 2.2.3.1 Decaffeination using $scCO_2$

The decaffeination process involves the following steps:

1. Green coffee beans are soaked in hot co-solvent (water or ethanol) inside a sealed extraction vessel till they are 50% saturated with co-solvent.
2. $scCO_2$ is pumped into the container at high pressure to dissolve the caffeine in $scCO_2$.
3. Water in absorption vessel removes the caffeine from the carbon dioxide.
4. After that the $scCO_2$ is moved into a low-pressure vessel to evaporate $scCO_2$.

Advantages

- There is no harmful residue because CO_2 is a safe and non-toxic material. It is completely removed from the decaffeinated coffee and also from the aqueous solution.
- The quality of product obtained by this method is superior to other decaffeination methods.

2.2.3.2 Drycleaning

Drycleaning is a process used to clean garments using a solvent other than water. The purpose of it is cleaning of garments without affecting the size, fabrics and colors of the garment. The process of dry cleaning was started in 1850s to remove stains and clean garments with petroleum-based solvents such as perchloroethylene, petroleum ether, and trichloroethane. In the early 1900s perchloroethylene (PERC) was widely used in the drycleaning industry due to its cleaning ability and potential to clean wide range of garments. The PERC is a carcinogenic and exposure to it causes irritation of the eyes, nose and throat. It also contaminates ground water.

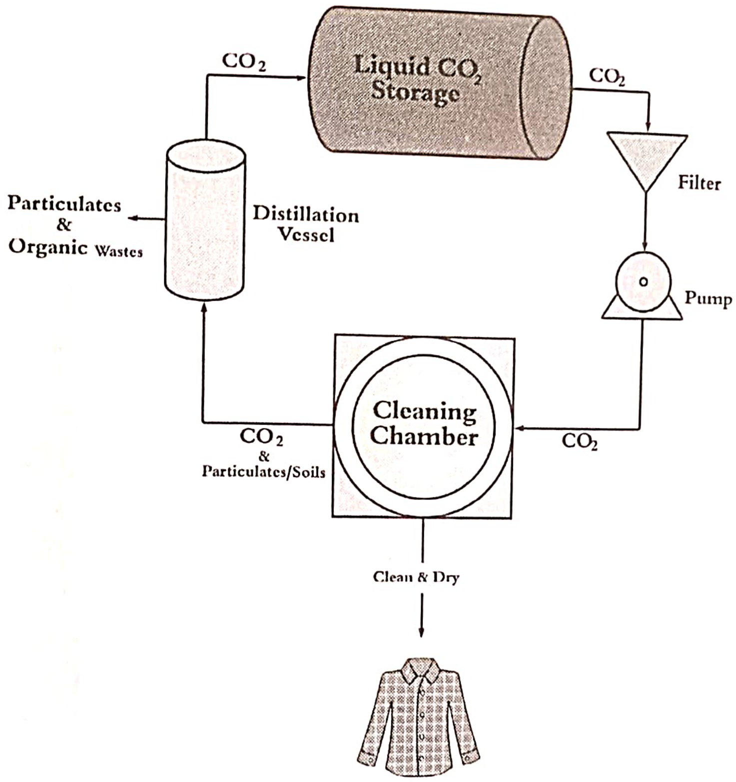


Fig. 2.2.3.2 Drycleaning using $scCO_2$

A green solvent supercritical carbon dioxide replaced PERC (perchloroethylene) and other petroleum-based solvents for drycleaning.The drycleaning process is similar to process involved in washing machine. It requires 3 steps: (1) washing the fabric in solvent (2) spinning to extract excess solvent, and (3) drying by tumbling in a hot air stream.

Disadvantage: Supercritical carbon dioxide sometimes inserts into buttons and when it is depressurized, the buttons are damaged.The major drawback of it is it has limited power to dissolve polar or non-volatile compounds.

2.3 GREEN ENERGY AND SUSTAINABILITY

Definition of Green Energy: Green energy is the energy generated from infinite renewable sources that does not produce carbon emissions and not negatively impacting the environment. It is generally originated from renewable, environmentally friendly and more sustainable natural sources like sunlight, wind, rain, tides, plants, algae, and geothermal heat.

Types of Green Energy: The main forms of green energy are wind, solar, geothermal, tidal and low-impact hydroelectric power energy.

- *Wind Power:* The generation of wind power is suitable at offshore and higher altitude areas. The flow air turns the blades and generates power. It is a renewable and a clean energy.
- *Solar Power:* Photovoltaic cells absorb energy from sunlight and turn it into electricity. The process is renewable and clean.
- *Geothermal Energy:* Hot water reservoir releases steam which rotates turbines and generates electricity. It is renewable since the earth has unlimited hot water reservoirs, and it is also clean because it emits minute amount of greenhouse gases (GHGs).
- *Tidal Energy:* The rise and fall of tides turn turbines and generate electricity. It is a renewable source of energy and a clean energy.
- *Low-impact Hydropower:* The hydropower project which generates 10 MW or less power is a green energy since it releases less amount of GHGs. It is renewable since water cycle is a continuous cycle.

Importance of Green Energy: Energy plays a crucial role in chemical reactions. All chemical reactions whether it is exothermic or endothermic need energy to convert reactants into products. The socio-economic development of a country depends on energy source. Recently, increase in population and economic growth accelerated increase in energy consumption. The demand of energy can be met by designing energy efficient processes or generation of green energy from renewable sources. Green energy is important for protection of environment because it replaces negative effects of finite fossil fuels such as oil, coal and natural gas.

Sustainability: It is the ability to exist and develop without depleting natural resources for the future. It is the development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

Environmental protection, social development and economic development are three pillars of sustainability. The United Nations designed 17 Sustainable Development Goals (SDGs) or Global Goals in 2015 to achieve a better and more sustainable future. The 7th Goal of SDGs aims at ensuring access to affordable, reliable, sustainable energy by using modern technology, improving energy efficiency and increasing share of renewable sources. The goal is achieved through generation of green energy.