Final Report

Investigation and demonstration of close coupled gasification and combustion of raw glycerin and canola hull fiber fuel pellets/briquettes
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Investigators

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ABSTRACT

Original canola meal (mixture of canola meal and canola hull fibers) and crude glycerol were characterized for their physical and chemical properties. Several process variables were examined for their effects on the bulk heating value and handling characteristics of fuel pellets made from canola meal using crude glycerol from the biodiesel production process as a binding agent. Pressure, temperature, average particle size and crude glycerol concentration were varied to determine the optimum operating conditions for pelletization process. The heating value of canola meal was found to be ~20 MJ/kg, whereas for pellets prepared with 5 and 10 %(w/w) of crude glycerol was in the range of 21.5-22.0 MJ/kg.

In the further study, protein extracted canola meal (deproteinated canola meal) was used to study the production of syngas from the gasification process in a fixed bed reactor system. The effects of gasification temperature and equivalence ratio (ER: Equivalence ratio is defined as the ratio of actual air fuel ratio to the stoichiometric air fuel ratio) on the gas products were investigated in a two-stage reactor system. It was observed that the yield of H_2 and CO increased with an increasing temperature and ER. A maximum H_2 content of 72.2 mole% (Mole of component ‘A’ in gas phase / Total moles of gas phase) and highest H_2/CO ratio were obtained at 735 °C and ER of 0.27. The optimum conditions for high lower heating value (LHV) of product gas obtained 11.4 MJ/Nm^3 was at 815 °C and ER of 0.2. For all operating conditions, LHV of product gas varied between 9-12 MJ/Nm^3. The suitable H_2/CO ratio of the product gas makes it suitable for applications such as methanol production. Use of dolomite as catalyst for tar cracking in the second reactor decreased tar yield by 50% and resulted in the total syngas production of 1.14 Nm^3/ kg of biomass, while the hydrogen gas yield increased to 0.78 Nm^3/kg.

In addition to this study, non-catalytic gasification of canola meal for the production of syngas was studied in lab-scale fixed bed gasifier and pilot-scale fluidized bed gasifier. Various experiments were undertaken in order to study the effects of different gasification parameters on gas composition, H_2/CO ratio, gas yield, syngas yield, LHV, and carbon efficiency (CE). Fixed-bed experiments were performed to study the effects of operating temperature in the range of 650–850°C and equivalence ratio in the range of 0.2–0.4. Steam, carbon dioxide (CO_2), and oxygen (O_2) were used as gasifying agents. The experimental results show that steam gasification delivers a gaseous product with a high H_2/CO ratio (2.7) and LHV (193.0 MJ/Nm^3).

Oxygen gasification attributed to maximum CE (65.5%). CO_2 gasification contributes to high gas yield (82.8 mol/kg biomass). During fluidized bed gasification study, it was found that using steam as gasifying agent leads to more H_2 production as compared to that for O_2 and CO_2 gasifying agents. Thus, it leads to high H_2/CO ratio, syngas yield, and LHV of product gas.

Finally, the study focused on pelletization of canola meal biomass to increase the bulk density, thereby reducing the transportation and storage costs, thus provide better material feeding with less dust formation. The study investigated the effects of additives as well as pelletization process parameters on canola meal pellets. The effects of additives such as binder, lubricant and moisture content along with effects of applied load and temperature on the quality of pellets were evaluated in terms of pellet density, durability and hardness. The effects of feed constituents of canola meal such as protein, fiber, fat, lignin and feed moisture content as well as feed conditioning temperature, added binder and lubricant (supplied by Evergreen Biofuels Inc.) and densification process parameters on the strength and durability of the densified product are investigated. The increased durability (99 %) of canola meal pellets was a result of added binder, 5 %(w/w) and the inherent protein, 40 %(w/w) and lignin, 12 %(w/w) content in the feed. Optimized pellets with 99% durability and 189 N hardness were produced at an applied load of 3500 N and a temperature of 90ºC with the 5% (w/w) binder, 2 %(w/w) lubricant and 12 %(w/w) moisture content. From the compression data at different temperature and pressure, Kawakita and Ludde model was developed to classify the feed material into groups. The R^2 value >0.999 showed good model fit. It was found that at temperature >70ºC, the particle undergoes rearrangement followed by fragmentation and particle plastic deformation during the compression process. The effects of coating agent on pellet durability, hardness and moisture uptake were studied to produce moisture-resistant pellets. Finally, the pellets were gasified in a fixed bed reactor using different gasifying agents such as steam, O_2 and CO_2 were assessed. Carbon dioxide was found to give maximum CE up to 82.7% and 50.7 MJ/Nm^3 LHV of gas at a temperature of 750 ºC and ER of 0.4. Whereas, O_2 gave 66.5 % of CE with 44.7 MJ/Nm^3 LHV of gas at 650 ºC and 0.4 ER and steam produced gas with LHV 40.8 MJ/Nm^3 with CE 27.4% at 650 ºC and 0.2 ER. Thus, by producing moisture-resistant canola meal pellets with reasonable fuel characteristics, pelletization of canola meal provides a promising alternative for the utilization of canola meal waste as an alternative source of renewable energy.

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ABBREVIATIONS

AAFC:	Agriculture and Agri Food Canada
AAFCO:	Association of American Feed Control Officials
ANOVA:	Analysis of Variance
ASABE:	American Society for Agricultural & Biological Engineering
BBD:	Box Behnken Design
CE:	Carbon efficiency
CEN:	European Committee for Standardization
CO_2:	Carbon Dioxide
DTG:	Differential themogravimetry
ER:	Equivalence ratio
FAME:	Fatty acid methyl ester
FFA:	Free fatty acids
FID:	Flame ionization detector
GC:	Gas chromatography
GY:	Gas yield
HHV:	Higher heating value
HPLC:	High-performance liquid chromatography
ICP-MS:	Inductively coupled plasma-Mass spectrometer
LHV:	Lower heating value
O_2:	Oxygen
SDS:	Sodium dodecyl sulfate
SDS:	Sodium Dodecyl Sulfate
SEM:	Scanning Electron Microscope
SY:	Syngas yield
SYNGAS:	Synthesis gas
TCD:	Thermal conductivity detector
TG-DTA:	Thermogarvimetric-Differential thermal analysis

1. INTRODUCTION

As demand for diversified, easily transported, carbon-neutral energy from biomass increases, there is increasing use being made of "waste" biomasses, such as sawdust, wheat and flax straw, as well as soy and almond hulls (Stelte, 2011; Shaw, 2008; Rentsen, 2010). One of the most cost-effective ways to use these waste materials is pelletization (densification). Biomass material is ground and pressed in a mill to allow cellular components to bond with one another. Pelletization drastically reduces storage space for the loose material and greatly increases the energy density per unit volume. It also improves handling characteristics, significantly reducing dust-related fire and health hazards. These biomass pellets are burnet for electricity in former coal-fired electrical plants and in domestic stoves for heating and cooking (Stelte, 2011; Shaw, 2008; Rentsen, 2010).

Canola seeds contain > 40 % (w/w) of oil, which is widely used as a vegetable oil. The solid product after oil extraction from canola seed is used to feed livestock due to its high protein content ~35 % (w/w). It includes fiber, carbohydrate, protein, moisture and ash (mineral compounds). Canada produces ~ 12.7×10^6 tonnes of canola seeds in 2010-11 which is estimated to reach a value of $15*10^6$ tonnes per year by 2015 (Stelte, 2011). As per the Agriculture and Agri Food Canada's (AAFC) canola outlook 2010-11 report, canola meal production for 2010-11 was 3.3×10^6 tonnes up by more than 20 % against previous year's 2.7×10^6 tonnes. In addition, excess use of protein can cause feed formulation challenges including reduced feed efficiency due to increased protein metabolism (Shaw, 2008). This puts an emphasis on looking into alternate applications of canola meal. Depletion of conventional energy resources with time and increasing demand for energy makes it logically viable to explore the use of a biomass such as canola meal as a renewable source of energy.

Canola meal, one of the industrial wastes, widely available and traded, usually sold in bulk form as a mash or in pellets. Canola meal generated from oil industries generally used for the animal feed and can be used as one of the abundantly available source of biomass for the production of syngas. Similar to the waste canola meal production, crude glycerol is one of the industrial waste by-product obtained during the production of biodiesel. Biodiesel is one of the alternative fuels used to meet our energy requirements and also carbon dioxide emission is much lesser when compared to regular diesel fuel. Biodiesel and glycerol are produced from the transesterification of vegetable oils and fats with alcohol in the presence of a catalyst. About 10 % (w/w) of vegetable oil is converted into glycerol during the transesterification process. An increase in biodiesel production would decrease the world market price of glycerol. For every tonne of biodiesel produced, approximately one hundred kilograms of crude glycerol are produced as a by-product. While there is demand for glycerol in pharmaceutical, hygiene and skincare products, there is not enough demand to keep up with the supply of glycerol created by current levels of biodiesel production. As biodiesel production increases, it will increase the amount of crude glycerol produced.

The low bulk density of biomass (< 150 kg/m^3), irregular shapes and different sizes limit their transportation, storage and utilization in actual form (Gilbert et al., 2009; Bowyer and Stockmann, 2001; Sokhansanj et al., 2006). To overcome these limitations, there is a need to develop more efficient methods for densification of biomass. The densification of biomass increases the density of biomass pellets typically > 600 kg/m^3 and helps to reduce the transportation costs with convenient material handling and less dust formation (Gilbert et al., 2009). Densification of biomass into pellets, briquettes or cubes makes the material in uniform shape and sizes for easy handling, which can be directly used for thermochemical processes such as combustion, gasification, pyrolysis or co-firing with coal (Kaliyan and Morey, 2009). Increase in natural oil and gas prices led to rapid development in biomass pellet industries with more emphasis to reduce greenhouse gas emission (Peng et al., 2013). Commercial densification of biomass is typically carried out by conventional pressure driven processes such as extrusion, pelletization and briquetting (Li and Liu, 2000; Kaliyan and Morey, 2009). To prepare the densified quality biomass product, it is essential to study desirable and dependent parameters such as density and durability in relation to independent parameters such as moisture content (Adapa et al., 2007).

Pellets are more vulnerable to physical wear and tear dust during transport and storage. This leads to the formation of fine particles or dust which can create problems in the boiler or combustion systems (Carroll and Finnan, 2012). In addition, it can be a source of both health and fire hazard. As per the European Committee for Standardization (CEN), CEN/TS 15210 method defines the physical durability as the ability of pellet to remain undamaged during transportation.

It means the ability of pellet to survive vibrations and shock. During the densification process, to a great extend the physical (thermal, mechanical or atomic) forces determines the strength of pellet produced (Adapa et al., 2002). Therefore, it is essential to understand the fundamental mechanism behind the biomass compression process, and to design energy efficient combustion process (Mani et al., 2004).

Continuous increase in demand for biomass pellets and the inadequate availability of agricultural resources has resulted in finding out new available raw materials for pellet production from various resources such as fibrous residue, straw, husks, stover, pulps, meal, grass, wastes from food industry, etc. The recent Canadian government directive to substitute 1.5 billion liters of petroleum based diesel per year (5%) with biodiesel by the year 2018 are projected to encourage biodiesel industries (Canola Council, 2012). The immense development of biodiesel industries in upcoming years will produce by-products in large quantity such as oilseed meal, for which their utilization will become uncertain. Particularly in Canada, biodiesel industries utilizes canola as a common feedstock for the biodiesel production, resulting in abundant quantities of waste canola meal. Apart from being more widely used as an animal feed, canola meal can be used as alternative feedstock for biofuel/ bioenergy production (Tilay et al., 2014; Azargohar et al., 2013). During the year of 2013, Canada has 41 pellet manufacturing plants with total capacity of > 3 million tonnes of annual production and has exported ~94% to overseas (Natural Resources Canada, http://cfs.nrcan.gc.ca/selective-cuttings/57).

Biomass pellets offer ecological advantages over traditional fuels such as heating oil and natural burning gas. Biomass pellets in a pellet stove, produces smaller volumes of hydrocarbons (methane) and CO_2. In general, pellet mills need a cheap and reliable source of waste materials due to rising competition for biomass. The competition and prices for renewable feedstock fluctuate as emerging applications such as alternative biomass, advanced biofuel, biochar from biomass, activated carbon made from the petcoke compete for these resources.

Thermochemical and biochemical processes are used for the production of renewable energy from biomass (Grassi et al., 1990). Biomass, one of the sources of renewable energy can be used for the production of syngas using a thermochemical process like combustion, pyrolysis and gasification because of its widespread availability (Kirubakaran et al., 2009). In comparison to other thermochemical processes, biomass gasification is of interest for the production of syngas (Kirubakaran et al., 2009). Gasification is the most effective process for hydrogen production from biomass. Syngas and biomass gasification were actually known before World War II and the first gasification plant was established in North America in 2001 (Thakur et al., 2012). Gasification operating conditions play an important role in the quality of syngas. The important parameters affecting the quality of gas produced are equivalence ratio (ER), operating temperature and pressure, gasifying agent and residence time (Devi et al., 2003; Lassa et al., 2011). It is a CO_2 neutral energy source. The CO_2 produced during biomass combustion or gasification is balanced by CO_2 uptake from the atmosphere during photosynthesis (Naczk et al., 1985). Gasification is the partial oxidation of biomass at high temperature using O_2 (Marono et al., 2010; Tavasoli et al., 2009; Zhou et al., 2009), steam (De Lasa et al., 2011; Ferdous et al., 2001; Franco et al., 2003), air (Hurley et al., 2012; Narváez et al., 1996; Xiao et al., 2007), steam-air (Lv et al., 2003; Lv et al., 2007; Campoy et al., 2009) or steam-oxygen (Lv et al., 2011; Meng et al., 2011; Lange et al., 2007) as gasifying agents. The gasifier process can be classified into three steps: drying, devolatilization and gasification. Upon heating, the biomass dries up, until the temperature reaches 120 °C. Up to 350 °C volatiles are produced and the resulting char formed is gasified above 350 °C. Gasification is a combination of pyrolysis and oxidation reactions. Besides gaseous end product rich in CO, CO_2, H_2 and methane, gasification also yields tar and char as products. Tar is a complex mixture of condensable hydrocarbons such as single ring to 5-ring aromatic compounds, some other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (Devi et al., 2003). It is highly undesirable because of the problems faced downstream in the process equipment, engine and turbines used in the application of syngas due to tar condensation, formation of tar aerosols and polymerization in the form of more complex compounds. Tar content can be reduced by catalytic cracking or by thermal cracking which includes partial oxidation or direct thermal contact (Bridgwater et al., 1995). Many catalysts such as dolomite, Fe-based and Ni-based catalysts are used for biomass gasification and tar cracking. Dolomite $CaO{\cdot}MgO(CO_2)_2$, is a naturally occurring active catalyst for tar conversion when it is in a calcined state as $CaO{\cdot}MgO$. Maximum tar conversion with dolomites can reach up to 95-98% (Caballero et al., 1997; Gusta et al., 2009).

Solid residue or the bio-char left behind after gasification is the only biomass product that retains the morphology of the original lignocelluloses (De Lasa et al., 2011). Char is the carbonaceous residue, formed through cross-linking reactions via condensation and water loss (Yung et al., 2009; Goyal et al., 2008). The char yield decreases with increasing temperature, the decrease being more rapid till 400°C is attained. Due to the removal of hydroxyl, aliphatic C-H bonds and carbonyl and olefinic C=C groups at higher temperatures, the char becomes more aromatic and high in carbon content (De Lasa et al., 2011). The inorganic components of the biomass are usually called ash content, which mostly includes compounds such as CaO, K_2O, P_2O_5, MgO, SiO_2, SO_3 and Na_2O. The specific fractions of products formed during gasification depend largely on operating conditions such as gasification temperature, pressure, amount of gasifying agent, reaction time and type of catalyst/additive used.

Synthesis gas ($CO+H_2$) from biomass can be used to produce essentially any product (chemical intermediates, polymers, fuel additives, or hydrogen) that would be produced from a petrochemical based synthesis gas. Hydrogen is widely used in the production of ammonia, fertilizers, manufacture of methanol, petroleum refining and various gas to liquid processes (Chen and He, 2011). It has a great potential to be a major energy source in the future as it is considered to be non-polluting, inexhaustible, efficient and affordable energy carrier. Syngas is one of the major building blocks for the production of majority of fuel and chemicals. Syngas is produced from a variety of feedstocks such as coal, oil shale, tar sands, heavy residual oil, low grade natural gas, or biomass. Syngas is further converted into useful chemicals by catalytic processes (using homogeneous and heterogeneous catalysts) including Fischer–Tropsch synthesis or by using microorganism as a suitable biocatalyst including syngas fermentation (Subramani and Gangwal, 2008; Munasinghe and Khanal, 2010). The produced syngas can be categorized based on its quality for use in engines and turbines, or as a chemical feedstock for the production of liquid fuels.

This final report comprises the study carried out in last six months as well as research work performed and submitted earlier in the following main areas:

1. Characterization and pelletization of canola meal using crude glycerol as binding agents and oxygen gasification of canola meal after protein extraction for synthesis gas production in a fixed-bed reactor.
2. Gasification of canola meal and factors affecting gasification process.

3. Canola meal moisture-resistant fuel pellets: Study on variables, effects of additives on the pellet quality and compression characteristics.

The results and discussions for the above three articles were submitted to ADF as interim reports. The 1st phase of the report covers the study characterization followed by pelletization of canola meal and crude glycerol. The ultimate analysis (CHNS), ash content, moisture content and ash elemental composition were performed for both the precursors. In addition, the amounts of free fatty acids, fatty acid methyl esters and methanol were determined in crude glycerol. Pelletization of canola meal using glycerol as binding agent was carried out at two temperatures (70 and 100 ºC), three pressures (1000, 3000 and 5000 N), two ranges of particle size (particles passed 0.83 and 3.2 mm screens) and three glycerol concentrations (5, 10 and 15 % (w/w)). The heating value, handling characteristics and mechanical strength (drop testing) were examined for pellets. In addition, the effects of gasification temperature (in the range of 650-900 ºC) and ER (in the range of 0.20-0.40) on the gas products of gasification for a deproteinated canola meal in a fixed-bed reactor was studied.

The 2nd phase of the report involves the non-catalytic gasification of canola meal for the production of syngas in lab scale fixed bed gasifier and pilot scale fluidized bed gasifier. Various experiments to study the effects of different gasification parameters on gas composition, H_2/CO ratio, gas yield, syngas yield, heating value and carbon efficiency were taken into consideration. Experiments were performed to study the effect of operating temperature in the range of 650-850 ºC and equivalence ratio in the range of 0.2- 0.4. Steam, oxygen (O_2) and carbon dioxide (CO_2) were used as gasifying agents.

Finally, the 3rd phase of the report focused on the study of pelletization of canola meal biomass to increase the bulk density, thereby reducing the transportation and storage costs, The study investigated the effects of additives as well as pelletization process parameters on canola meal pellets. The effects of additives such as binder, lubricant and moisture content along with effects of applied load and temperature on the quality of pellets were evaluated in terms of pellet density, durability and hardness. From the compression data at different temperature and pressures, Kawakita and Ludde model (1971) was developed to classify the feed material into groups. The effects of coating agent on pellet durability, hardness and moisture uptake were studied to produce moisture-resistant pellets. Finally, the pellets were gasified in a fixed bed reactor and the effect of different gasifying agents such as steam, O_2 and CO_2 on the volume and quality of product gas were assessed.

All characterizations and experiments were carried out in the Department of Chemical and Biological Engineering, University of Saskatchewan. The research work is described in this report and the major findings are given in the Abstract and conclusion sections.

2. MATERIALS AND METHODS

2.1 Characterization and pelletization of canola meal using crude glycerol as binding agent

2.1.1 Feedstock

Canola meal was obtained from Cargill's crushing facility (Clavet, Saskatchewan). Crude glycerol was provided by Milligan Biotech (Foam Lake, Saskatchewan). All characterization was carried out in the Department of Chemical and Biological Engineering, University of Saskatchewan.

2.1.2 Characterization

The canola meal was characterized for elemental composition (CHNS), heavy metal content (ICP-MS) as well as ash and moisture contents. Similarly, the crude glycerol was analyzed for metal content using ICP-MS as well as moisture and fatty acids contents using Karl-Fischer method and HPLC, respectively. The heating values of the raw materials were determined using bomb calorimetry.

The meal was ground in a Wiley mill to two different ranges (one passed through 0.83 mm and the other from 3.20 mm screens). Density of the raw material was measured. Particle size distribution of ground meal was determined using a Mastersizer 9000 laser-scanning particle size analyzer. The ground meal was then mixed with crude glycerol at 0, 5, 10 and 15 % (w/w), and densified with a computer-controlled Instron 3366 press, using a 6.38 mm diameter mill. The densification or pelletization, was carried out at 1000, 3000 and 5000N (corresponding to 31.6, 94.7 and 157.9MPa, respectively), and pelletization temperatures of 70 and 100°C. The temperature of the mill was controlled using an insulated thermal tape wrap, controlled by an external thermocouple. Pellets were weighed and measured immediately after densification, then stored for two weeks to simulate industrial storage conditions, before being weighed and measured again to determine relaxation and bulk density. Pellets were burned in a Parr 1341 calorimeter with an 1108 oxygen bomb to determine higher heating values (HHV). HHV is the heat released from combustion of unit mass/mole when the combustion products are cooled to ambient temperature. Basic durability characteristics were evaluated by drop testing from a height of 1.8 m and the handling characteristics were observed by the physical method. The drop testing consisted of dropping ten successive pellets from a height of 1.8 m into a steel collection basin and comparing the size of the largest surviving piece to the size of each pellet before dropping. Drop testing was conducted only for the pelletes with excellent handling characteristics. When the pellets broke apart, it was usually normal to the longitudinal axis, as shown in **Fig. 2**. Handling characteristics refer to how well the pellets stood up to transport and manipulate while being measured to determine their bulk density. The range of handling characteristics was as follows:

- **Fragile** - pellets have a tendency to break apart or crumble when touched, and when pressure is applied, come apart easily. Surface of pellets are rough and looks porous.
- **Fair** - Pellets tend to shed small amounts of material, particularly from the ends, when handled. When handled gently, pellets tend not to break or split, but still come apart easily under slight pressure.
- **Good** - pellets rarely break apart and have a homogeneous, smooth surface.
- **Excellen**t - pellets never break apart during handling, surface is smooth and shiny.

Fig. 2.1: Drop testing basin

Fig. 2.2: Pellet after drop testing

2.1.3 Protein removal

To compare the properties of pellets made from original meal and de-proteinated meal, 67 % (w/w) of protein was removed from meal and it was ground and used for above mentioned tests. The extraction method is described in section 2.2.1 of the second part of this report.

2.2 Oxygen gasification of canola meal after protein extraction for synthesis gas production in a fixed-bed reactor

2.2.1 Extraction of protein from canola meal

Raw de-oiled canola meal was obtained from Cargill Inc. (SK, Canada). Alkaline extraction method was used to extract the protein from canola meal (Xu and Diosady, 2002; Ghodsvali et al., 2005). 100 g of overnight dried canola meal was stirred with 1800 g water for 2 hours at 300 rpm and 45 °C. The pH of solution was kept constant at 12 by adding a 1N NaOH solution containing 1 % (w/w) surfactant sodium dodecyl sulfate (SDS). The pH was checked after every one hour. The slurry was separated by centrifugation at 3000 g and 8 °C for 20 minutes. The residue collected was vacuum filtered using excess water. To reduce the effect of oxidation, Na_2CO_3 at a concentration of 0.1 % (w/w) was added to the extraction solution as a reducing agent (Xu and Diosady, 2002). After filtration, the meal was dried overnight in a furnace at 100 °C. The amount of protein extracted was calculated using Bradford method. Processed canola meal is the product obtained after removal of protein from the canola meal is called processed canola meal or deproteinated canola meal.

2.2.2 Biomass characterization

Ultimate (CHNS) analysis: Carbon, hydrogen, nitrogen, and sulphur percentages were measured by Elementar Vario EL III. Through quantitative high temperature decomposition, solid substances are changed into gaseous combinations. ~ 0.1 g sample was burned at 1000 ^{o}C and the released gases were separated into their components.

2.2.3 Heating value measurement

The calorific value was determined in a static bomb calorimeter, a sealed Parr 1108, based on the procedure described by Hubbard and Scott (1956). The sample (1.0 g) was put in a stainless steel crucible and then placed inside the bomb. A 1.0 mL portion of water was added into the bomb, and the bomb was filled with oxygen (2 MPa pressure) at room temperature (25 ^{o}C). The calorimeter was placed in an isothermal jacket. The electrical energy (40 V) was applied for ignition using a platinum wire. The bomb calorimeter was submerged in a calorimeter cane filled with distilled water.

2.2.4 Particle size analysis

Particle size distribution of sample was determined based on the laser beam diffraction pattern of particles, by the Malvern Mastersizer S Long Bench Particle Size Analyzer (Malvern instruments Ltd., Malvern, UK) using wet method. The sample cell mounts in front of lens, and the sample passes through the laser beam by flowing through this cell. The flow cell is used with samples dispersed in a liquid. The sample is maintained in suspension and circulated continuously through the flow cell by the “Small volume sample dispersion unit” or “Wet feeder”. The particle size of samples was analyzed by the 1000-mm lens (04.19-3473.45 μm). The Mastersizer measures the concentration of a sample by measuring the amount of laser light that has been lost by passing it through the sample.

2.2.5 Thermogravimetric (TG-DTA) analysis of canola meal

The thermogravimetric analyzer (Pyris Diamond TG/ DTA, PerkinElmer Instruments, USA) consists of a micro thermobalance with an electric furnace connected to a computer. Helium was used as a carrier gas to sweep the product gases. He flow rate was set at 44 ml/min and the heating rate was set at 25°C/min as per the operating conditions used in the gasification process of the biomass. The canola sample was kept in a platinum sample holder. The sample size was ~ 25 mg approximately in all experiments. The final pyrolysis temperature of the sample in all experiments was set at 900 °C and the sample was kept on hold for 10 minutes.

Gas chromatography technique: Teddler bags were used to collect the product gas from the gasification unit and injected into the gas chromatograph (Agilent 7890A) equipped with two TCD (Thermal conductivity detector) and one FID (Flame ionization detector) detectors. Inductively coupled plasma-Mass spectrometer (ICP-MS): The ICP-MS analysis of bio-char samples was performed using an inductively coupled plasma-mass spectrometer (ICP-MS, Model Sciex Elan 5000 provided by Perkin Elmer (USA).

2.2.6 Experimental set-up

The experiments were carried out at atmospheric pressure in two-stage fixed bed reactor system. The schematic diagram for the setup is shown in **Fig. 2.3**. The first stage and second stage reactors were made of Inconel tubing having 10.5 mm ID as well as 500 mm and 370 mm lengths, respectively. Each reactor had 3 pins welded inside it to support the fixed bed. 2 g of dried protein extracted canola meal was loaded into the first reactor. Inert Ottawa sand was used to form a 70 mm high packed bed in second reactor. The temperature was measured and controlled using K-type thermocouple placed at the heating zone in the furnace and connected to temperature controller (Eurotherm model 2132, USA). Helium and oxygen were fed to the reactor at the desired flow rates using separate mass flow controllers. The second reactor was heated to the desired final temperature and then the heating of first reactor was started. Both the reactors were heated to the same final temperature at same heating rate of 25 °C/min.

After the first reactor had reached a temperature of 250 °C, injection of oxygen was started and collection of product gas was started at this point. The injection of oxygen and a collection of product gases was then carried out for the next 60 minutes. It took approximately 30-40 min to achieve the desired operating temperature after the reactor had reached 250 °C. At the end of 60 minutes, injection of oxygen was stopped and flow of helium was continued for cooling. Liquid tar from the reaction was cooled and collected in a liquid trap, cooled with ice bath and gaseous product was collected over saturated brine solution of sodium chloride. The volume of gas collected was measured at 25 °C and 1 atm pressure conditions. The reactor system was washed with acetone to collect tar. Tar and acetone were separated using rotavapour.

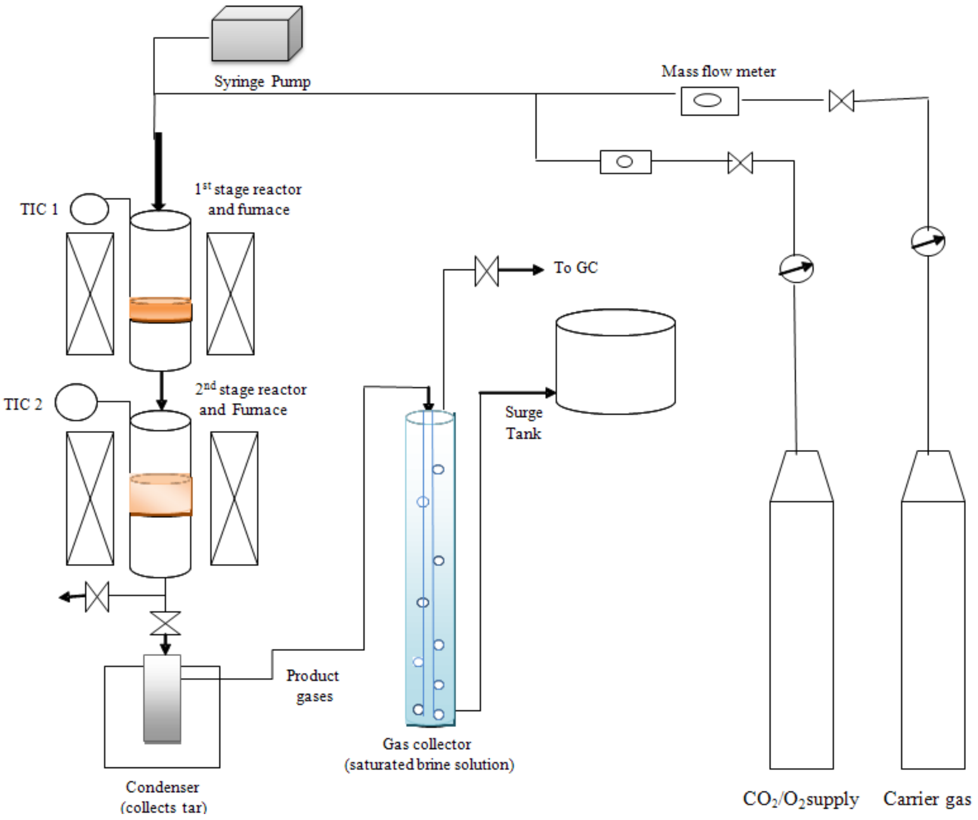


Fig. 2.3: Schematic diagram of the experimental setup

2.2.7 Activation of dolomite

Dolomite was obtained from a local gardening store where it is sold as garden potting soil. It is basically a dolomitic limestone. Raw dolomite was activated by calcination at 800 °C for 1 hr under 300 ml/min N_2 flow. One gram of activated dolomite was used for the experimental runs.

2.2.8 Experimental design

The effects of gasification temperature and equivalence ratio (ER) on the gas product composition were investigated in this work. Equivalence ratio is the oxygen used relative to the amount required for complete combustion. It is dimensionless parameter. To change ER, the oxygen flow rate into the reactor was changed. The gasification temperature was varied from 650 °C to 900 °C (650, 735, 815 and 900 °C). The ER for oxygen was varied from 0.20-0.40 with an increment of 0.07. Total 16 experiments were performed at four different temperatures and four ER values and were repeated randomly to check the reproducibility of results. Average values of the results are reported in repeated experiments. An experiment was performed at 735 °C and ER of 0.20 with dolomite to check the impact of catalyst on tar cracking. One gram of dolomite was mixed with Ottawa sand to form a 70 mm packed bed in second reactor. The run was repeated to check its validity.

2.3 Gasification of canola meal and factors affecting gasification process

2.3.1 Feed material and characterization methods

Canola meal was obtained from Milligan Biofuels Inc. (Saskatchewan, Canada). Silica sand (100-45 mesh from Selkirk Silica) as a bed material was procured from Manitoba, Canada. The particle size distribution of canola meal was determined by Mastersizer 9000 laser-scanning particle size analyzer (Malvern Instruments Ltd., Malvern, UK) confirms 60.3% particles were in range of 700-900 µm. The volume of fine (< 700 µm) and coarse (> 900µm) particles were determined to be 30.1% and 9.6%, respectively. Characterization of canola meal biomass was presented in **Table 2.1**.

Table 2.1: Characterization of canola meal biomass

Proximate analysis (% (w/w) dry basis)		**Ultimate analysis (% (w/w) dry basis)**	
Fixed carbon	17.6±0.98	C	49.03±0.1
Volatile	71.1±1.12	H	6.42±0.3
Ash	6.7±0.01	N	6.61±0.2
		S	0.82±0.2
Moisture content (% (w/w) wet basis)	4.3±0.05	O*	30.40±0.2
Higher heating value (MJ/kg)	19.9±0.14	Ash	6.73±0.01

* Calculated by difference

ASTM 3173-87 method was used for determination of moisture content of canola meal. Ash content was determined in a laboratory muffle furnace (Holpack, USA) as per ASTM 3174-04. For determination of ash content, approximately, 1.0g of canola meal was taken in weighed crucible and placed in a muffle furnace maintained at 575±5 °C for 4 h and the difference in weight indicated its ash content. After completion of this process, the crucible was removed and placed in desiccators to avoid moisture absorption. Repetition of heating and cooling step was done until constant weight was obtained which helps in removal of volatiles and carbon (Naik et al., 2010). Elemental analyses for carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) were performed using a PerkinElmer Elementar CHNS analyzer (Vario EL III, Elementar Americas Inc., NJ) and amount of oxygen was obtained by differentiating. The HHV of canola meal was measured by oxygen bomb calorimeter (insert makers). The sample was burnt in Parr 1108, placed inside a Parr 1341 isothermal calorimeter. 1mL of water was added to the bomb and pressurized to 2.5 MPa, before placing in an isothermal jacket filled with 2000 ml of water at room temperature (25±1 ºC). When depressed, the ignition switch sent 40 V of electrical energy through a 100 mm platinum ignition wire and a 75 mm cellulose thread.

2.3.2 Laboratory scale gasification unit

A schematic flow diagram of the fixed bed gasification setup used was shown in **Fig. 2.3**. The experiments were carried out at atmospheric pressure in two-stage fixed bed reaction system. The first stage reactor (10.5 mm ID × 500 mm length) and second stage reactor (10.5 mm ID × 370 mm length) were made of Inconel tubing. The first stage reactor was loaded with 2.0 g of dried canola meal. Silica sand was used to form a 70 mm high packed bed in the second stage reactor. The temperature was measured and controlled using K-type thermocouple placed in the heating zone in the furnace and connected to a temperature controller (Eurotherm model 2132, USA). Argon used as the inert carrier gas at the flow rate of 44 ml/min. When the second reactor attains the desired final temperature, heating of first reactor was started. Both reactors were heated to the same final temperature at the same heating rate of 25 °C/min. Injection of gasifying agent (steam/ CO_2/ O_2) started once the first reactor reached to 250 ºC and collection of product gas was started. The injection of gasifying agent (steam/ CO_2/ O_2) and a collection of product gases were then carried out. It took approximately 30-40 min to achieve the desired operating temperature after the reactor had reached 250 °C. After completion of 60 min, injection of the gasifying agent (steam/ CO_2/ O_2) was stopped and the flow of argon was continued for cooling the reactors. The volume of gas collected was measured at 25±2 °C and 1 atm using water displacement method. For steam gasification, syringe pump was used to inject water into the gasifier.

2.3.3 Sampling and gas analysis

Gas samples were collected in tedlar bags and were analyzed for the permanent gases H_2, N_2, CO_2, CO, CH_4, CmHn (light hydrocarbons) using GC (Agilent 7850) flame ionization detector and thermal conductivity detector. Tar was collected in condenser placed in an ice bath and gaseous product was collected over solution of sodium chloride (17%). After cooling down the reactor, the system was washed with acetone to collect remaining tar. There was collected by evaporating acetone using a rotary vacuum evaporator. Char sample remained in gasifier was weighed and subjected to ultimate analysis (CHNS). The GC calibration was performed prior to analysis using certified standard gas.

2.3.4 Experimental Procedure

To study the effect of operating parameters on canola meal gasification, parameters along with ranges studied are described in **Table 2.2**. The experiments were carried out at atmospheric pressure. The experiments were performed at optimized conditions obtained from lab scale gasification unit. The experiments were conducted using different gasifying agents at optimum parameters obtained at the fixed bed gasification unit. Steam, CO_2 and O_2 were chosen as gasifying agents. Syngas can be produced from biomass with varying degree of heating value depending upon the type of gasifying agent (air, steam, oxygen, CO_2) used (McKendry, 2002; Lassa et al., 2011). To study the effects of temperature and ER, three levels of each parameter including 650, 750, 850 ºC and 0.2, 0.3, 0.4 respectively were used. Temperature was adjusted at 750 ºC whereas ER was adjusted by varying flow rate of gasifying agent. Thus, creating 27 combinations of experiment are shown in **Table 2.2**.

2.3.5 Pilot scale gasification unit

The fluidized bed gasifier was made of a cylindrical stainless steel tube with a height of 1.5 m and in which the fluidized bed has an inner diameter of 7 cm and height of 0.5 m, and the freeboard section has 15 cm diameter and 1 m height (**Fig. 2.4**). Heating was managed by means of electric furnace encapsulating the cylindrical stainless steel gasifier. Canola meal was charged in a hopper and fed constantly into the reactor above the distributor with the help of screw feeder. Calibration of feeder was done before starting each experiment by varying the rotation speed of the screw feeder. The condenser and cyclone were attached externally to the column. The bed temperature was continuously monitored to reach steady-state condition. The silica sand used as bed material with a particle density of 2600 kg/m^3 and average particle size of 250 µm. The minimum fluidization velocity of the sand particles use was 0.04 m/s and the bed height of sand was kept constant at 11 cm for all experiments.

Table 2.2: Design of experiments to study the effects of temperature, ER and gasifying agents on syngas quality

Exp. No.	Gasifying Agent	Temp. (°C)	ER
1	Steam	650	0.2
2	Steam	650	0.3
3	Steam	650	0.4
4	Steam	750	0.2
5	Steam	750	0.3
6	Steam	750	0.4
7	Steam	850	0.2
8	Steam	850	0.3
9	Steam	850	0.4
10	O_2	650	0.2
11	O_2	650	0.3
12	O_2	650	0.4
13	O_2	750	0.2
14	O_2	750	0.3
15	O_2	750	0.4
16	O_2	850	0.2
17	O_2	850	0.3
18	O_2	850	0.4
19	CO_2	650	0.2
20	CO_2	650	0.3
21	CO_2	650	0.4
22	CO_2	750	0.2
23	CO_2	750	0.3
24	CO_2	750	0.4
25	CO_2	850	0.2
26	CO_2	850	0.3
27	CO_2	850	0.4

2.3.6 Experimental Procedure

During gasification, biomass were continuously fed at the bottom of the gasifier, 3 cm above the distributor. All experiments were conducted at atmospheric pressure. Gasifying agent (steam/ O_2 or CO_2) preheated to 750 ºC was injected into the bed through a distributor. The rate of inert gas (argon), gasifying agent (steam/ O_2 or CO_2) and the biomass feed rate was kept constant for all experiments (gasification temperature of 750 ºC and ER of 0.4). The gasifier temperature was manually controlled during experiments. Sampling of the outlet gas was done 10, 20, 40, 60 and 70 min during each experiment and the samples were analyzed using Gas Chromatograph (GC).

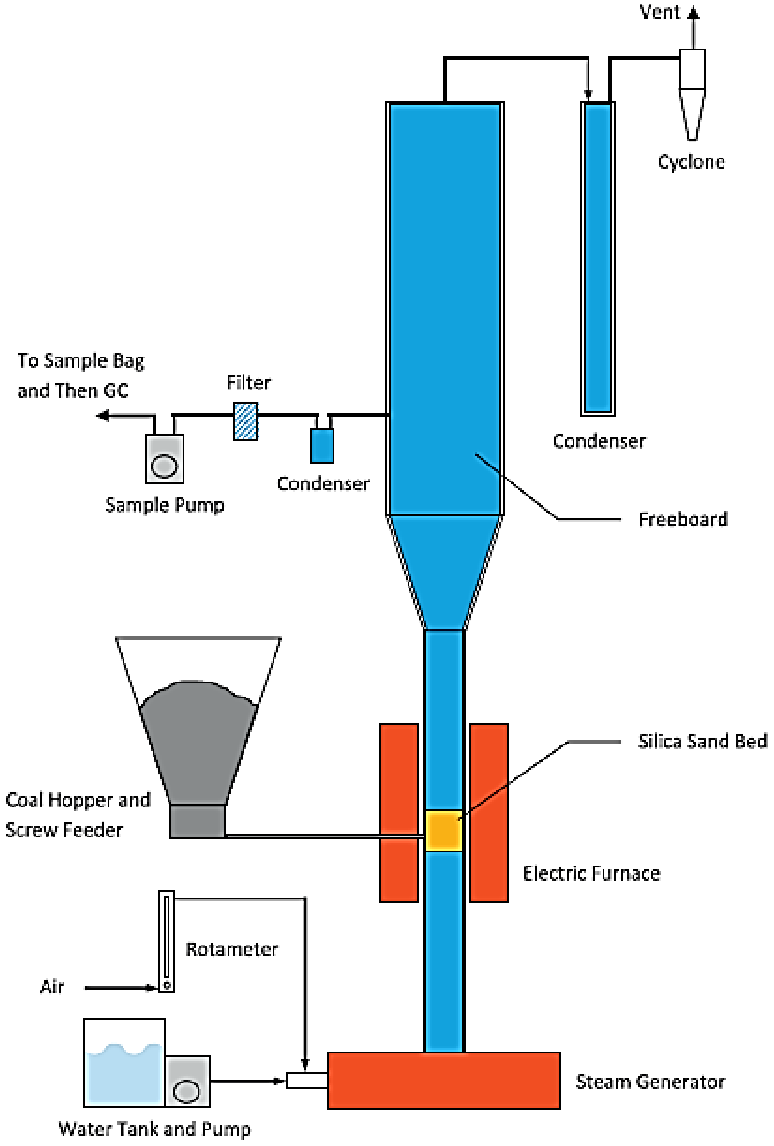


Fig. 2.4: Schematic diagram of the fluidized bed gasifier used in the present work.

2.4 Production of moisture-resistant canola meal fuel pellets

2.4.1 Materials

The waste canola meal biomass from Milligan Biofuels Inc. (Saskatchewan, Canada) were used as raw materials for the present study. The proximate analysis of biomass was previously carried out using AAFCO (Association of American Feed Control Officials) standard (Tilay et al., 2014). The canola meal material was ground by means of knife mill (Retsch GmbH, 5657 HAAN, West Germany) and passed through 0.8 mm mesh. Further, the particle size distribution of the ground canola meal was determined using Mastersizer 9000 laser-scanning particle size analyzer (Malvern Instruments Ltd., Malvern, UK) which confirms that 80.3 % particles were in the range of 100-800 µm. The volume of fine (<100 µm) and coarse (>1000µm) particles was determined to be 14.2 % and 5.5 %, respectively. The moisture content of the ground canola meal was determined using ASTM 3173-87 method and was 5.19±0.8 % as received. Similarly, ash content of the manufactured pellet was determined as per ASTM 3174-04 in a laboratory muffle furnace (Holpack, USA) and was in the range of 5.5 to 5.7 % (w/w), depending upon the composition of feed and additives. The additives (binder, lubricant and coating agent) used in this study were procured from Evergreen BioFuels Inc. (Montreal, QC, Canada). The elemental analysis of procured binder and pellet for carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) was performed using a PerkinElmer Elementar CHNSO analyzer (Vario EL III, Elementar Americas Inc., NJ) and the analyzer calibration was done using standard sulfanilic acid. The elemental analysis of binder showed 2.3±0.05 % (w/w) of N; 49.0±0.2 % (w/w) of C; 0.2±0.07 % (w/w) of S and 5.3±0.07 % (w/w) of H. In case of canola meal pellet using optimized formulation, the composition elements were found to be around 6.1±0.07 % (w/w) of N; 46.6±0.8 %w of C; 0.9±0.3 % (w/w) of S and 6.6±0.2 % (w/w) of H. The HHV of produced canola meal pellet was measured by oxygen bomb calorimeter (Parr® 6400 Calorimeter, IL, United States) using ASTM D 5865. The canola meal pellet sample was burnt in a Parr 1108, placed inside a Parr 1341 isothermal calorimeter. Approximately 1mL of water was added to the bomb and pressurized to 2.5 MPa, before placing in an isothermal jacket filled with 2000 ml of water at room temperature (25±1 ºC). The electrical energy (40 V) was applied for ignition using a platinum wire. The test was carried in three replicates. All the produced canola meal pellets were found to have HHV of ~ 20.3±0.18 MJ/kg.

2.4.2 Preparation of sample and densification

The desired quantity of moisture was added to the formulation to make the final moisture content in the range of 8 to 12 % (w/w). The additives (binder and lubricant) were added to the pre-adjusted moisture of canola meal, in the range of 2 to 5 % (w/w) and 1 to 3 % (w/w), respectively and kept in air tight seal bags for 12 h. All samples were densified in a lab scale single-pelleting unit used in previous studies as described by Adapa et al. (2013) and Kashaninejad and Tabil (2011). The densification unit was composed of a plunger-die assembly. The internal diameter and length of a steel cylinder assembled on the Instron testing machine (3360 Dual Column Tabletop Testing Systems, Instron Corp. Norwood, MA) is 6.5 mm and 135.3 mm, respectively, and fitted with a 10000 N load cell. The die was surrounded with a dual element heating tape (Cole-Parmer Instrument Company, Vernon Hills, Ill.) to maintain the desired temperature during the densification process. One thermocouple (type-T) was connected to the outer surface of the die and another to a temperature controller. The die was positioned on a raised base which consist of sliding gate at the bottom allowing the ejection of pellet after the densification process. The plunger was attached to the upper moving crosshead of the testing machine.

Once die reached a constant set temperature of 60±1 °C, a weighed quantity of sample (0.8±0.02 g) was loaded into the die. During the densification process, initially compressive force of 500 N (equivalent pressure 15.8 MPa) was applied to the sample. The plunger moves down to the pre-set speed 50 mm/min and stops for 15 s at the applied load of 500 N (**Fig. 2.5**). This allows material to reach the desired set temperature. After 15 s, the plunger moves down with the same set speed and the pre-set final compressive force of 3000 N (equivalent pressure 94.7MPa) was applied to densify the samples. Once the pre-set load was attained, the plunger stops and retains in place for 60 s for the relaxation test (Kashaninejad and Tabil, 2011) and in addition prevents spring back action of compressed sample (Mani et al., 2006). The plunger was withdrawn to release the applied load and the sliding gate was opened. After 30 s, the plunger moves down to eject the pellet. Each sample was determined in fifteen replicates. Following ejection, once the pellet sample attains ambient temperature, the mass, length, and diameter of pellet were measured using digital caliper.

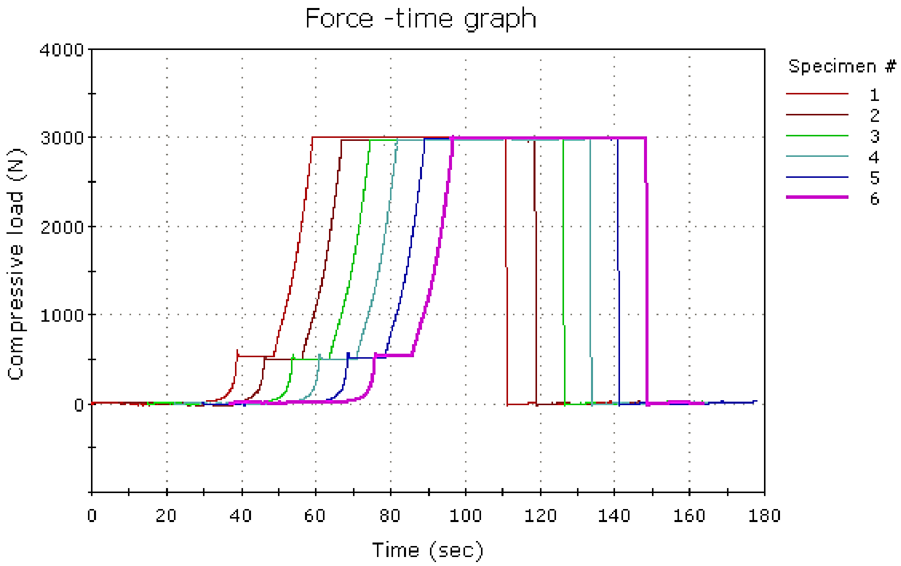


Fig. 2.5: Force-Time graph (densification method)

2.4.3 Box-Behnken design to study the effect of additives and moisture content on pellet quality

Box–Behnken design (BBD) matrix was used to examine the influence of most important chemical parameters such as concentration of additives and moisture content. The three parameters: binder (A), lubricant (B) and moisture content (C) were considered to find the most suitable combination of these variables resulting high quality pellets. Different formulations were prepared (**Table 3.13**) using BBD (Stat-Ease, Inc., version 6.0.8) at three levels, coded as -1, 0, and +1. BBD creates designs with desirable statistical properties with only a fraction of the experiments required for a three-level factorial with the appropriate quadratic model. The design comprised of three factors with three levels together with five replicates at the center point. These experiments were used to assess the linear and interaction effects of these factors considered and to fit a second order quadratic model. These factors were considered as an independent variable and pellet quality parameters (durability and hardness) were dependent variable. Lower, middle and high level of each variable was coded as −1, 0 and +1 respectively. The actual values along with coded level were described in **Table 3.13**. A second order polynomial equation was adopted to find the effects of independent variables to the response.

For predicting the best suitable combination, the following second-order polynomial equation was developed to correlate the relationship between selected independent variables and the dependent responses (durability and hardness):

$$Response = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (1)$$

Where, the response is either durability or hardness of the pellet;
β_0- Constant term;
β_1, β_2 and β_3- Coefficient of linear terms;
β_{11}, β_{22} and β_{33}- Coefficient of quadratic terms;
β_{12}, β_{13} and β_{23}- Coefficient of cross product terms (two variables) respectively.
The quality of fit of the polynomial equation was expressed with the coefficient of determination R^2.

A sample without binder, lubricant and the desired moisture contest was considered as control. Each formulation was prepared (1 to 17, **Table 3.13**) and kept in an airtight sealed bags for 12 h at room temperature for even distribution of moisture before densification. Further, the densification process was carried for all formulations at applied preset load of 3000 N and a temperature of 60 ºC, using a lab-scale single pelleting unit as mentioned above. The optimized combination of formulation was selected on the basis of pellet durability and hardness.

2.4.4 Effect of physical parameters on pellet quality

The optimized combination of pellet formulation obtained from BBD was used to study the effects of pressure and temperature on pellet quality. The preset loads used for these tests were 3500, 4000 and 4500 N and a temperature of 60 ºC, at a crosshead speed of 50 mm/min. Further, the optimized load was considered depending on pellet durability and harness, to study the effects of temperature (70, 80 and 90 ºC) at an optimized preset load. In each compression test, the sample (0.8 ± 0.02 g) was fed into the heated die and compressed up to the stated preset load and held for 60 s to arrest the spring back effect. Specified samples from each study were tested for density, durability and hardness measurement.

2.4.5 Durability and pellet density measurement of a single pellet

The durability test was carried out as previously described in section 2.1.2. There are different methods investigated for durability test (Temmerman et al., 2006). The tumbling method for pellet durability test (ASABE 269.4) described by the American Society for Agricultural and Biological Engineering (ASABE) was mostly accepted with high accuracy level and limited test replicates required. Due to the limited quantity of pellets, drop test as described by Adapa et al. (2010) was performed to measure the durability of canola meal pellets obtained after pelletization. Pellet sample (ten replicates) was dropped from a height of 1.85 m on a metal plate. The ratio of mass retained with the initial weight was expressed as the percentage durability of the pellet (Adapa et al., 2010; Al-Widyan and Al-Jalil, 2001).

Following the extrusion of the pellets, the length, mass and diameter of the pellets were measured using a calibrated digital caliper to determine the density in kg/m^3. Each five replicates (pellets) from each different experiments were considered. The process is repeated to find out the change in pellet density (% expansion/ relaxed density) after a storage period of two weeks (Adapa et al., 2010; Serrano et al., 2011).

2.4.6 Pellet hardness test

The internal strength of the produced pellets was measured using compression test by applying a load at a constant rate, until the test pellet breaks. The load at fracture is recorded as the hardness and reported as force (N). Hardness was related to the chewability or palatability of pellets previously (Adapa et al., 2006; Mahapatra et al., 2010). The hardness of canola meal pellets was measured using a TA-XT2i texture analyzer (Stable Micro Systems, Scarsdale, NY). A single pellet 20 ±1 mm in length and 6.4 ± 0.05mm in diameter was placed by positioning horizontally on a flat surface (Fig. 2.6) under the disc shaped metal probe (dia- 35 mm) attached to 100 kg load cell. A test was carried out by increasing the applied load at a constant rate of 2 mm/s, until the pellet failed by cracking or breaking and stopped after pellet failure. The average force required to break the pellet was calculated based on five replicated per sample (Mahapatra et al., 2010). Post run, the load cell comes to its original position with the preset speed of 10 mm/s. The maximum force needed to break the pellet sample was determined directly by the software (Stable Microsystem version 2.64) and taken as hardness (Adapa et al., 2006).

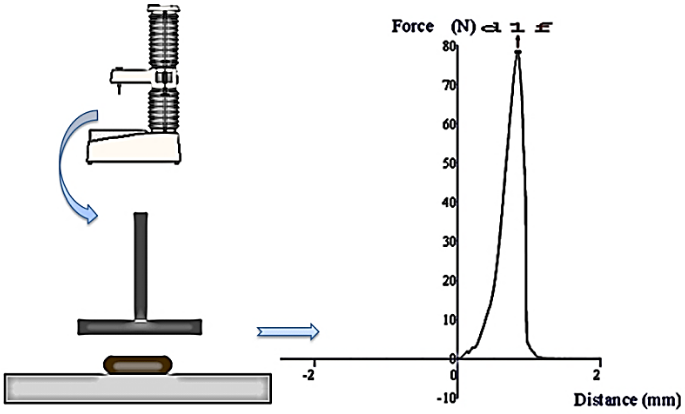


Fig. 2.6: Hardness testing of pellets using a texture analyzer and recorded force-distance curve to determine the force required to break the pellet

2.4.7 Bulk and Particle Density

The bulk density (kg/m^3) of biomass was determined using a 250 ml graduated measuring cylinder filled using a funnel. The cylinder was tapped on a table for approximately 15 times to let the material to settle down and subsequently the container was weighed. The bulk density was determined in replicates of five. Similarly, the particle density (kg/m^3) of the ground canola meal was measured using a gas multi-pycnometer (Quanta Chrome, Boynton Beach, FL), by calculating the displaced volume of nitrogen gas with a known mass of sample (Adapa et al., 2010). The particle density measurements were performed in three replicates.

2.4.8 Compression Model

This study represents a protocol for the assessment of mechanical properties of a ground canola meal, and evaluates the pelleting relevant information carried forward by compression data. This is useful in a pelletization process to enhance and understand the process and also applicable for monitoring of the pelletization process. Various compression models applied to pharmaceutical and biomass materials have been studied and reviewed earlier in detail (Adapa et al., 2002; 2009; Mani et al.; 2003; Denny, 2002). For agricultural non-treated biomass such as barley, canola, oat, and wheat straw (1.98 mm grind size), Kawikita and Ludde (1971) model was delivered as best fit in addition to deformation characteristics using Cooper-Eaton (1962) and Jones (1960) model by Adapa et al. (2009). Kawakita and Ludde (1971) compression model was developed to explain the compaction process during the pelletization.

Kawakita and Ludde Model

One of the ways of representing compression data observed on the relationship between applied pressure and reduction of a powder bed. The proposed equation for compaction of powders based on pressure and volume (Kawakita and Lüdde, 1971; Kawakita and Tsutsumi, 1965) (Equation 2):

$$\frac{P}{C} = \frac{1}{ab} + \frac{P}{a} \tag{2}$$

Where, C is the degree of volume reduction: $C = \frac{Vo-V}{Vo}$,

Vo is the initial volume of the powder bed,
V is the volume under applied pressure,
P is the applied pressure, and
a and b are parameters.

The Kawakita equation includes two compression parameters referred to as 'a' and 'b'. The parameter 'a' characterizes the engineering strain or degree of compression at infinite pressure (C_∞), while the inverted b-parameter characterizes the applied pressure required to achieve an engineering strain of C/2 (Nordstrom et al., 2008). The importance of Kawakita parameters has been discussed in terms of the physical properties of the particles (fracture strength) and the yield pressure of the particle (Nordstrom et al., 2008). Thus, it is reasonable that the original size of the feed particles can affect the compression process, and consequently the values of the Kawakita parameters. It is hypothesized that the corresponding effects on the Kawakita parameters during compression of a fine powder will be a low value of parameter 'b^{-1}' and a high value of the parameter 'a'(Nordstrom et al., 2009). The combination of Kawakita parameters 'a' and 'b' reveal the occurrence of particle rearrangement during the compression process. This is relatively important depicting the initial stage for the overall compression behavior.

The value of parameters ‘a’ and ‘b’ can be derived from a linear relationship between $\frac{P}{C}$ and P. Materials for which particle rearrangement has a substantial influence on the overall compression process, are related to the low value of parameter ‘b^{-1}’ and high value of parameter ‘a’. The product of these Kawakita parameters called as an index (ab_I) from which a material can be classified as either Class I ($ab_I > 0.1$) or Class II ($ab_I \leq 0.1$). A material showing a combination of $ab_I > 0.1$, $a > 0.6$ and $b^{-1} < 7$ is thus typical features for a Class I powder (Nordström et al., 2012).

The optimized formulation obtained from BBD was used for this study. The single pelleting unit was used to make pellets from canola meal. The sample loading for making pellets was kept constant 0.8 ± 0.02 g. The experimental parameters (temperature and applied pressure) were studied at different ranges. The pellet die temperature was studied at different temperature of 60, 70, 80 and 90 (±1 °C) in order to simulate the heating during the commercial pelleting process. Four preset pressure of 2500, 3000, 3500 and 4000 N corresponds to pressures of 75.37, 90.44, 105.52 and 120.59 MPa were used to compress samples. The crosshead speed was set to 50 mm/min. Once the preset load was attained, the plunger remains in place for 60 s in order to avoid spring-back effect of biomass (Adapa et al., 2006). Later, the pellet was ejected and kept for cooling at ambient temperature. The weight, length and diameter of pellet were measured.

2.4.9 Pellet coating and storage study

The final pellet formulation obtained from BBD were used to make pellets at an optimized temperature of 90 ºC and applied load of 3500N. These pellets were used for coating studies. Freshly prepared pellets were coated using the coating agent (4% dissolved in ~85% isopropyl alcohol). Further, pellets were heat cured in an oven at a temperature of 100 ºC for 30 seconds. Obtained coated pellets were stored in an open atmosphere and at an ambient temperature with humidity ~60%. To study the effect of coating agent on moisture resistant canola meal fuel pellets, about three replicates were measured at an interval of 1 week for each set of moisture content, durability and hardness study following up to 8 weeks. For comparison, control pellets i.e. without coating was stored and analyzed in the same way.

2.4.10 Gasification of pellets in fixed bed reactor

Fixed bed combustion is generally used for energy production from waste biomass at various scales (Gilbert et al., 2009). In this study, the gasification of the canola meal pellets was investigated in the fixed bed reactor. The fixed bed reactor has been frequently applied for fundamental studies of biomass gasification process (Gilbert et al., 2009; Dalai et al., 2009; Dalai et al., 2003). Details of fixed bed gasification set up are mentioned before in section 2.3.2 (Tilay et al., 2014). The experiments were carried out using different gasifying agents, including steam, oxygen (O_2) and carbon dioxide (CO_2), at atmospheric pressure in a two-stage reactor system. The operating parameters were chosen based on the maximum LHV for syngas obtained by Tilay et al. (2014) for canola meal (steam/ 650 ºC/ 0.2 ER; O_2/650 ºC/ 0.4 ER and CO_2/ 750 ºC/ 0.2 ER). Both reactors, first stage (10.5 mm ID × 500 mm length) and second stage (10.5 mm ID × 370 mm length) were made of Inconel tubing. Previously weighed two pellets were loaded in the first stage reactor and silica sand (100-45 mesh) was used to form a 70 mm high fixed bed in the second stage reactor. The temperature of both furnaces was controlled by two temperature controllers (Eurotherm model 2132, USA). Carrier gas (Argon) was used at the flow rate of 44 ml/min. Both reactors were heated up to same final temperature with the same heating rate (25 ºC/ min). The injection of the gasifying agent (steam/O_2/CO_2) and simultaneous collection of gas sample was started as soon as the first reactor reaches to a temperature of 250 ºC. Total run time was set 60 min after injection of gasifying agent. The volume of gas collected was measured at 25±2 °C and 1 atm in the water column over a solution of sodium chloride (17 % (w/w)) and gas samples were collected in sampling bags for GC analysis. The reactors were cooled down with the continuous flow of argon. In case of steam gasification, a pre-calibrated syringe pump was used to inject water into the gasifier.

The product gas samples were analyzed for the permanent gases H_2, N_2, CO_2, CO, CH_4, CmHn (light hydrocarbons) using GC (Agilent Technologies, model 7890A, ON, Canada) with FID and TCD. The tar sample was collected in a condenser placed in an ice bath. After cooling down the system, tubings were washed with acetone to collect residual tar. Acetone was evaporated using a rotary vacuum evaporator to collect tar free from acetone. Char sample remaining in gasifier was weighed and subjected to elemental analysis (C, H, N, S). The GC calibration was performed prior analysis using certified standard gas procured from Praxair Products Inc., Saskatoon, SK, Canada.

2.4.11 Scanning electron microscope (SEM)

SEM was performed to study the binding characteristics of the canola meal pellets by fracture surface analysis. The fracture surface was prepared by manually snapping a pellet into two parts. Each pellet for analysis was snapped in the similar way. A tiny notch was given in the center of the pellet using a sharp blade and the pellet was snapped. The fractured surface was examined away from the notch carefully. The pellet samples were placed on carbon tapes and then coated with a thin layer of gold – carbon in an inert (argon) atmosphere using Agar Sputter Coater (Desk-1 sputter coater, Denton, USA). Electron micrographs were recorded using a SU 6600 Hitachi Field Emission SEM (Hitachi High-Technologies Europe GmbH, Krefeld, Germany) operated at 12 kV.

3. RESULT AND DISCUSSION

3.1 Characterization and pelletization of canola meal using crude glycerol as binding agent

3.1.1 Characterization of canola meal

The meal obtained from Cargill had average moisture content of 8.8 % (w/w) and ash content of 7.3 % (w/w). Comparatively, the deproteinated meal had average moisture content of 7.2 % (w/w) and ash content of 8.5 % (w/w). The optimum moisture content for industrial-scale densification usually falls between 7-15 % (w/w), with the optimum for most biomasses at approximately 10 % (w/w) (Shaw, 2008). Some moisture is necessary to facilitate bonding processes, such as starch gelatinization and fiber solubilization (Shaw, 2008; Rentsen, 2010).

3.1.2 Characterization of crude glycerol

Table 3.1 shows the chemical characterization of crude glycerol. The crude glycerol obtained from Milligan Biotech had a methanol content of 1.3 % (w/w). An average moisture content of 5.5 % (w/w) was found using Karl-Fischer Titration. Gas chromatography (GC) showed an average free fatty acids (FFA) content of 15.4 % (w/w). HPLC was used to evaluate the glycerol and fatty acid methyl ester (FAME) contents of the crude. The average FAME content ranged from 39.8 % (w/w).

Table 3.1: Chemical characterization of crude glycerol, concentrations in % (w/w)

MeOH	**Moisture**	**FFA**	**FAME**	**Ash**
1.3	5.5	15.4	39.8	4.9

The CHNS elemental analysis and heating value are presented in **Table 3.2**. The heating value of crude glycerol (27.1 MJ/kg) was found to be higher than the canola meal (20.1 MJ/kg). From **Table 3.3**, the ICP-MS analysis results showed that, canola meal contains reasonable quantity of heavy and alkali metals. Crude glycerol showed higher carbon and hydrogen contents compared with canola meal. The larger nitrogen content of canola meal is due to its high protein content. Sulfur and ash content of canola were also larger. Phosphorus, calcium and magnesium concentration in the ash part of canola meal were larger.

Table 3.2: CHNS Elemental analysis and heating value results for canola meal from Cargill and crude glycerol from Milligan biotech. All values for elements' content are in % (w/w).

	C	H	N	S	O	Ash	HHV (MJ/kg)
Canola meal	47.6	6.5	6.4	0.7	31.5	7.3	20.1
Crude glycerol	55.2	10.0	1.5	< 0.1	28.3	4.9	27.1

Table 3.3: ICP-MS analysis results, in ppm

Sample	**Na**	**Mg**	**Al**	**P**	**Ca**	**Ti**	**Mn**	**Fe**	**Fe**	**Cu**
Canola Meal	ud	5004	82	12065	6561	11	58	359	337	61
Crude Glycerol	145	121	21	1142	ud	9	ud	165	153	27
Sample	**Zn**	**Rb**	**Sr**	**Mo**	**Sn**	**Ba**	**Ta**	**Tl**	**Pb**	**U**
Canola Meal	69	10	22	1	2	11	0	0	19	1
Crude Glycerol	ud	4	1	ud	2	ud	0	ud	6	ud

3.1.3 Pelletization

During the initial phase of experimentation, it was observed that pellets with any amount of crude glycerol could not be made at 5000 N. It was also discovered that crude glycerol content above 10 % (w/w) would also cause pelletization to fail. The pellets produced were cylindrical in nature, with an average diameter of 6.72 mm. The length varies with mass, but for example, pellets made at 3000 N and at 70 °C with an average mass of 0.6 g, had length of 13.5 and 13.9 mm for glycerol concentration of 5 and 10 % (w/w), respectively. The deproteinated pellets (prepared using 10 % (w/w) glycerol at 100 °C and 3000 N) were ~15.6 mm long. All pellets were measured and accounted for calculating the volume. The physical dimensions of pellets are shown in **Table 3.4**.

After storage, pellets made with 0 % (w/w) crude glycerol disintegrated when handled, preventing them from being analyzed for handling characteristics or heating value. Deproteinated canola without a binding agent (glycerol) demonstrated significantly poorer handling characteristics than the standard canola meal, regardless of average particle size. It is due to the lack of protein in the treated meal, in addition to starches, hemicellulose, and lignocellulosic material, cellular protein content contributes significantly to the structural integrity of the final product, plasticizing under heating and improving the quality of the pellets (Shaw, 2008; Naczk et al., 1985). Initial experiments determined that at 5000 N and/or crude glycerol content higher than 10 % (w/w), the canola meal/crude glycerol mixture would not form solid pellets. Attempts to pelletize under these conditions repeatedly failed, due to premature extrusion from the mill. Untreated canola meal pellets disintegrated under handling, making them unsuitable for marketing as a densified biomass product. However, densification with crude glycerol produced stable pellets that saw roughly a doubling of the energy of combustion produced per unit volume. Plain meal and the meal ground to pass the 0.83 mm and 3.2 mm screens had similar heating densities of approximately 12000 MJ/m^3. Pellets made with 5 and 10 % (w/w) glycerol, that would pass either screen also all showed similar values, around 21500 to 22000 MJ/m^3.

Table 3.4: Average pellet dimensions for the experimental range.

Max particle size mm	**Glycerol Content** % (w/w)	**Force** N	**Temp** °C	**Mass (average)** g	**Diameter (average)** mm	**Length (average)** mm
0.83	5	1000	70	0.66	6.72	16.70
0.83	10	1000	70	0.67	6.72	16.90
0.83	5	1000	100	0.70	6.77	16.75
0.83	10	1000	100	0.70	6.65	16.27
0.83	5	2000	100	0.64	6.85	16.41
0.83	10	2000	70	0.67	6.69	15.14
0.83	5	3000	70	0.65	6.71	13.51
0.83	10	3000	70	0.57	6.69	13.91
0.83	5	3000	100	0.64	6.72	14.40
3.2	5	1000	70	0.61	6.69	15.54
3.2	5	1000	100	0.61	6.73	14.92
3.2	10	1000	70	0.61	6.75	15.23
3.2	10	1000	100	0.63	6.75	14.91
3.2	5	3000	70	0.63	6.72	14.65
3.2	5	3000	100	0.62	6.72	14.70
**deproteinated meal*						
0.83	10	3000	100	0.61	6.82	15.64

* Data for pellets made at 2000 N was acquired before the experiment was restructured, but has been included here for comparison.

Handling property, heating value and density of pellets produced from canola meal using different concentrations of glycerol are given in **Table 3.5**. This shows pellets made with 5 % (w/w) crude glycerol demonstrated the best handling characteristics of all the samples, with a drop test survival rate of ~92%, as compared to 82% for 10 % (w/w) glycerol and 76% survival for deproteinated pellets. The drop test results for pellets prepared using 5 % (w/w) of glycerol are shown in **Tables 3.6** and **3.7**.

Table 3.5: Density, HHV, Volumetric HV and handling characteristics

Particle Screen mm	**Glycerol Content** % (w/w)	**Force** N	**Temp** ºC	**Density (average)** kg/m^3	**HHV (average)** MJ/Kg	**Bulk HV (average)** MJ/m^3	**Handling (average)**	**Drop Test** % survival
0.83	5	1000	70	1050.6	18.76	19707.5	Fragile	n/a
0.83	10	1000	70	1095.9	19.18	21023.4	Fragile	n/a
0.83	5	1000	100	1099.9	19.40	21335.9	Fragile	n/a
0.83	10	1000	100	1099.9	19.40	22332.7	Fragile	n/a
0.83	5	2000	100	1073.8	19.12	20528.6	fair	n/a
0.83	10	2000	70	1110.5	19.74	21917.8	good	n/a
0.83	5	3000	70	1142.8	19.02	21741.1	excellent	91.99
0.83	10	3000	70	1132.1	19.39	21948.2	good	83.01
0.83	5	3000	100	1175.2	19.28	22653.2	good	n/a
3.2	5	1000	70	1071.9	19.28	20668.2	Fragile	n/a
3.2	5	1000	100	1085.2	19.16	20792.4	Fragile	n/a
3.2	10	1000	70	1095.7	19.87	21766.6	Fragile	n/a
3.2	10	1000	100	1099.9	19.62	21584.4	Fragile	n/a
3.2	5	3000	70	1147.3	18.96	21756.5	Good	n/a
3.2	5	3000	100	1160.1	19.77	22933.9	Good	n/a
**deproteinated meal*								
0.83	10	3000	100	1037.8	18.85	19561.60	Fragile	76.45

Tables 3.6 and **3.7** shows, dimensions of the samples prepared for one operating condition (70 ^{O}C and 3000 N using particles passed 0.83 mm) before and after drop testing. It can be seen that the % survival for each operating condition, calculated based on the results of 10 samples.

Table 3.6: Mass and dimensions for the 5 % (w/w) crude glycerol, plain canola meal pellets (prepared at 70 °C and 3000 N using particles passed 0.83 mm) before drop testing

Before Drop testing					
Mass g	**Length mm**	**Base[1] mm**	**Tip[2] mm**	**Volume mm^3**	**Density kg/m^3**
0.576	13.63	7.36	6.74	498.9	1154.7
0.56	13.2	7.15	6.72	476.6	1174.9
0.585	13.88	7.30	6.72	503.9	1160.9
0.569	13.75	7.24	6.71	496.8	1145.4
0.568	13.32	7.38	6.68	481.0	1180.8
0.568	13.39	7.51	6.71	490.0	1159.2
0.56	13.27	7.65	6.71	489.0	1145.2
0.564	13.68	7.39	6.68	493.9	1142.0
0.56	13.57	7.34	6.68	488.9	1145.4
0.563	13.39	7.48	6.71	489.3	1150.6

[1] Average diameter of pellet base; [2] Average diameter of cylindrical part of pellets

Table 3.7: Mass and dimensions of largest surviving fragment of 5 % (w/w) crude glycerol, plain canola meal pellets (prepared at 70 °C and 3000 N using particles passed 0.83 mm) after dropping

After drop testing						
Mass g	**Length mm**	**Base mm**	**Tip mm**	**Volume mm^3**	**Density kg/m^3**	**% survival (mass)**
0.57	13.69	7.30	6.72	497.2	1148.5	99.13
0.55	13.21	7.49	6.72	484.9	1131.4	97.86
0.42	10.08	6.68	6.68	353.3	1180.4	71.28
0.53	12.87	6.84	6.68	454.1	1173.9	93.67
0.56	13.33	7.40	6.68	481.8	1170.6	99.30
0.53	12.57	7.31	6.76	462.2	1135.9	92.43
0.51	12.50	7.15	6.73	452.9	1128.2	91.25
0.50	12.19	6.68	6.68	427.2	1168.0	88.48
0.53	12.72	6.68	6.68	445.79	1184.42	94.29
0.52	12.75	6.71	6.71	450.86	1151.12	92.18
					average	**91.99**

3.2 Oxygen gasification of canola meal after protein extraction for synthesis gas production in a fixed-bed reactor

3.2.1 Extraction of protein from canola meal

Several batches of canola meal were treated for protein extraction. Bradford method was used to determine the content of protein in the filtrates left after extraction. The average value of protein removed was 67% of the protein content of the original canola meal.

3.2.2 Characterization of canola meal feed after protein extraction

The results for ultimate analysis of biomass sample are given in **Table 3.8**. From the analysis, the empirical formula for the biomass was calculated to be $CH_{1.79}O_{0.59}N_{0.11}$.

Table 3.8. Ultimate analysis of protein extracted canola meal

Ultimate analysis	% (w/w), dry, ash-free basis
C	48.2
H	7.2
N	6.4
S	0.4
O*	37.8 (* by difference)

It was determined from particle size analysis that the particle size for biomass was in range of 0.041 to 2.197 mm with the average particle size of 0.781mm (**Fig. 3.1**). From the thermogravimetric analysis for canola meal after protein extraction (**Fig. 3.2**), it can be observed that thermal decomposition starts at around 250 °C and major weight loss of about 50 % (w/w) was observed between 250 to 550 °C. So, the injection of O_2 and collection of product gases started at 250 °C. In this figure, TG stands for weight of sample (mg) and DTG shows the rate of change in sample weight based on the time (mg/min).

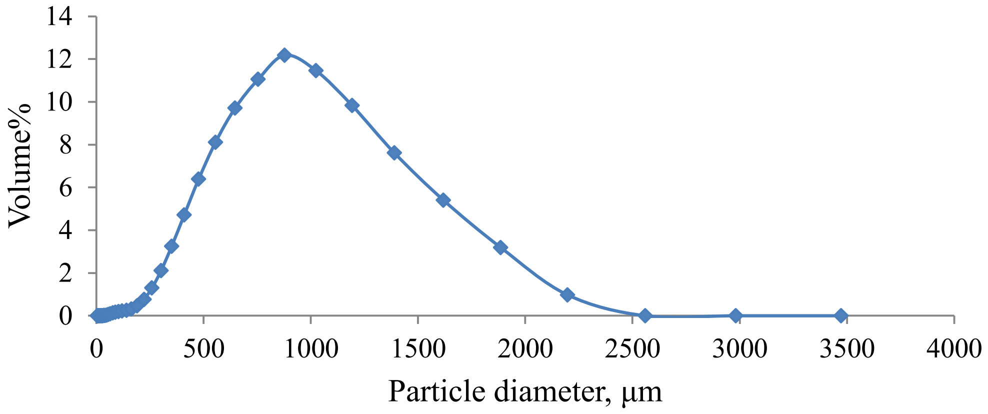


Fig. 3.1: Particle size distribution of feed used for the gasification experiments

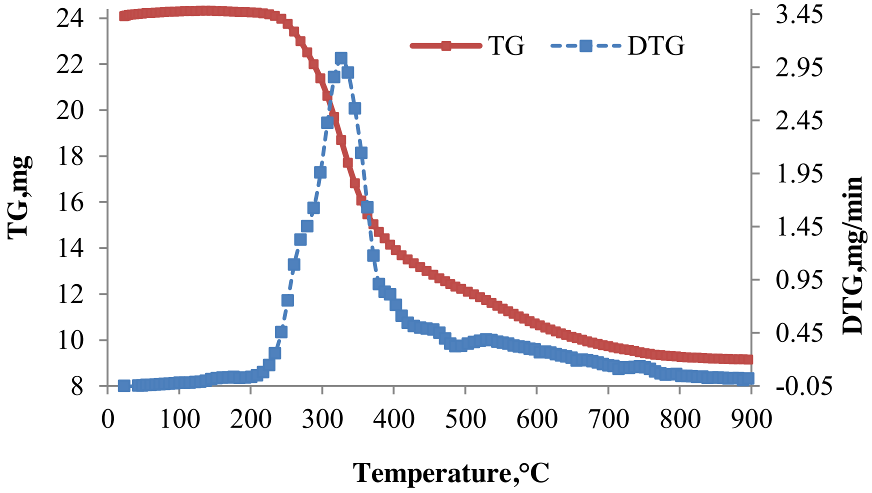


Fig. 3.2: Thermogravimetric analysis results for canola meal feed after protein extraction under inert atmosphere (He)

3.2.3 Gasification of canola meal

In this work, product yield distribution of gas, tar and char at four different temperatures (in the range of 650-900 ^{o}C) and four different ER values (in the range of 0.20-0.40) was investigated. The results for each compound in gas phase such as H_2, CO and concentration (mol %) of the chemical compounds are given in **Table 3.9**.

Table 3.9: Results for oxygen gasification of canola meal after protein extraction

Run	1	2	3	4	5	6	7	8
Reaction time(min)	60	60	60	60	60	60	60	60
ER	0.20	0.20	0.20	0.20	0.27	0.27	0.27	0.27
Temperature, °C	650	735	815	900	650	735	815	900
Yields								
Char/biomass (g/g)	0.15	0.14	0.11	0.07	0.09	0.08	0.08	0.07
Tar/biomass (g/g)	0.22	0.15	0.10	0.08	0.21	0.15	0.10	0.08
Gas/biomass (Nm^3/g)	0.74	0.78	0.90	1.06	0.78	0.93	0.99	1.10
Gas composition (mole%)								
H_2	70.99	58.03	65.57	64.12	72.19	66.82	61.35	59.55
CO	12.58	17.51	16.81	17.45	11.59	16.84	20.52	21.73
CO_2	6.88	5.75	5.22	4.21	10.04	7.25	6.69	5.74
CH_4	1.90	3.57	3.21	3.62	1.55	2.31	2.85	2.82
C_2+	1.42	2.19	1.62	0.96	1.19	1.54	1.53	0.82
LHV (MJ/Nm^3)	10.83	11.14	11.38	11.03	10.56	11.14	11.20	10.70
Carbon conv. efficiency(η_c)	22.11	30.70	31.09	34.70	24.46	33.50	39.60	42.87
H_2/CO	5.67	3.32	3.90	3.69	6.23	3.97	2.99	2.67
Syngas (H_2+CO), Nm^3/kg	0.62	0.59	0.74	0.86	0.66	0.78	0.81	0.90

Run	9	10	11	12	13	14	15	16
Reaction time (min)	60	60	60	60	60	60	60	60
ER	0.33	0.33	0.33	0.33	0.40	0.40	0.40	0.40
Temperature, °C	650	735	815	900	650	735	815	900
Yields								
Char/biomass (g/g)	0.08	0.08	0.07	0.07	0.08	0.08	0.07	0.06
Tar/biomass (g/g)	0.17	0.15	0.09	0.06	0.16	0.12	0.09	0.04

Gas/biomass (Nm^3/g)	0.93	0.98	1.03	1.23	0.99	1.03	1.15	1.35
Gas composition (mole%)								
H_2	65.5	61.7	55.9	59.1	64.6	58.1	53.7	60.8
CO	13.2	19.5	22.7	23.2	12.8	20.9	20.7	23.0
CO_2	11.5	8.2	6.9	6.9	14.6	10.3	8.7	9.6
CH_4	1.56	2.21	2.89	3.13	1.54	2.36	2.75	2.44
C_2+	1.13	1.51	1.48	0.50	1.08	1.61	1.41	0.94
LHV (MJ/Nm^3)	10.01	10.87	10.88	10.74	9.83	10.78	10.29	10.94
Carbon Conv. efficiency(η_c)%	32.3	39.3	44.0	52.71	37.2	47.7	48.7	60.3
H_2/CO	4.87	3.16	2.46	2.52	5.04	2.58	2.59	2.65
Syngas (H_2+CO) Nm^3/kg	0.73	0.79	0.81	1.01	0.76	0.81	0.86	1.13

Products' yield are shown in **Fig. 3.3**. Gas yield is defined as Nm^3 of dry and inert free gas produced per kilogram of dry biomass. As expected, the gas yield increased with an increase in temperature as well as ER values. This increase can be attributed to the following factors (Tavasoli et al., 2009; Franco et al., 2003; Xiao et al., 2007): (i) increase in endothermic char gasification reactions at higher temperatures, (ii) cracking and reforming of higher hydrocarbons and tars at elevated temperatures. The gasification of canola meal can be broadly described through given reactions (Tavasoli et al., 2009):

$$\text{Canola meal} \rightarrow \text{Gas + Tars + Char} \tag{1}$$

$$\text{Tars} \rightarrow \text{Light and heavy hydrocarbons} + CO + CO_2 + H_2 \tag{2}$$

$$\text{Heavy hydrocarbons} \rightarrow \text{light hydrocarbons} + H_2 \tag{3}$$

$$\text{Char} \rightarrow CO + CO_2 + H_2 + \text{solid residue} \tag{4}$$

By increasing the temperature from 650 to 900 °C, the gas yield increased from 0.74 to 1.06 Nm^3/kg at ER of 0.2 and from 0.98 to 1.35 Nm^3/kg at ER of 0.4. Tar yield (tar collected/biomass sample, kg/kg) decreased from 22 to 8 % (w/w) and char yield decreased from 15 to 7 % (w/w) as the temperature increased from 650 to 900 °C at ER of 0.20. Similar results were observed for other ER values, as it can be seen in **Fig. 3.3**. Such trend in results is due to tar cracking and steam reforming reactions given below (Narváez et al., 1996):

$$C_nH_x \leftrightarrow nC + (x/2)\,H_2 \tag{5}$$

$$C_nH_x + mH_2O \leftrightarrow nCO + (m + x/2)H_2 \tag{6}$$

Ottawa sand packed bed used in second stage increased the residence time of tar and promoted thermal cracking which lead to low tar percentage. Soni et al. (2009) used similar arrangement for 2-stage gasification and reported a 57.3 % reduction in tar content and 40.9 % increase in gas yield over single stage using 2-stage gasification setup. Ultimate analysis results for tar and char samples obtained at 650 °C and ER of 0.20 are reported in **Table 3.10**. The char remained after the gasification has more than 40 % (w/w) carbon content. Therefore, it can be used for the production of activated carbons or for soil remediation.

Table 3.10: CHNS analysis of tar and char sample at 650 °C and ER of 0.20

Element	Tar (% (w/w))	Char (% (w/w))
C	72.7	42.1
H	9.6	0.7
N	3.1	3.6
S	0.2	0.4

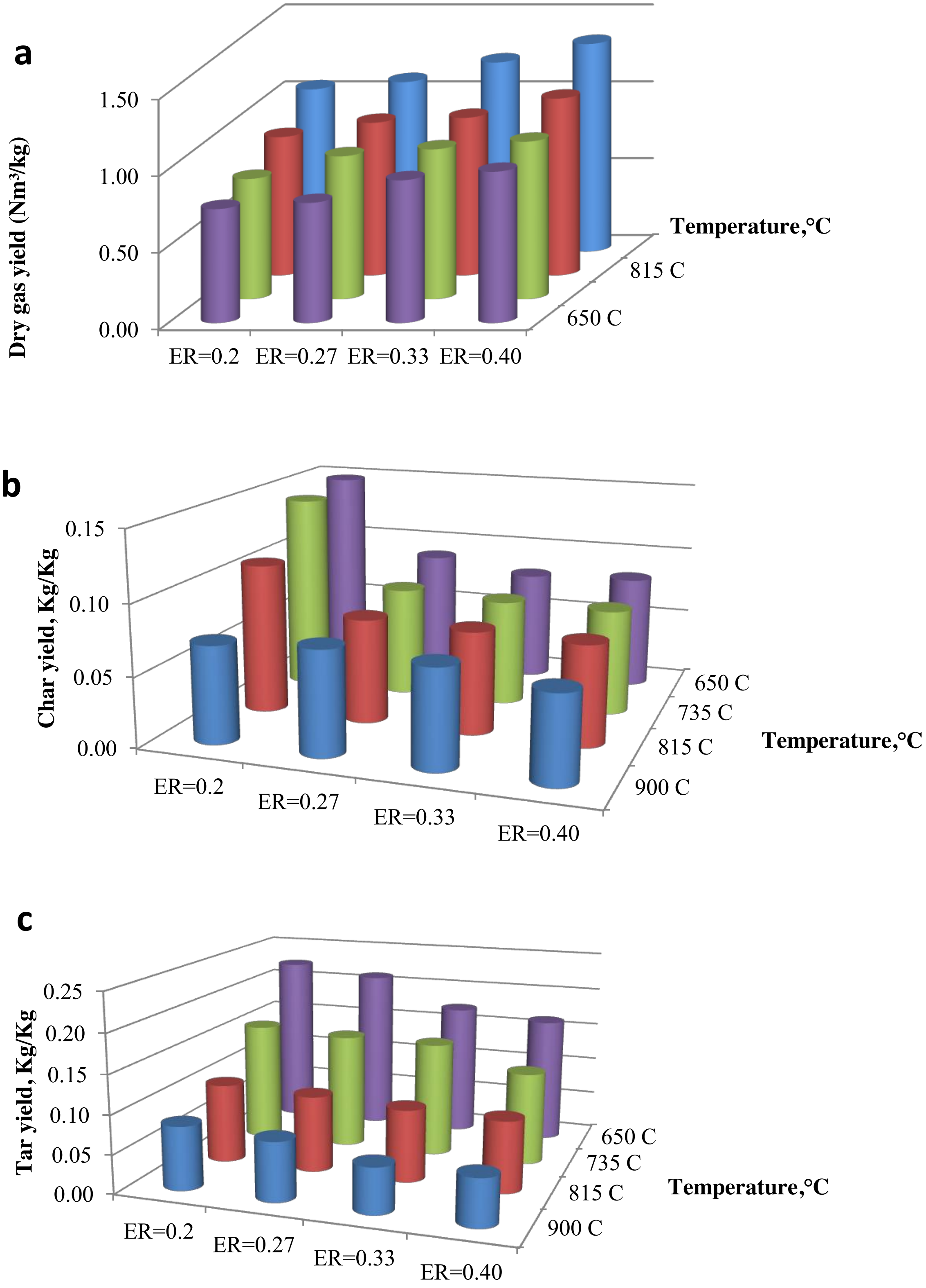


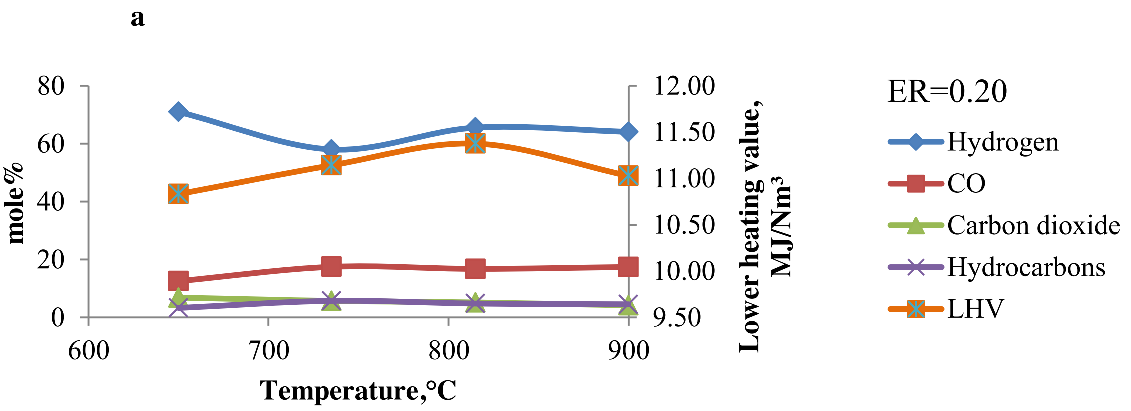
Fig. 3.3: Variation in product yield for a) gas, b) char and c) tar with temperature and ER

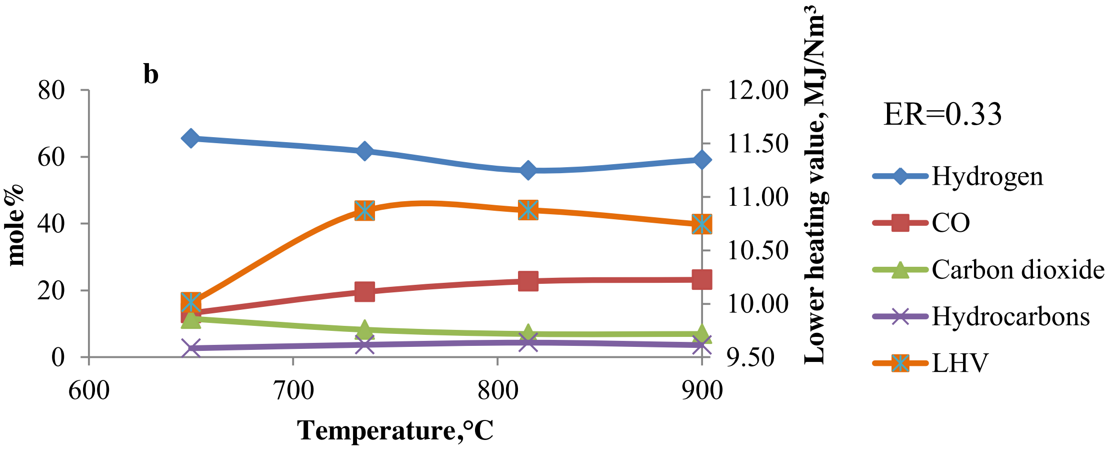
% (w/w) difference for replicate run is as follows: dry gas yield = ±2.5%, char yield = ±3%, tar yield = ±2%.

3.2.4 Gas composition and LHV

The gas composition at various temperature and ER values is given in **Table 3.9**. The gas composition is reported on dry and inert free basis. Gas product included CO, H_2, CO_2, CH_4 and a small percentage of other higher hydrocarbons such as C_2H_2, C_2H_6, C_2H_4 and C_3H_8 as the main products. **Fig. 3.4** shows the trend for composition of product gas for various values of ER and temperature. CO content increased from 13.2 to 23.2 mole% as the temperature increased from 650 to 900 °C whereas the CO_2 content decreased from 11.5 to 7.0 mole% for ER equal to 0.33. Similarly, CO increased from 12.6 to 17.5 mole% and CO_2 decreased from 6.9 to 4.2 mole% as the temperature increased at ER of 0.20. This trend can be studied via given chemical reactions, occurring to a varying degree during gasification (De Lasa et al., 2011; Franco et al., 2003; Salaices et al., 2010):

Reaction name	**Chemical equation**	**$\Delta H_{f\ (298°C)}$ KJ/mol**	
Oxidation	$CO + 1/2O_2 \rightarrow CO_2$	-254.0	(7)
Oxidation	$C + ½\, O_2 \rightarrow CO$	-111.0	(8)
Boudouard	$C + CO_2 \leftrightarrow 2CO$	172.6	(9)
Combustion	$CnHm + [n+(m/2)]O_2 \rightarrow nCO_2 + (m/2)H_2O$		(10)
Dry reforming of methane	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	123.8	(11)
Water gas shift reaction	$CO + H_2O \leftrightarrow H_2 + CO_2$	-42.2	(12)
Steam reforming of methane	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	205.3	(13)


a
ER=0.20
Hydrogen
CO
Carbon dioxide
Hydrocarbons
LHV
mole %
80
60
40
20
0
600
700
800
900
Temperature,°C
Lower heating value, MJ/Nm³
12.00
11.50
11.00
10.50
10.00
9.50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Hydrogen
CO
Carbon dioxide
Hydrocarbons
LHV
mole %
80
60
40
20
0
600
700
800
900
Temperature,°C
Lower heating value, MJ/Nm³
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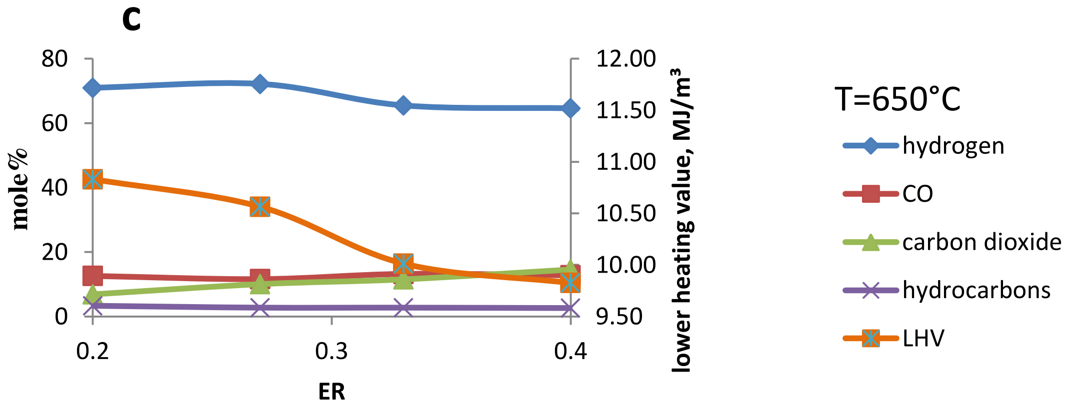
11.50
11.00
10.50
10.00
9.50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T=650°C
hydrogen
CO
carbon dioxide
hydrocarbons
LHV
mole %
80
60
40
20
0
0.2
0.3
0.4
ER
lower heating value, MJ/m³
12.00
11.50
11.00
10.50
10.00
9.50

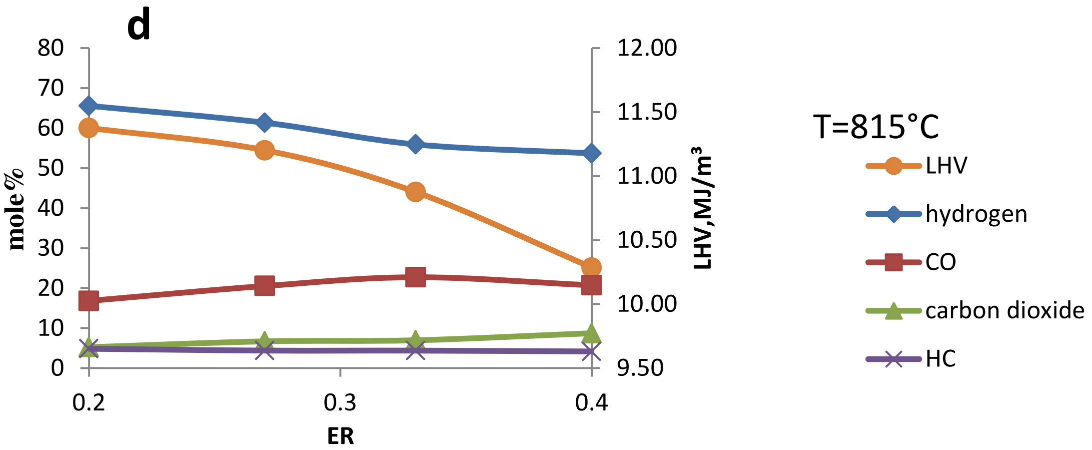


Fig. 3.4: Gas composition and heating value at different temperatures at a) ER= 0.20 & b) ER= 0.33; Gas composition and heating value at different ER values for c) T= 650°C & d) T= 815°C. The % difference in replicating run is as follows: H_2 = ±7%, C0 = ±2.3%, CO_2 = ±1.3%, Hydrocarbons = ±0.2%.

Reactions (7) and (8) are exothermic in nature which leads to production of CO_2 and CO at lower temperatures. At higher temperatures, CO_2 reacts with carbon in char to form CO which leads to increase in yield of CO and decrease in CO_2 content (reaction 9). As evident from data provided in **Table 3.9**, increase in amount of CO is almost two times of the decrease in CO_2 content which is in accordance with mechanism of reaction (9) where one mole of CO_2 gives 2 moles of CO for this reaction. As reported by Tavasoli et al. (2009) rate of reaction of reaction (9) is independent of quantity of char and is zero with respect to carbon for considerable extent of reaction. This shows the importance of reaction (9) during last periods of gasification when the amount of char left behind is low.

As it is shown by reaction (10), by complete combustion, light hydrocarbons will be converted to water and CO_2, if there is enough oxygen in the system. If the amount of oxygen is not enough (partial combustion), the possible reactions for light hydrocarbons depend on the composition of gas phase and they should compete with compounds such as H_2 and CO for combustion. Obviously, these hydrocarbons have less chance for reaction at higher temperatures because they are highly exothermic compared with the above mentioned gases. For example heat of combustion for ethane and methane is -1560 and -2219 kJ/mol, respectively. At given constant temperature, content of CO_2 increases with an increase in ER. The molar concentration of CO_2 increased from 6.9 to 14.6 % at 650 °C and from 5.2 to 8.7 % at 815 °C, with an increase in ER from 0.20 to 0.40. The increase in ER gives rise to combustion (reaction 10) of carbon and hydrocarbons due to higher availability of oxygen, which leads to more CO_2 production. This can be verified from the decrease in the concentration of C_nH_m (including CH_4) at higher ER values (**Table 3.9**). The concentration of hydrocarbons produced had a narrow range of 2.6 to 5.8 mole% at all temperatures and ER values. While the concentration of hydrocarbons decreased with an increase in ER, it first increased and then decreased with increasing gasification temperature. Xiao et al. (2007), Tavasoli et al. (2009) and Narvaez et al. (1996) reported similar results for CO and CO_2 formation, but for different feedstocks and operating conditions.

The CO content almost remained constant with an increase in ER, as it can be seen from **Table 3.9**. It was observed that the content of H_2 decreased with an increase in ER, from 71 to 64.6 % at 650 °C and from 65.6 to 53.7 % at 815 °C. This can be attributed to oxidation of CO and H_2 to CO_2 and H_2O (Mahishi and Goswami, 2007). Also, combustion reactions are more dominant at higher ER values to form CO_2 which limit the availability of O_2 for CO formation. It was observed that concentration of H_2 was maximum at the lowest temperature 650°C irrespective of the ER value. The H_2 concentration first decreased and then increased with temperature at a constant ER value. The H_2 concentration decreased from 65.5 % at 650 °C to 55.9 % at 815 °C and then increased to 59.1 % at 900 °C for ER value 0.33. The highest concentration of 72.2 % was observed at 650 °C and 0.27 as an ER. Water gas reaction (WGS) and steam reforming reaction are the two important reactions of gasification process that affect the concentration of CO and H_2. WGS is exothermic in nature (reaction 12) which can be a reason for high content of H_2 at lower temperature. Abuadala et al. (2010) reported decrease in H_2 content with an increase in temperature for steam gasification. They attributed this trend to other reactions taking place at elevated temperatures where H_2 reacts to form other byproducts. Also, all the reactions involved do not attain equilibrium during the actual gasification process and reactivities of tar and char can have a significant effect on product composition (De Lasa et al., 2011). Even ash can have a catalytic effect in the pyrolysis step and influence the synthesis gas composition. ICP-MS result for ash content of protein extracted canola meal is reported in **Table 3.11**.

Table 3.11: ICP-MS results for ash content of protein extracted canola meal

Element	Na	Mg	Al	P	Ca	Fe
Content (ppm)	675	81095	1465	193481	99558	2198
Element	Ni	Cu	Zn	Ba	Pb	
Content (ppm)	22	252	818	175	66	

Also, decrease in H_2 content at higher temperatures can be justified by volatilization of alkalies to gaseous phase at higher temperatures and ER (Arvelakis et al., 2004; Tanaka et al., 2008), iron sintering or even reduced porosity of char due to increased crystallinity and thus reactivity loss at higher temperature. This leads to this fact that ash is an active catalyst for gasification at lower temperature which gets deactivated at higher temperatures. Increase in tar cracking at higher temperature can be a reason for increase in H_2. The work done by Tanaka et al. (2008) indicated that biomass ash acts catalytically and lowers temperature for steam reforming reactions. Although, the gas composition showed a definite trend with change in ER and temperature, it was observed that the total yield of each gas component increased with an increase in both parameters. This can be attributed to increase in total gas yield due to increase in tar cracking at higher temperatures and ER. As shown in **Fig. 3.5**, H_2 yield increased from 0.5 to 0.7 Nm^3/Kg of biomass with an increase in temperature at an ER of 0.20.

LHV is calculated for the gas produced in the gasification process. It is the heating value of material after subtracting the latent heat of water formed during the combustion. The LHV depends on the composition of dry product gas and is calculated as follows (Lv et al., 2007):

$$\text{LHV (KJ/m}^3\text{)} = (30*CO+25.7*H_2+85.4*CH_4+151.3*CnHm)*4.2 \qquad (3)$$

Where CO, H_2, CH_4 and CnHm are the molar concentration of the gas components.

The value of LHV varied from 9.8 MJ/Nm^3 (650 °C, ER= 0.40) to 11.2 MJ/Nm^3 (815 °C, ER = 0.27). This makes it suitable as feedstock in subsequent conversions into chemicals such as methanol and methane (Mckendry, 2002). Overall, heating value decreases with an increase in

ER due to combustion of hydrocarbons into CO_2 and decrease in the content of fuel gases such as H_2 and CO. So, on one hand increase in ER leads into reduction in content of tar and char and on other side, it lowers the heating value of product gas. In case of increase in temperature, there was an overall increase in LHV at higher temperatures with a little fluctuation in results at some points due to change in content of hydrogen. The heating value increased from 9.8 to 11.1 MJ/Nm^3 as the temperature increased from 650 to 900 °C at ER of 0.40. This is due to increase in the content of CO and H_2 at higher temperature values as discussed in previous studies (Marono et al., 2010; Tavasoli et al., 2009; Zhou et al., 2009).

3.2.5 Carbon conversion efficiency [η_c (%)]

Carbon conversion efficiency is defined as the ratio of the weight of carbon in product gas to the weight of carbon in the original biomass sample on the dry ash free basis. It was calculated by following equation (4)

$$\eta_c = (Vg \times 1000[CH_4\% + CO\% + CO_4\% + 2(C_2H_4\% + C_2H_6\%) + 3(C_3H_6\% + C3H8\%) + 4 * C_4H_{10}\%] \times 12) / (22.4 * W * C\ \%\ (w/w)) \quad (4)$$

Where CH_4%, CO% and concentration of hydrocarbons are vol. %. Vg is the dry product gas collected (Nm^3) per dry, ash-free biomass fed (g), and C % (w/w) is the carbon content in the ultimate analysis (dry ash free) of biomass.

Fig.3.6 shows carbon conversion efficiency increases with an increase in ER as well as temperature. At higher temperatures, char reaction is promoted due to the endothermic nature of reaction (4), therefore, one can observe an increase in carbon efficiency by temperature. At higher ER, the efficiency increased due to increase in oxidation of char to form CO_2 but the quality of product gas degrades, thus reducing LHV. It was observed that by increasing the temperature from 650 to 900 °C, the carbon efficiency increased from 37.2 % to 60.3 % (i.e. 38.2 % increase) at ER equal to 0.40. Similar trend was observed at ER equal to 0.20 where the efficiency increased from 22.1 to 34.7 %. The efficiency increased from 22.1 to 37.2% as the ER increased from 0.20 to 0.40 at a constant temperature of 650 °C. Similar results can be seen for other values of temperature and ER in **Table 3.9**.

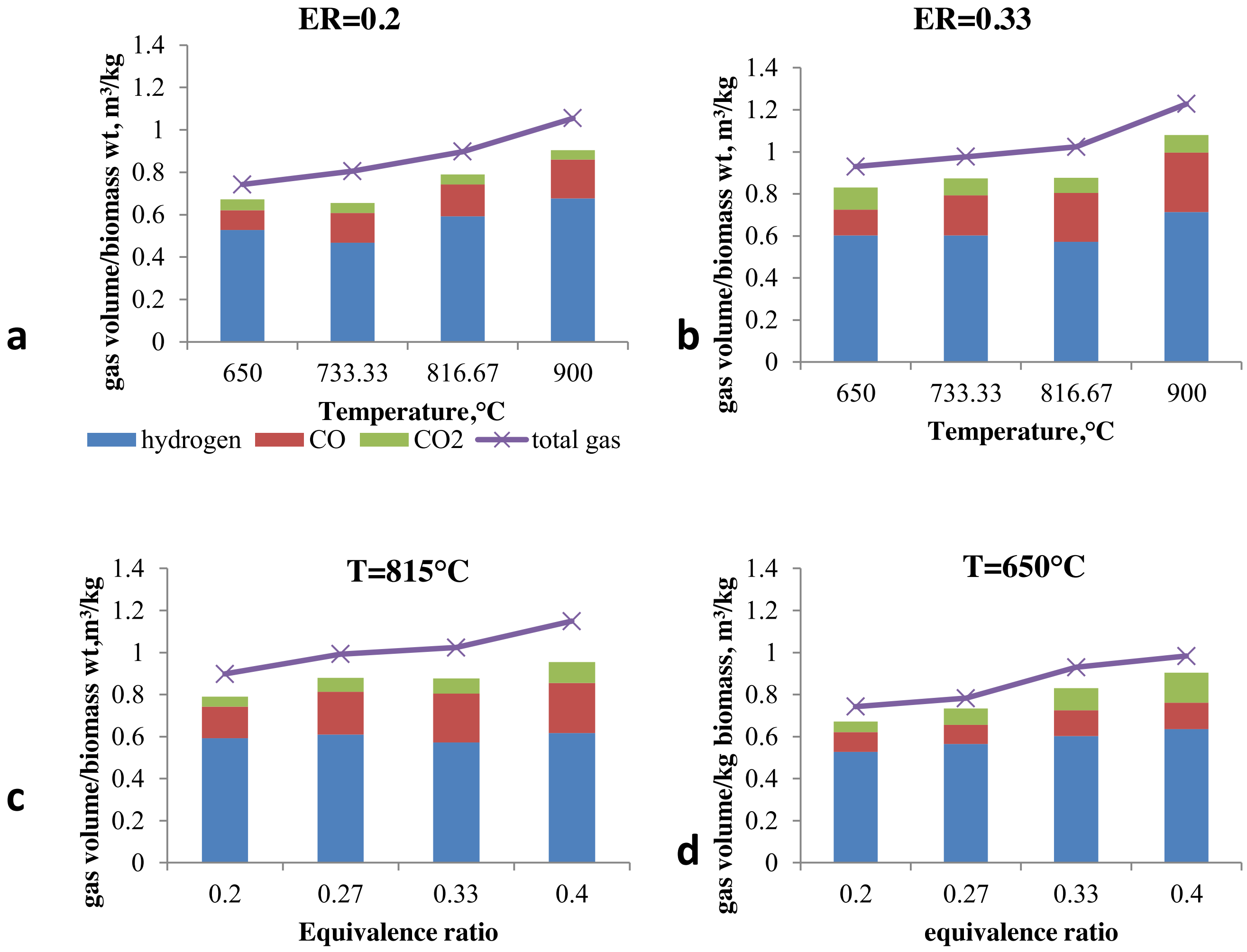


Fig. 3.5: Total volume of gaseous product per unit of biomass fed (Nm³/Kg) with temperature at a) ER=0.20, b) ER=0.33 and with ER at c)T=815°C and d) T=650°C

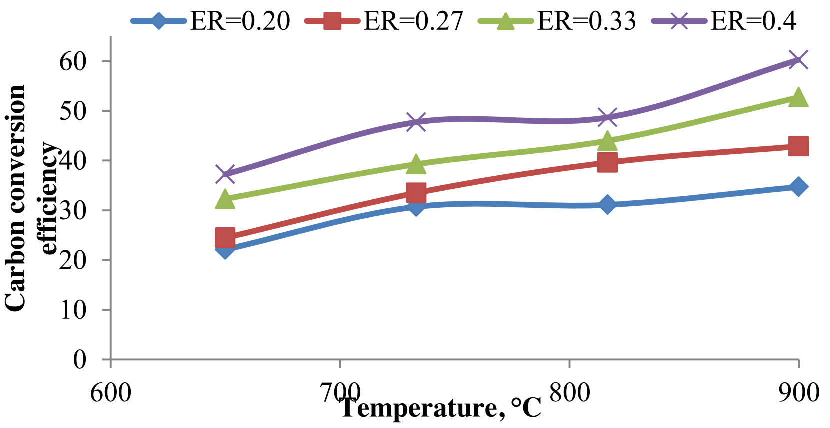


Fig.3.6: carbon conversion efficiency vs. temperature for various ER values

3.2.6 H_2/CO molar ratio

The H_2/CO ratio is important for syngas application in Fischer-Ttropsch process. For instance, the H_2/CO ratio for ethanol synthesis is 3 and 2 for methanol synthesis. **Fig. 3.7** shows the H_2/CO ratio for total gas produced at all temperature and ER values. The value of this ratio is maximum at the lowest temperature, i.e. 650 °C, because the mole fraction of H_2 is maximum at this temperature and CO content is minimum for all ER values. The total syngas yield increases with temperature and equivalence ratio (**Fig. 3.8**). The yield is almost doubled from 0.62 Nm^3/kg biomass at 650 °C and ER of 0.20 to 1.13 Nm^3/kg at 900 °C and ER of 0.40.

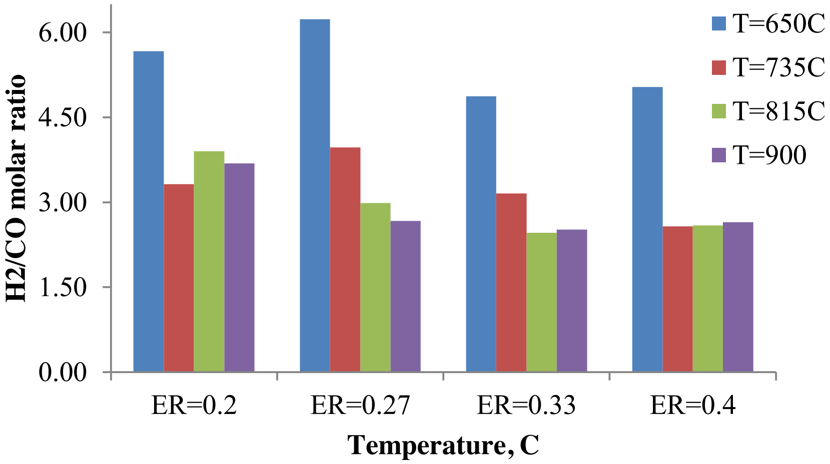


Fig. 3.7: H_2/CO ratio at different ER and temperature values

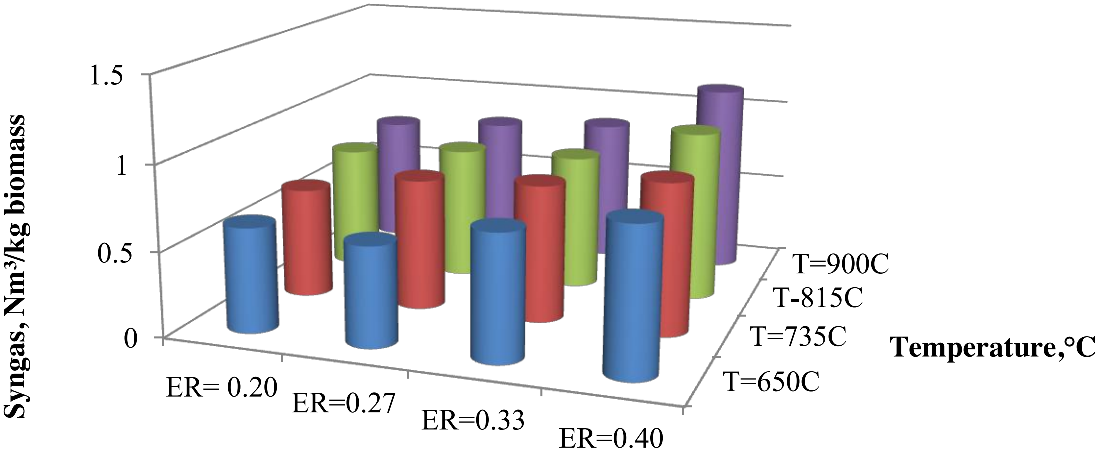


Fig. 3.8: Syngas yield at different temperature and ER values

3.2.7 Use of catalyst

Dolomite was used to study its impact on tar reduction and the experiment was carried out at 735 °C and ER of 0.27. It was observed that the tar yield reduced by around 50 % (w/w) from 15 to 7 % (w/w). The gas yield increased from 0.93 to 1.14 Nm^3/kg biomass. H_2 yield increased by 23.5 % from 0.62 to 0.78 Nm^3/kg biomass. The catalytic effect of dolomite for tar cracking can be due to the trace minerals found in dolomite such as potassium and iron oxides which are active for tar-removal reactions, including steam/dry reforming reactions, and steam/thermal cracking reactions.

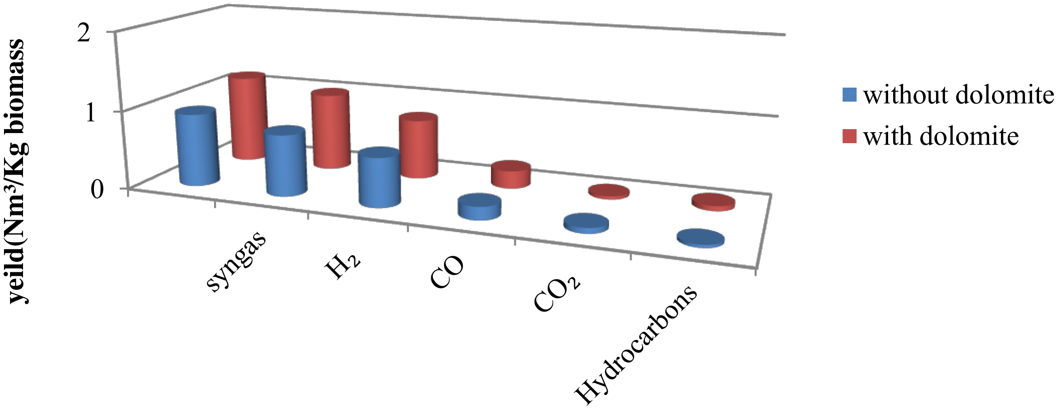


Fig. 3.9: Comparison of gas composition with and without use of dolomite (T=735 °C & 0.2 ER)

3.3 Gasification of canola meal and factors affecting gasification process

3.3.1 Steam Gasification

3.3.1.1 Effects of ER and temperature on gas composition

In steam gasification, several reactions take place due to the carbonaceous nature of the feedstock. The concentration of different components in gas differs depending on the extent of reactions taking part during gasification process. The effects of temperature and ER on gas composition are shown in **Fig. 3.10a**. As can be seen from the graphs, the effects of increasing temperature from 650 to 850 ºC and ER from 0.2 to 0.4 are investigated. Since it is challenging to propose the exact governing reaction during gasification process, based on the literature, authors have suggested the following reactions in case of canola meal feed stock. Steam gasification of canola meal involves reactions 14 to 19:

Water gas

Primary

$C + H_2O \rightarrow H_2 + CO$ ΔH= +130.1 KJ/mol (14)

Secondary

$C + 2H_2O \rightarrow CO_2 + 2H_2$ ΔH= -96.6 KJ/mol (15)

Methanation

$C + 2H_2 \rightarrow CH_4$ ΔH= -74.9 KJ/mol (16)

$2CO + 2H_2 \rightarrow CH_4 + CO_2$ ΔH=-247.5 KJ/mol (17)

$CO + 3H_2 \rightarrow CH_4 + H_2O$ ΔH= -206 KJ/mol (18)

Water-gas shift

$CO + H_2O \rightarrow CO_2 + H_2$ ΔH= -40.2 KJ/mol (19)

Higher ER favors the high concentration of H_2 in product gas due to dominated reactions 14 and 15. Generally H_2 concentration is correlated to ER and carbon from biomass, char and tar (Dellavedova et al., 2012). CO_2 in product gas mainly comes from oxidation reaction of char components (reaction 15). Hence around lower temperature (650 ºC), the CO2 concentration is high in product gas while it decreases as the temperature increases to 850 ºC. As the temperature inside gasifier increases, it favors the CO_2 reaction with the char to produce CO (Senapati and Behera, 2012). This reaction was well explained by using the Le Chatlelier principle of higher temperature favoring endothermic reaction. Then, around 600-700ºC the endothermic Boudouard reaction (reaction 20) dominates the process and increases the concentration of CO in product gas (Franco et al., 2003).

Boudouard

$C + CO_2 \rightarrow 2CO$ ΔH= +172.5 KJ/mol (20)

The rate of carbon oxidation reaction by steam and CO_2 are of same magnitude, whereas hydrogenation reaction (reaction 16) is of several magnitude slower than the steam-char (reaction 14 and 15) and CO_2-char reaction (reaction 20) (Senapati and Behera, 2012). Apart from the endothermic hydrogenation and methanation reaction, the following reaction helps in increasing concentration of CO at higher temperature and ER, which can be clearly seen from **Fig 3a**.

Steam reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = +206 \text{ KJ/mol} \qquad (21)$$

Therefore, temperature and oxidizing agent play important role with regard to the final composition of product gas. Reaction 14 is strongly endothermic which as dominant reaction was accompanied by other exothermic reactions, making formation of H_2 and depletion of CH_4 and CO_2 as temperature rises. The decomposition gases like CO_2 and CO, and some double bond and triple bond series matter in biomass may lead to formation of light hydrocarbons (Xiang and Zhao, 2009). This might be applicable to formation of CH_4 from cracking of volatile components and higher temperature favors less CH_4 formation which was previously reported by Huang et al. (2003) and Kim et al. (1997). As temperature and ER increase, the rates of several reactions (oxidation, reforming, cracking etc.) also increase, thus reduce CH_4 concentration (6.6% from 18.3%) and others light hydrocarbons to almost negligible levels (1.2% to 0%) from the product gas (see **Fig 3.10a**) (Gil et al., 1997). The composition of product gas is as follows: H_2 (27.9-54.1 mol%), CH_4 (18.3-6.6 mol%), CO_2 (19.4-11.8 mol%), CO (18.8-25.0 mol%). It is observed that increase in temperature from 650ºC to 850ºC, favors increase in H_2 concentration from 27.9 to 54.1 mol%, whereas, contrary effect was observed in case of CH_4 i.e., its concentration decreased from 18.3 to 6.6 mol% with increase in gasification temperature. Similar trend for H_2 and CH_4 was observed by Senapati and Behera (2012) in case of steam gasification using coconut coir feed stock. It is also observed that, concentration of CO increases from 18.8% to 25.0% as temperature and ER increase in the range of, 650-850 ºC and 0.2-0.4 respectively.

Steam gasification

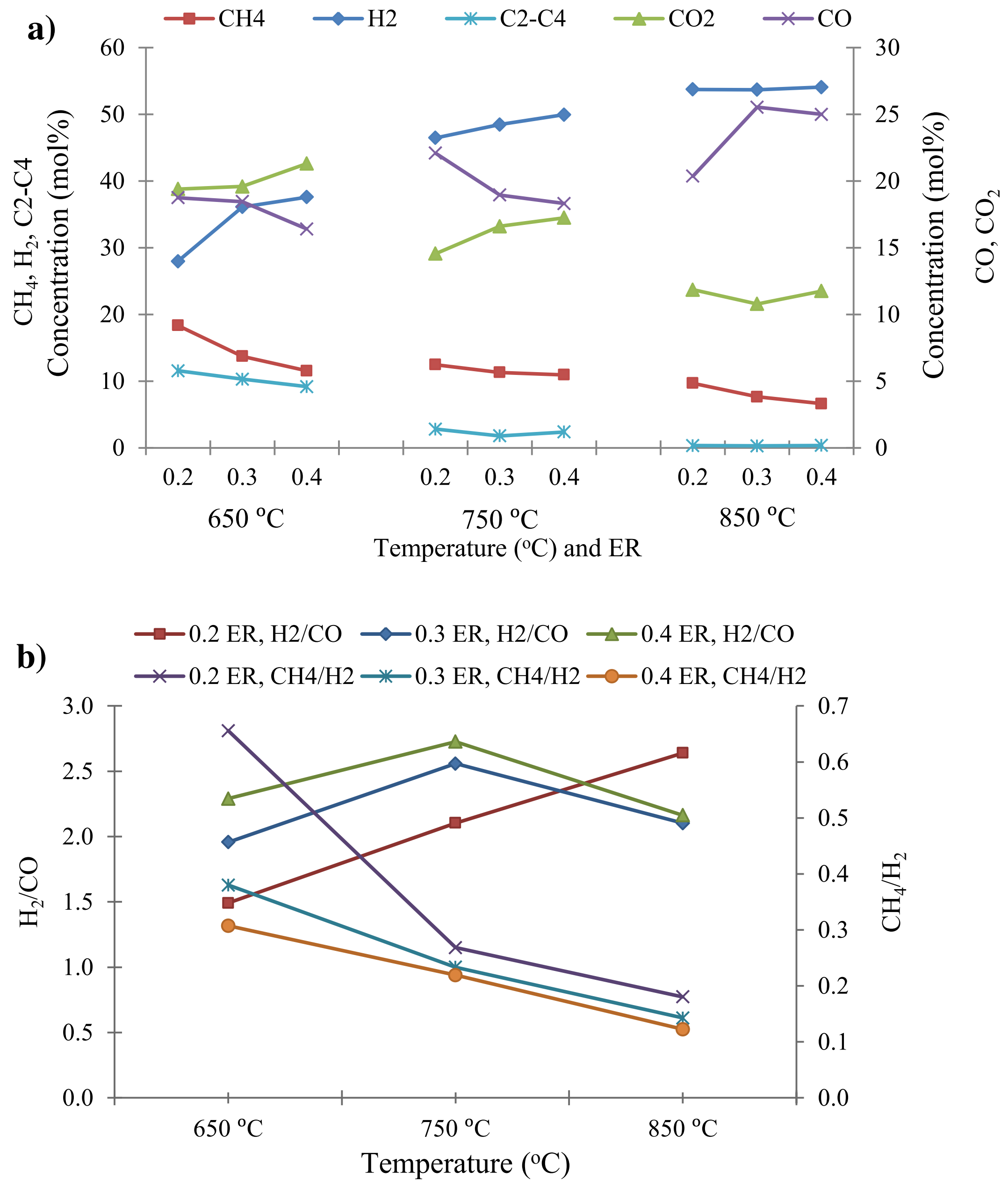


Fig 3.10: Effect of temperature and ER on gas composition H_2/CO and CH_4/H_2 ratio using steam gasification

3.3.1.2 Effects of ER and temperature on H_2/CO and CH_4/H_2 ratio

The H_2/CO and CH_4/H_2 ratio in the product gas is important for further possible end applications like production of liquid fuels or chemicals such as higher alcohol via Fischer–Tropsch process

(Spivey and Egbebi, 2007). Effects of temperature and ER are shown in **Fig. 3.10b** for H_2/CO and CH_4/H_2 ratio. In case of steam gasification, the H_2/CO ratio ranges between 1.49 and 2.73. Syngas having molar ratio of H_2/CO in higher range is desirable for production of H_2 and NH_3 (Encinar et al., 2002). Also, it is highly required as feedstock for Fischer-Tropsch synthesis to produce liquid fuels. In case of ER from 0.2 to 0.4, rise in temperature from 650 ºC to 850 ºC caused increase in H_2/CO ratio with increase in concentration of H_2 (27.9% to 53.8%) and CO (18.8% to 20.4%) in product gas. The small rise in CO as compared to H_2 was attributed to Boudouard reaction. At higher ER, the extra steam available alleviates the bed temperature and prevents the formation of CO and thus increasing the H_2/CO ratio (Zhou, 2005).

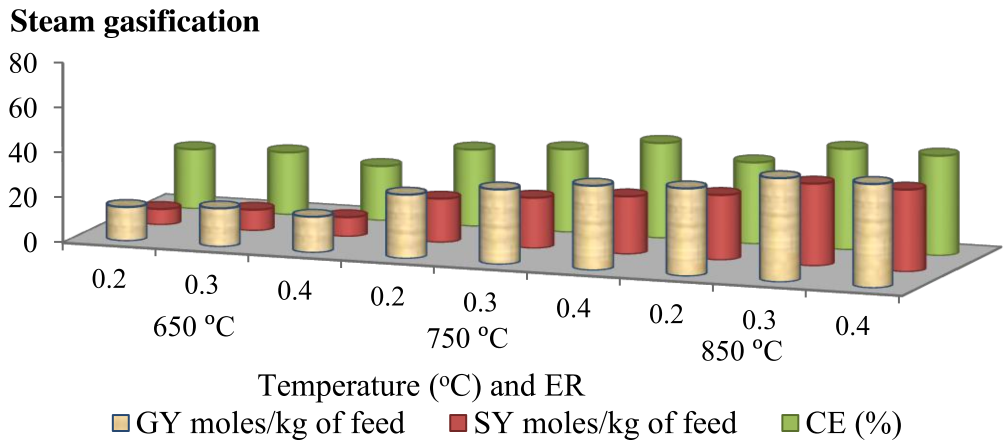
Indeed opposite trend was observed in case of CH_4/H_2 ratio. Increase in both ER and temperature values decreased the CH_4 concentration in product gas from 18.3% to 9.7%, thus leads to decrease in molar ratio of CH_4/H_2 from 0.66 to 0.12. Higher temperature and ER favor more cracking of light hydrocarbons and leads to formation of H_2 and CO in product gas (reactions 20 and 21). The similar trend is also observed by other researchers (Franco et al., 2003).

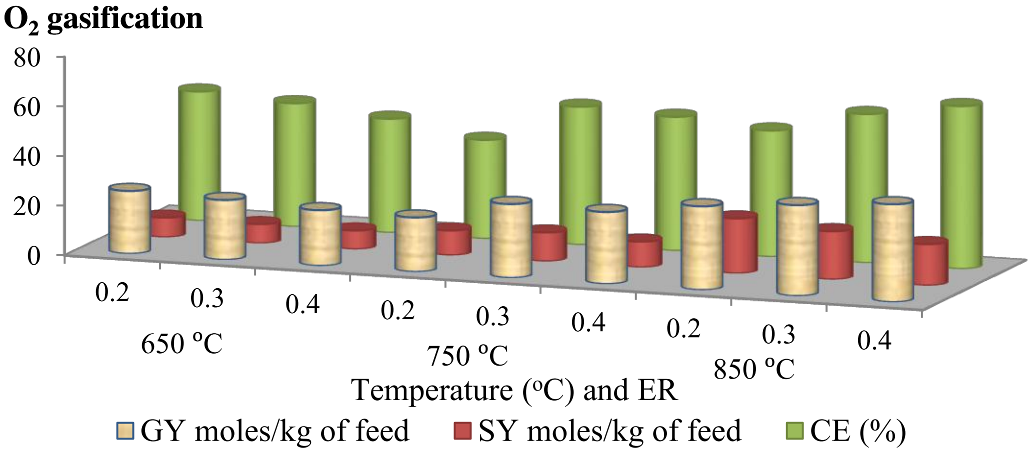
3.3.1.3 Effect of ER and temperature on gas and syngas yield

Total gas yield (GY) and syngas yield (SY) are important parameters to be considered in the gasification process. The gas yield or syngas yield is defined as the moles of gas or syngas produced on the inert free basis per gram of dry and ash free (daf) biomass. The effects of ER and temperature on GY and SY are shown in **Fig. 3.11a**. The GY and SY increase rapidly with increase in temperature and ER, which proves that gasification temperatures as well as ER are the main factors affecting gasification of canola meal. The GY increased from 15.2 moles/kg biomass (0.2 ER and 650 ºC) to 46.4 moles/kg biomass (0.4 ER and 850 ºC) by 32%, whereas SY increased from 7.1 moles/kg biomass (0.2 ER and 650 ºC) to 36.7 moles/kg biomass (0.4 ER and 850 ºC) by 19.3%. Encinar et al. (2002) and Xiang et al. (2009) observed similar trend. The increase in GY and SY can be correlated to a) initial reaction of carbon oxidation as well as cracking of volatile matter, b) further cracking of tars at the elevated temperature and formation of H_2 and CO, and c) accelerated rate of reactions due to high temperature (Xiang et al., 2009).

3.3.1.4 Effect of ER and temperature on carbon efficiency

Carbon efficiency (CE) is one of the parameters to describe the degree of gasification reaction. Carbon efficiency is defined as ratio of the weight of carbon in product gas to the weight of carbon in the original biomass sample on the dry ash free basis (Lv et al., 2007). CE has increased from 26.6% at lowest ER value 0.2 and temperature 650 ºC to 44.6% at highest ER value 0.4 and temperature 850 ºC (refer **Fig. 3.11a**). This stipulates gasification temperature and ER play important role in gasification impacting carbon efficiency. Higher ER and temperature increases the reaction rate increasing CE in the gasification process.





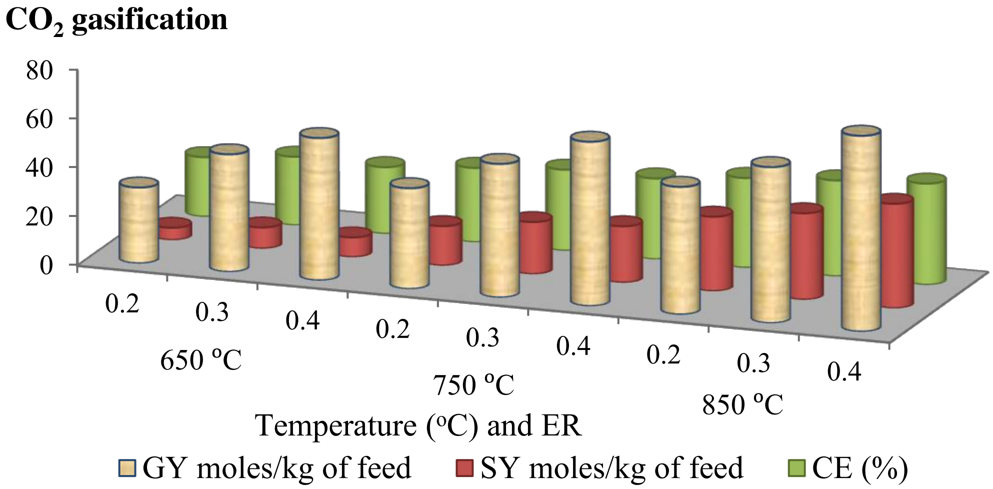


Fig. 3.11: Effect of ER and temperature on gas yield, syngas yield and carbon efficiency

3.3.2 Oxygen (O_2) Gasification

3.3.2.1 Effects of ER and temperature on gas composition

In case of oxygen gasification, oxygen is the strong gasifying agent generally favoring exothermic reaction. Oxygen reacts with carbon in biomass to form CO which further reacts with excess of oxygen present in the surroundings to form CO_2. This can be well explained by the following reaction mechanisms:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -393.8 \text{ KJ/mol} \qquad (22)$$

$$C + 0.5O_2 \rightarrow CO \qquad \Delta H = -283.3 \text{ KJ/mol} \qquad (23)$$

$$CO + 0.5O_2 \rightarrow CO_2 \qquad \Delta H = -110.5 \text{ KJ/mol} \qquad (24)$$

$$H_2 + 0.5O_2 \rightarrow H_2O\ (g) \qquad \Delta H = -242.0 \text{ KJ/mol} \qquad (25)$$

Above all reactions make the whole oxygen gasification process strong exothermic. This heat is released from the reaction of char and oxygen (reaction 22) which is most dominating reaction in the oxygen gasification process. Reaction 24 and 25 may consume produced CO and H_2 and increase the amount of CO_2 and water in product gas. This increase in concentration of CO_2 and simultaneous decrease in concentration of CO and H_2 was well exposed in **Fig. 3.12a**. For example, at 850 ºC, increase in ER surges the concentration of CO_2 (21.2 to 46.8%) due to consumption of produced CO (38.9 to 22.5%) and H_2 (26.8 to 19.8%) at the initial phase of gasification process. This might be due to excess amount of oxygen present around at higher ER value, causing more depletion of H_2 and CO from product gas. High temperature and ER, promotes more diffusion of oxygen to the surface of feed particle causing more absorption of the oxygen molecule. As the gasification reaction process further, residual char particles come more easily in contact with oxygen molecules. This causes more absorption of oxygen followed by increases rate of dominating reaction (reaction 22) of carbon from char and oxygen molecules. In addition, water gas shift reaction due to water formed though reaction 25 might produce H_2. Xiang et al. (2009) explained surface diffusion reaction mechanism behind the oxygen gasification process. The formation of other hydrocarbons along with CH_4 was similar at the initial phase as explained earlier in steam gasification. Concentration of CH_4 has slightly changed, though remains in the range of 6.5 to 10.9%. In precise, the effective gas composition (CH_4, CO and H_2) decreases in product gas and CO_2 content increases as the temperature and ER value increases during gasification process.

3.3.2.2 Effect of ER and temperature on H_2/CO and CH_4/H_2 ratio

Use of oxygen as gasifying agent has improved the H_2/CO from 0.3 to 0.9 but decreased the CH_4/H_2 ratio from 1.0 to 0.3. The increase and decrease trends with H_2/CO and CH_4/H_2 were depicted in **Fig. 3.12b**. The H_2/CO ratio was smallest 0.3 during the lowest reaction parameters (ER 0.2, 650 ºC). Increase in temperature increases the rate of reaction causing formation of more H_2 and CO. This is also responsible for the breakdown of CH_4 thus decreasing the CH_4/H_2. Although oxygen consumes CO and H_2 in combustible/ effective gas as temperature increases, the CO and H_2 content in product gas increases due to accelerated reactions and produces gas with highest H_2/CO ratio 0.9.

O_2 gasification

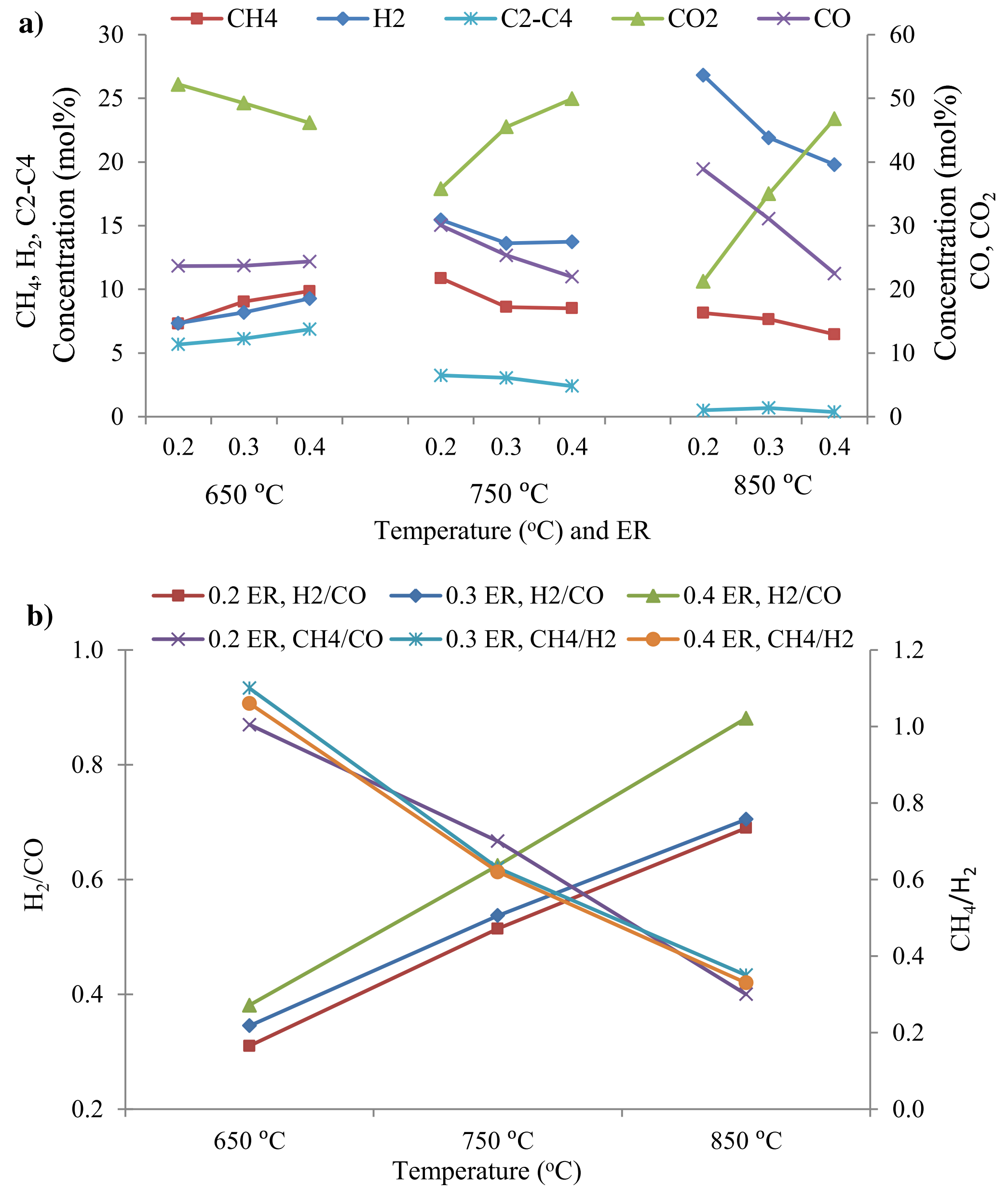


Fig. 3.12: Effect of temperature and ER on gas composition H_2/CO and CH_4/H_2 ratio using oxygen gasification

3.3.2.3. Effect of ER and temperature on gas and syngas yield

The effects of ER and temperature on GY and SY are shown in **Fig. 3.11**. Certainly, similar trend is observed in case of GY during oxygen gasification of canola meal. Increase in temperature increases the GY. The GY at ER 0.2 and temperature 650 ºC reached 25.3 moles/kg biomass, whereas at highest operating parameters (ER 0.4 and temperature 850 ºC), it reached to 39.4 moles/kg biomass. The increase in GY by 64% was due to more produced gas components in product gas. The similar mode was observed in case of the SY. Although maximum SY for canola meal feed was obtained at ER 0.2 and 850 ºC. Further increase in ER at 850 ºC consumes the CO and H_2 from product gas thus decreasing the SY.

3.3.2.4 Effect of ER and temperature on carbon efficiency

The carbon efficiency during oxygen gasification progresses slowly with increasing in temperature and ER. At temperature 650 ºC and ER 0.2, carbon efficiency was almost 52% and increased to 65.5% at 850 ºC, ER 0.4 by a 79.4 % increase (see **Fig. 3.11**). This shows carbon efficiency was higher in oxygen gasification of canola meal as compared to steam gasification. When ER increases from 0.2 to 0.4 at 850 ºC, carbon efficiency increases gradually, the yield of the product gas generated slows down because the CO and H_2 concentration tends to decrease.

3.3.3 Carbon dioxide (CO_2) Gasification

3.3.3.1 Effects of ER and temperature on gas composition

The use of CO_2 as gasifying medium is of interest these days. Temperature and ER are very crucial in the case of CO_2 gasification because the lower value of temperature and ER decreases the H_2 and CO yields and increases the CO_2 concentration in product gas and vice versa. CO_2 gasification in presence of catalyst and a mixture of steam-CO_2 was previously studied by some researchers (Minkova et al., 2000; Garcia et al., 2001). There was substantial reduction in CO_2 concentration with increase in temperature (850 ºC) and ER (0.4) indicating that CO_2 itself gets converted into other products. The gas composition for CO_2 gasification at different temperatures and ERs are represented in **Fig. 3.13**. The principle chemical reactions for CO_2 gasification are as follows:

$$CO_2 + C \rightarrow 2CO \qquad \Delta H = +172.46\ \text{KJ/mol} \qquad (26)$$

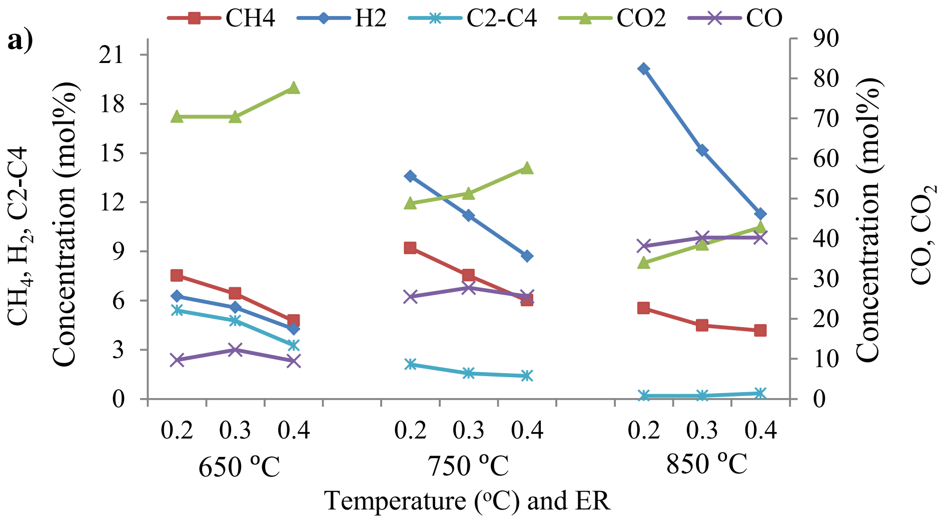
$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H = +41.16\ \text{KJ/mol} \qquad (27)$$

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H = +246.98\ \text{KJ/mol} \qquad (28)$$

$$C_2H_4 + 2CO_2 \rightarrow 2H_2 + 4CO \qquad \Delta H = +292.41\ \text{KJ/mol} \qquad (29)$$

A similar trend was observed by Davy et al. (2003). At lowest temperature and ER (650 ºC, 0.2) concentration of CO_2 in product gas reaches to 70.4%, which further reduces to 42.8% with increase in temperature and ER (850 ºC, 0.4). Reactions 26 and 27 dominated at higher temperature leading to self-participation of CO_2 in gasification process and increasing the concentration of CO (9.7% at 650 ºC; 40.2% at 850 ºC) in the product gas. Higher temperature and ER increases breakdown of light hydrocarbons which substantially reduced to negligible value in product gas and formed increase in H_2 and CO concentrations (reactions 28 and 29).

CO_2 gasification



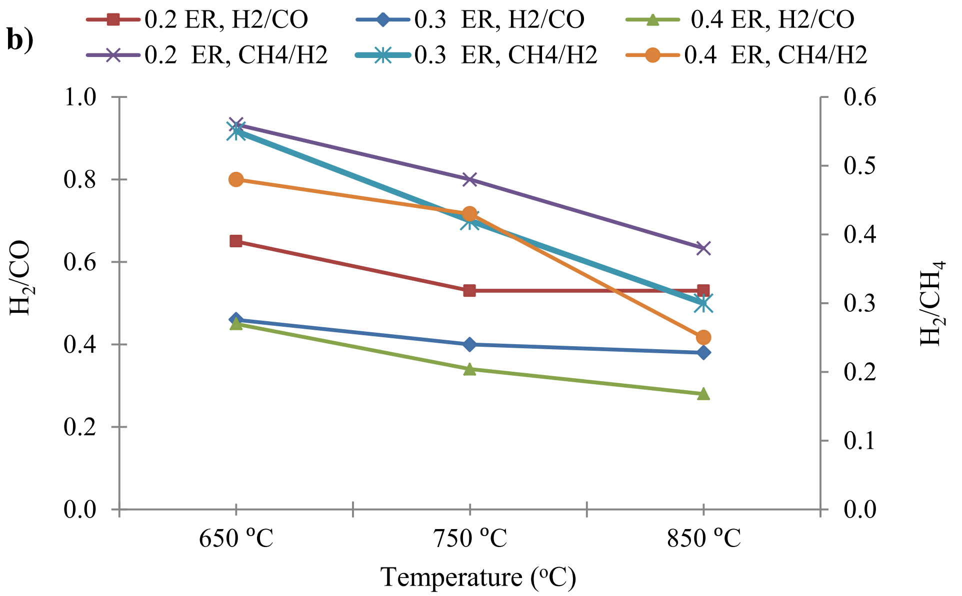


Fig. 3.13: Effect of temperature and ER on gas composition H_2/CO and CH_4/H_2 ratio using CO_2 gasification

3.3.3.2 Effects of ER and temperature on H_2/CO and CH_4/H_2 ratio

The effects of different temperatures along with ERs on H_2/CO and CH_4/H_2 ratios for CO_2 gasification of canola meal are shown in **Fig. 3.13b**. It is observed that temperature and ER play crucial role in H_2/CO and CH_4/H_2 molar ratio. At the higher temperature and ER values both H_2/CO and CH_4/H_2 ratios are decreased. The substantial increase in CO content in product gas (9.7 to 40.2%) decreases the H_2/CO from 0.6 to 0.3. Whereas a slight change in CH_4 (4.2 to 9.2%) content with the higher temperature, considerable increase in H_2 (6.3 to 20.1%) content was observed thus reducing CH_4/H_2 ratio from 1.2 to 0.4 as temperature and ER increases.

3.3.3.3 Effects of ER and temperature on gas yield and syngas yield

Temperature and ER show their strong impact on GY and SY (see **Fig. 3.11c**). It can be clearly observed that, at each temperature study 650, 750 and 850 ºC, with increase in ER from 0.2 to 0.4, GY increases 31.0 to 58.2, 41.2 to 67.1 and 52.2 to 82.8 moles/kg biomass respectively. The SY increased from 4.9 to 42.6 moles/kg biomass with increase in temperature and ER from 650 ºC, ER 0.2 to 850 ºC, ER 0.4. Increase in SY at higher temperature was due to more production of CO due to increase in rates for reactions 26-29 (Devi et al., 2003).

3.3.3.4 Effects of ER and temperature on carbon efficiency

The carbon efficiency in CO_2 gasification is found to be close with steam gasification (**Fig. 3.11c**). Higher temperature increased the rate of reaction thus increasing the CE. The CE increased from 24.3 to 41.3% i.e. by 58.7%. At higher temperature and ER, CO_2 reacts with more carbon from biomass and produces light hydrocarbons leading to more production of CO and H_2 in product gas.

3.3.4 Effects of different gasifying agents (steam, O_2, CO_2) on LHV

The LHV of the product gas was calculated using the equation (3). As shown in **Fig. 3.14**, the LHV of product gas using three different gasifying agents (steam, O_2, CO_2) for canola meal gasification at temperature range 650-850 ºC and ER of the range 0.2-0.4 vary from 193.0 MJ/m^3 to 54.3 MJ/m^3.

In case of steam gasification, highest LHV was obtained at 650 ºC with an ER 0.2. The low temperature and the ER value for steam gasification process promote more formation of hydrocarbons and thus increases the LHV (193.0 MJ/m^3) of product gas (Turn et al., 1998). Higher temperature 850ºC and ER 0.4 favors more tar and other hydrocarbon breakdown thus decreasing the amount of light hydrocarbons and CH_4 from product gas, hence decreases the LHV to 115.9 MJ/m^3.

Slightly different trend was observed in case of oxygen gasification of canola meal. At temperature 650 ºC, as ER increases from 0.2 to 0.4, the LHV value increases from 100.0 MJ/m^3 to 119.7 MJ/m^3. However, at temperature 750 ºC and 850 ºC, with increase in ER from 0.2 to 0.4 LHV decreases due to further breakdown of hydrocarbons and tar in product gas.

In case of CO_2 gasification, ER rather than temperature was very essential because its higher value declines concentration of H_2, CO and surges CO_2 content in the product gas, thus decreasing the LHV of product gas. Maximum LHV 93.1 MJ/m^3 was reached at ER 0.2 and 750 ºC, whereas lowest was 54.3 MJ/m^3 at ER 0.4 and 650 ºC.

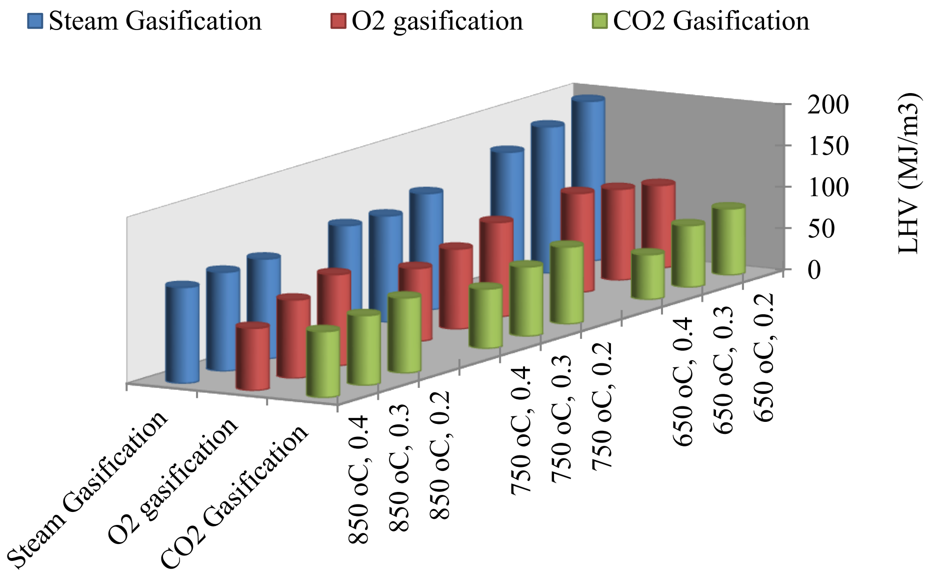


Fig. 3.14: Effect of temperature, ER and gasifying agents on LHV of syngas

3.3.5 Fluidized bed gasification of canola meal, gas composition and product yield

The effects of experimental conditions like temperature and ER on gasification process were evaluated. Results from fluidized bed gasification studies are represented in **Table 3.12**. H_2 concentration (40.3 mol%) in product gas was found to be highest in case of steam gasification as compared to other gasifying agents O_2 and CO_2. It is well known fact that steam produces relatively high concentration of H_2 in syngas produced which makes it more effective. CO concentration was found to be in range of 9-20 mol% in case of all gasifying agents. O_2 gasification produces more CO_2 as the reaction progress and decreases the CO and H_2 produced in the product gas. This was well explained by the reaction 11 and 12 as mentioned earlier. This consumption of H_2 and CO from product gas increases CO_2. Methane content was highest in case of steam gasification (7.4 mol%) and was lower in case of O_2 (1.5 mol%) and CO_2 (3.6 mol%) gasification. This is due to participation of O_2 and CO_2 in the reactions as the gasification progresses, consuming the produced light hydrocarbons in product gas and converting it to CO and H_2.

Table 3.12: Fluidized bed gasification of canola meal, gas composition and product yield

	750 °C, 0.4 ER		
	Steam Gasification	**O_2 gasification**	**CO_2 Gasification**
Gas composition*			
H_2	40.3	1.6	6.5
CO	19.9	9.8	13.0
CO_2	21.9	73.8	71.4
CH_4	7.4	1.5	3.7
Hydrocarbons[#]	6.9	2.0	3.6
H_2/CO	2.0	0.2	0.5
CH_4/H_2	0.2	1.0	0.6
GY (Moles/kg of biomass)	22.1	31.3	43.9
SY (Moles/kg of biomass)	13.3	3.5	8.5
Carbon Efficiency (%)	31.9	64.0	49.2
LHV (MJ/Nm^3)[$]	139.2	32.3	59.6

*mole%; [#]Hydrocarbons except methane; [$]Ar and He free basis

The syngas ratio, 2.0 was highest in case of steam gasification due to the introduction of H_2 from steam comparative to O_2 and CO gasification. During O_2 gasification process, some CO produced was burned thus decreasing the CO concentration in syngas and increasing CO_2 concentration in the product gas (Cao et al., 2008). Hydrogen may experience burnout since H_2 can burn under an oxygen atmosphere at lower initial temperatures and have a lower active energy of burnout than CO (Sánchez et al., 2000). This leads to high syngas yield (13.3 moles/kg biomass) during steam gasification. Consumption of more carbon from biomass, char and light hydrocarbon during O_2 gasification increases the carbon efficiency of gasification process. CE in case of O_2 gasification was found to be highest (64.0%) as compared to steam (31.9%) and CO_2 (59.6%) gasification. Steam gasification process promote more formation of hydrocarbons and thus increases the LHV (139.2 MJ/m^3) of product gas (Turn et al., 1998). LHV was observed in case of O_2 (32.3 MJ/m^3) and CO_2 gasification (59.6 MJ/m^3).

3.4 Production of moisture-resistant canola meal fuel pellets

3.4.1. Box-Behnken design to study the effect of additives and moisture content on pellet quality

It can be seen that (see **Table 3.13**), added binder (A), lubricant (B), and moisture content (C) in the formulation have shown noticeable effects on the density, durability and hardness of the produced canola meal pellet. It is well known fact that the moisture content affects to a great extent on pelletizing properties and product quality, thus has been the subject of several studies (Larsson et al., 2013; Mahapatra et al., 2010; Serrano et al., 2011; Mani et al., 2006). These studies comprised on densification of variety of biomass at different moisture content and their effects on pellet quality were analyzed. It was found that, the optimum level of moisture content varies with the different raw material. In case of canola meal, the low amount of moisture content (8 % (w/w)) was found to be less effective to compact the canola meal particles and produced less durable pellets with decreased relaxed density and pellet hardness (see formulations 5-6 and 9-10, **Table 3.13**).

Each formulation with variable concentrations of additives and moisture content has behaved differently. In addition to the formulation composition, the inherent feed composition (various biomass constituents) also exhibits different characteristic behavior during the compression process in the presence of moisture and heat. The feed composition of canola meal used in this study contains about 12.0 % (w/w) of lignin, 15.7 % (w/w) of cellulose, 10.0 % (w/w) of hemicellulose, 40.3 % (w/w) of crude protein and about 9.5 % (w/w) of residual canola oil (Tilay et al., 2014). In the presence of moisture, protein molecules tend to denaturate with high temperature. Denaturation of protein involves the actual breakdown of three-dimensional protein structure. Upon further cooling of pellets after densification, the protein molecules re-associate and establish the bonds with the other feed particles (Thomas et al, 1998). Along with the added binder, the protein present in the canola meal acts as an additional binding agent, building pellet more durable and better pellet hardness. According to Thomas (1998), the increased mechanical stability of proteins, increases the pellet quality characteristics, mainly due to the covalent binding, electrostatic interactions, van der Waals forces and hydrogen bonds.

Table 3.13: Effect of binder, lubricant and moisture content on pellet density, pellet relaxed density, durability and hardness of canola meal pellets made in the single pelleting unit

Formulation	**Binder (A) (%w/w)**	**Lubricant (B) (%w/w)**	**Moisture (C) (%w/w)**	**Pellet Density (kg/m^3)**	**Relaxed Density (kg/m^3)**	**Durability (%)**	**Hardness (N)**
1	2	1	10	1160±17	1165±13	61±7	23±6
2	5	1	10	1183±7	1177±4	66±11	48±1
3	2	3	10	1161±13	1170±17	45±7	41±3
4	5	3	10	1161±12	1181±12	63±4	47±7
5	2	2	8	1172±6	1155±15	41±10	30±0
6	5	2	8	1172±7	1144±9	64±5	25±2
7	2	2	12	1173±10	1193±8	58±13	30±6
8	**5**	**2**	**12**	**1181±6**	**1190±8**	**64±13**	**71±3**
9	3.5	1	8	1167±7	1151±20	49±6	21±2
10	3.5	3	8	1160±10	1145±15	44±10	52±1
11	3.5	1	12	1185±5	1214±8	61±13	63±5
12	3.5	3	12	1168±8	1195±2	48±15	35±7
13	3.5	2	10	1163±8	1168±23	61±9	40±1
14	3.5	2	10	1162±7	1167±13	60±10	40±1
15	3.5	2	10	1163±8	1168±9	60±8	39±0
16	3.5	2	10	1163±7	1169±14	61±7	41±2
17	3.5	2	10	1165±6	1169±12	60±8	41±1

These feed components such as proteins, lignin and hemicellulose of canola meal exhibit different properties in the presence of water. Thomas et al. (1997) have described that, water during compression changes the structure of the surrounding particles to such as extend that makes to bound feed particles to each other. In addition, the applied heat during the process enhances the binding properties and consequently increases the pellet quality. In case of canola meal pellets, it was observed that (see formulation 8 and 11, **Table 3.13**) high moisture content (12 % w/w) pellets with larger concentration of binder (3.5-5.0 % w/w) produced good quality pellets with comparatively high durability (>61%) and hardness (>63N). This might be due to the enough amount of binding agent (protein and binder) available to bind the feed particles firmly to each other and more moisture (12 % (w/w)) favors this bonding additionally. Cavalcanti and Behnke (2005a) reported that, formulation is the single most significant variable which can affect the physical quality of the pellet. Cavalcanti and Behnke (2005a) investigated the effects of the feed composition such as proteins, fats, starch, fibers, etc. on the corn meal pellet quality using the simplex mixture design. It was observed that, increased in protein concentration did lead to negative effects on pellet durability whereas an increase in starch concentration did lead to improved pellet durability. A similar experiment by Cavalcanti and Behnke (2005b) observed the effects of nutrients on soybean meal and yellow dent corn pellet durability. In this case, the highest durability was found with added protein showing a positive impact on overall pellet quality.

The reasonably good quality pellets were observed with 12 % (w/w) moisture and 5 % (w/w) binder having a pellet durability 64% and pellet hardness 71 N (formulation 8) where as poor quality pellets having a pellet durability 41% and pellet hardness 30 N were observed with 8 % (w/w) moisture content and 2 % (w/w) binder (formulation 5) in case of formulation study using BBD. The pellets extruded from the pellet mill are generally at high temperature due to applied heat and the friction between the biomass and the press channel wall. This elevated temperature helps in redistribution of moisture present in the feed via evaporation and condensation. This causes an increase in the movement of water molecules between the feed particles (Thomas and van der Poe1, 1998). In the case of low moisture content (8 % (w/w)), total binding forces available are less. Thus, it makes pellets with lower quality with more brittle and loosely bound particles. Furthermore, applied load, heat and moisture during the process, facilitate the plastic deformation of the feed particles. In this manner it enables the inter-particle contact area. In the case of biomass pellets, plastic deformation occurs at the glass transition temperature of the amorphous material (like hemicellulose, starch, lignin etc.) in the biomass (Thomas, 2010). Kaliyan and Morey (2009) reported that, apart from the traditional reasoning behind requirement of moisture for the binding of feed particles with van der Waals forces and hydrogen bonds during the densification process, the glass transition temperatures of inherent polymers present in the feed are also responsible for the compressibility of the feed material.

Therefore, in addition to the role of moisture, which facilities the binding between the feed particles, the physico-chemical changes, i.e. thermal softening (glass transition) of the inherent canola meal biomass polymers (lignin and hemicellulose) and binder plays important role in densification. Kelley et al. (1987) investigated dynamic mechanical thermal analysis of the lignin and hemicellulose polymers in the wood cell wall. The relationship between the glass transition temperature and moisture was studied using the Kwei equation. From the study it was observed that, moisture affects the glass transition temperature of the lignin and hemicellulose to a great extend. In case of canola meal, less moisture content (< 8 % w/w), glass transition temperature of polymers is high and thus low melting of the lignin and hemicellulose produces less durable pellets with low hardness values (see formulations 5-6 and 9-10). Some pellets have a tendency to expand after pelletization, a phenomenon called as "spring back effect" of pellet (Wolfgang et al., 2012). It signifies the binding quality between the biomass feed particles within a pellet.

In this study, the lubricant was found to give mixed effects depending on the concentration of binder and moisture content available in the formulation. The most common lubricant utilized for densification of biomass is vegetable oil to reduce the friction between the die wall and feedstock. Generally, lubricants are used by hardwood pellet manufacturers due to the fibrous nature of the feedstock (Thomas, 2010). An overall lubricant added to the canola meal formulation and inherent residual oil content, show improvement in the throughput and thus assist in decreasing the energy consumption. Similar effects were observed by Cavalcanti and Behnke (2005b) with the addition of proteins in the feed formulation. However, Briggs et al. (1999) reported that, the addition of oils or fat in the feed formulation will not always affect pellet energy consumption. This might result of an interaction with other processing parameters or due to physical properties of the fats used.

The regression prediction equation was developed for dependant parameters such as durability and hardness with independent parameters such as moisture content, binder and lubricant concentration for quality canola meal pellets.

Final equation in terms of actual factors of response surface quadratic model:

$$\text{Durability (\%)} = -171.84 + 7.44 * A + 14.01 * B + 38.28 * C + 0.98 * A^2 - 4.02 * B^2 - 1.47 * C^2 + 1.94 * A * B - 1.39 * A * C - 0.91 * B * C \quad (5)$$

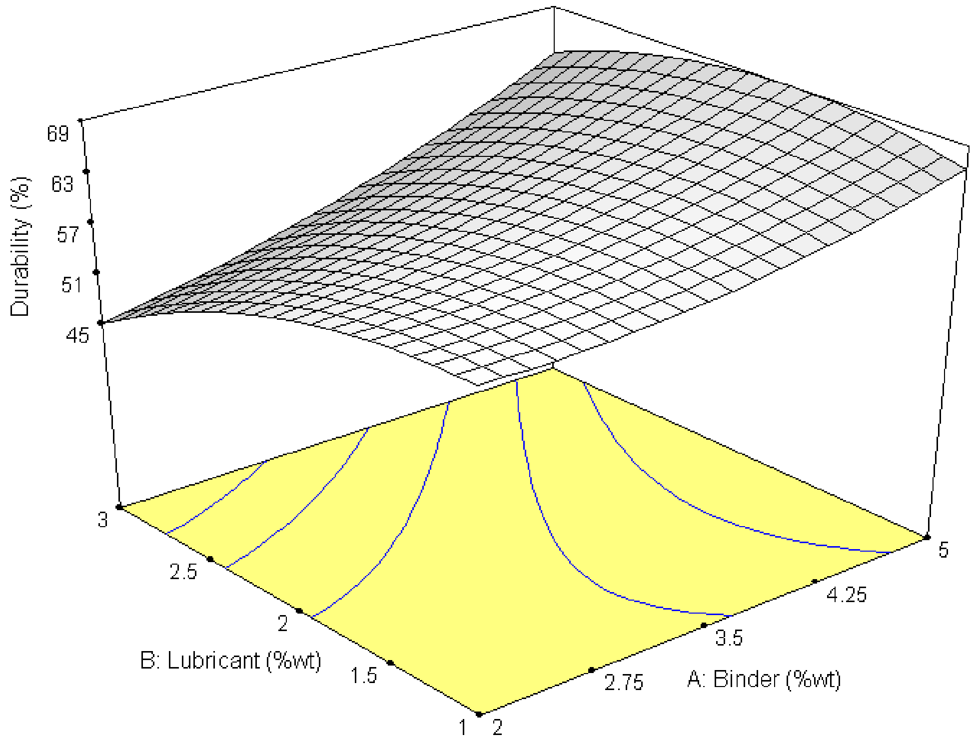
Pellet hardness response after square root transformation:

$$\text{Hardness (N)} = -12.84 - 1.73 * A + 9.21 * B + 1.93 * C - 0.01 * A^2 - 0.04 * B^2 - 0.05 * C^2 - 0.28 * A * B + 0.28 * A * C - 0.75 * B * C \quad (6)$$

These equations can be utilized to get the maximum value of canola meal pellet durability and hardness with R^2 value 0.997 and 0.999 respectively. The "Pred R^2" of 0.963 for durability was in reasonable agreement with the "Adj R^2" of 0.993. "Adeq Precision" value of 49.9 measures the S/N ratio. The S/N ratio greater than 4 is required. In case of durability, the S/N ratio of 49.9 indicates an adequate signal. Similarly, in case of hardness response, the "Pred R^2" of 0.988 was in reasonable agreement with the "Adj R^2" of 0.997. Besides durability, "Adeq Precision" value 102.7 indicates an adequate signal. The analysis of variance (ANOVA) for the response surface quadratic model was described in **Table 3.14**. The probability values less than 0.05 indicates significant model terms. The durability and hardness model F values 263.7 and 610.8 indicate that the model is significant. The “Lack of Fit F-Value” 4.1 and 1.6 indicates that “Lack of Fit” is non-significant and non-significant “Lack of Fit” is desirable for the model. The interaction graphs of independent parameters are shown in **Figs. 3.15** & **3.16**.

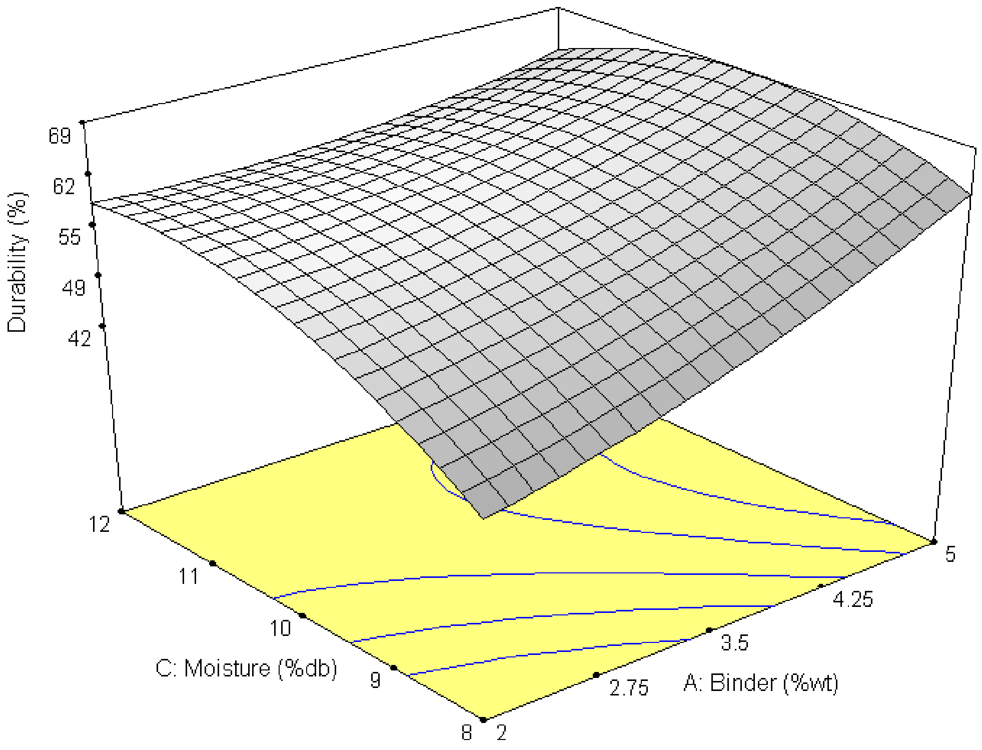
Table 3.14: ANOVA obtained from BBD for durability and hardness response

	Durability		**Hardness**		
Source	**F Value**	**Prob > F**	**F Value**	**Prob > F**	
Model	263.72	< 0.0001	610.79	< 0.0001	Significant
A (Binder)	802.23	< 0.0001	778.00	< 0.0001	
B (Lubricant)	378.45	< 0.0001	367.57	< 0.0001	
C (Moisture Content)	342.49	< 0.0001	1335.20	< 0.0001	
A^2	49.82	0.0002	0.98	0.3545	
B^2	163.90	< 0.0001	2.44	0.1624	
C^2	351.07	< 0.0001	38.01	0.0005	
AB	81.10	< 0.0001	171.46	< 0.0001	
AC	167.22	< 0.0001	671.55	< 0.0001	
BC	31.95	0.0008	2129.70	< 0.0001	
Lack of Fit	4.07	0.1042	1.60	0.3217	Not significant



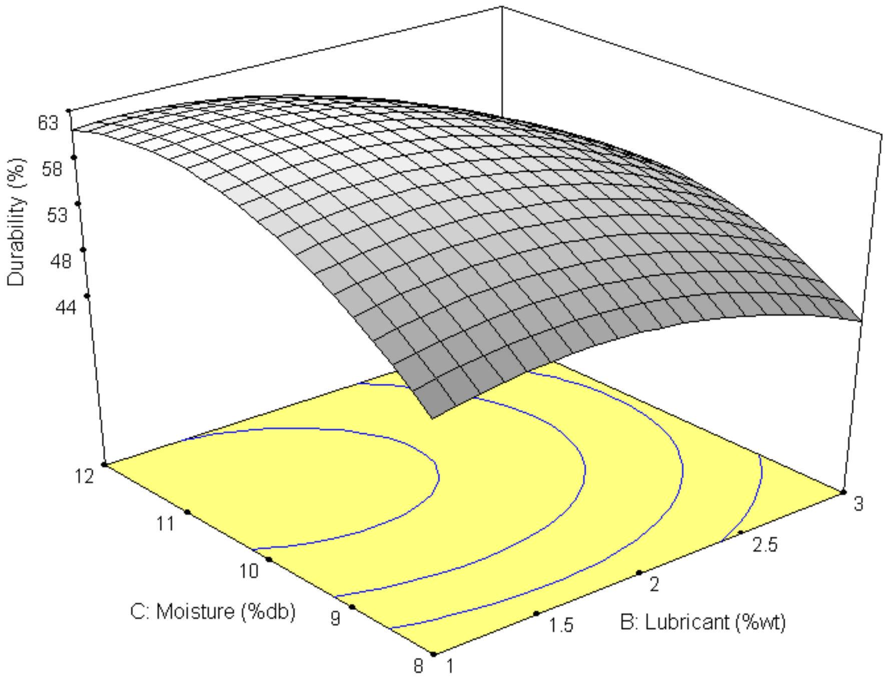
Durability (%)
69
63
57
51
45
3
2.5
2
1.5
1
B: Lubricant (%wt)
2
2.75
3.5
4.25
5
A: Binder (%wt)

(a)



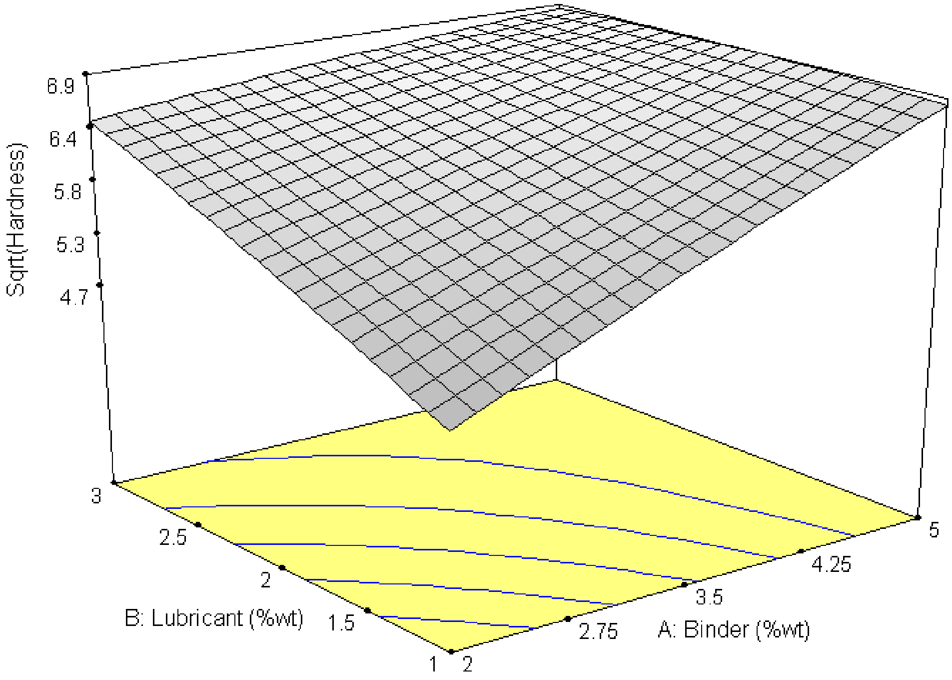
Durability (%)
69
62
55
49
42
12
11
10
9
8
C: Moisture (%db)
2
2.75
3.5
4.25
5
A: Binder (%wt)

(b)

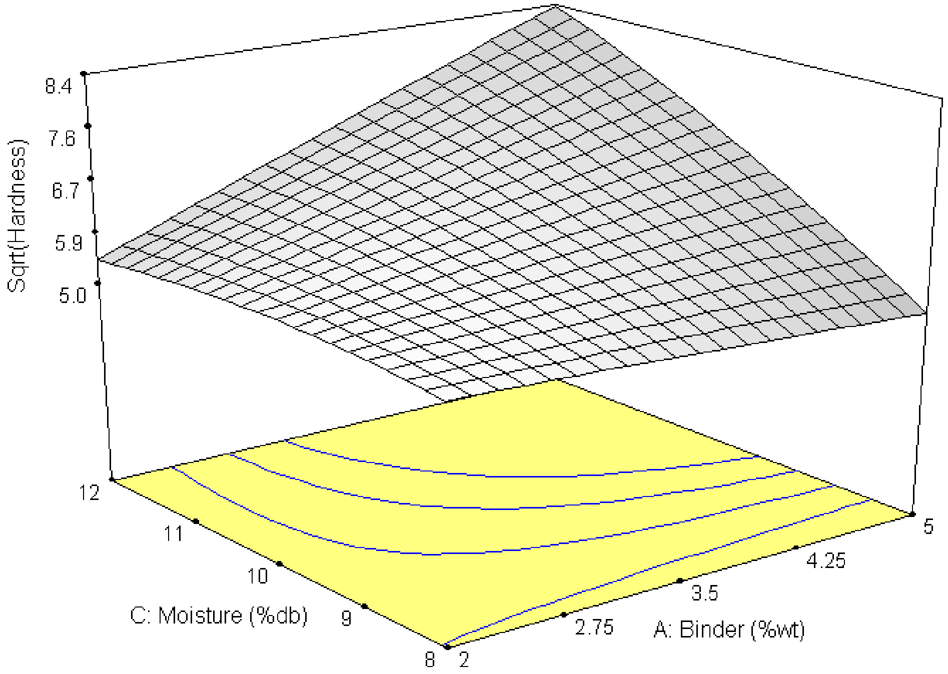


(c)

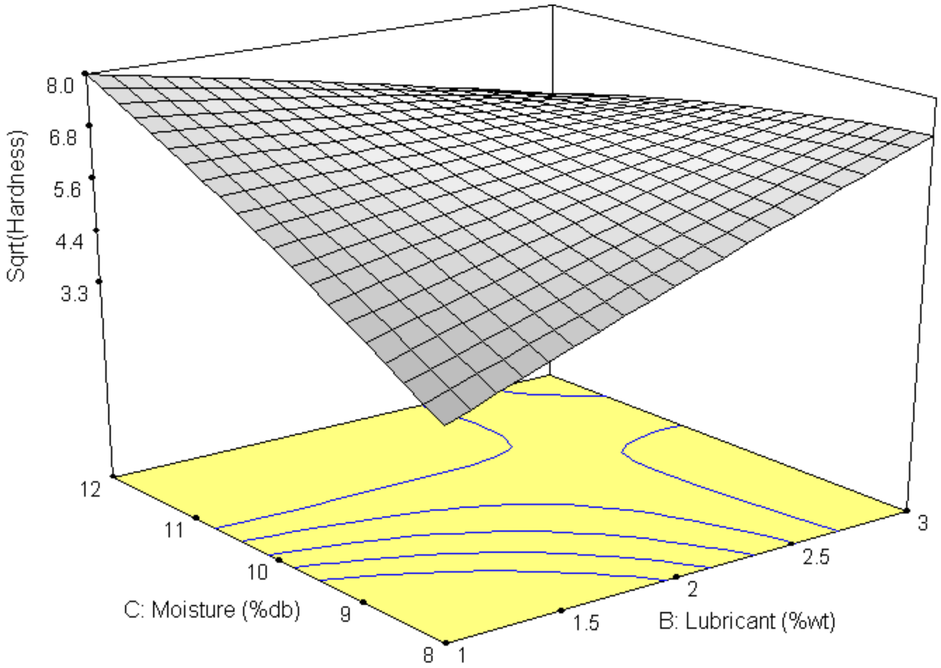
Fig. 3.15: Response surface interaction graphs for durability response obtained for canola meal pellet



(a)



(b)



(c)

Fig. 3.16: Response surface interaction graphs for hardness response obtained for canola meal pellet

3.4.2 Effect of physical parameters on pellet quality

Like other studies, it was observed that applied load and temperature were found to be the key processing parameters affecting both the compression process and pellet quality of canola meal. The formulation 8 (binder- 5 % (w/w); lubricant- 2 % (w/w) and moisture- 12 % w/w) obtained from BBD was considered as an optimized formulation and used further for all studies. From **Table 3.15**, it was found that with increase in applied load, pellet quality decreases. When the applied load increased to 4000 N and 4500 N, sometimes the feed material from the die wall had a tendency to come out, and failed to form a pellet. This might be due to the over applied load on feed material make it more flowable due to plastic deformation and can not sustain at high pressure. This led to a pellet with loosely bound feed particles and thus produces less durable and low density pellet. In this case, due to poor adhesion, the pellet expands similar to a spring after compression or during storage. Hence, the optimum applied load was found to be 3500 N with high pellet density- 1205±6 Kg/m^3, durability- 67±4% and hardness 76±2 N. The pellet density of biomass compressed at different applied pressures has been studied extensively before (Adapa et al., 2009; Mani et al., 2006, Kaliyan and Morey, 2009b). In all studies, it was observed that, increase in applied load or pressure, increases the pellet density, whereas in case of canola meal, it was the contradictory due inability to feed to sustain at high applied load (> 4000 N).

Table 3.15: Effect of applied load and temperature on pellet density, pellet relaxed density, durability and hardness of canola meal pellets made in the single pelleting unit

Temp. (°C)	**Load (N)**	**Density Kg/m^3**	**Density Kg/m^3**	**Durability (%)**	**Hardness (N)**
	3500	1195±7	**1205±6**	**67±4**	**76±2**
60	4000	1177±19	1200±10	62±2	69±2
	4500	1189±12	1192±5	54±5	73±9
Load (N)	**Temp. (°C)**	**Density Kg/m^3**	**Density Kg/m^3**	**Durability (%)**	**Hardness (N)**
	70	1243±7	1215±9	97±1	111±10
3500	80	1254±10	1223±7	99±4	154±6
	90	1260±8	**1247±2**	**99±0**	**189±6**

Pellets compressed at higher temperature (90 ºC at 3500 N), expanded considerably less. This indicates that canola meal particles adhere much stronger to each other and make pellet more compact. This was reflected by a greater unit density 1247±2 Kg/m^3 of pellets pressed at 90°C with durability 99±0% and hardness 189±6 N. Generally, pellet leaving the press channel is at a lower temperature than the actual applied heat to the die wall. This may be due to the poor heat transfer between the metal surface of the press channel and the feed (Serrano et al., 2011). Thus, in the case of applied temperature of 90 ºC, the pellet leaving the press channel was around 70 ºC. This temperature is sufficient for crude protein present in canola meal to denaturate and melts lignin, hemicellulose to form the highly compact canola meal pellet.

3.4.3 Compression Model

The pressure-density data for canola meal densification process was fitted to the Kawakita and Ludde (1971) model as described in equations (2). The Kawakita compression 'a' and 'b^{-1}' parameters and the derived compression index 'ab_I' along with pellet height, diameter, mass and densities were described in **Table 3.16** at the different temperature and pressure used. These parameters represent the behavior of the canola meal feed particles in different stages during the compression process, and classified according to Nordstrom et al. (2009).

Table 3.16: Bulk density (ρ_b) and particle density of canola meal (ρ_t); canola meal pellet density (ρ_p); compression characteristics of canola meal using Kawakita-Ludde Model

Temp	**Pressure**	**Pellet mass**	**Pellet height**	**Pellet Dia.**	**Density (ρ_p)**	**Kawakita compression parameters and suggested classification of feed material**				
(°C)	**(MPa)**	**(g)**	**(mm)**	**(mm)**	**(kg/m^3)**	**a**	**b^{-1}**	**ab$_I$**	**R^2**	**Class$^@$**
60	75.4	0.80±0.00	20.06±0.10	6.41±0.00	1233.6±6.2	10^6	(-) 2	(-) 5×10^5	0.9988	II
	90.4	0.80±0.00	20.14±0.04	6.42±0.03	1222.7±7.9					
	105.5	0.80±0.00	20.03±0.10	6.41±0.00	1231.6±8.5					
	120.6	0.81±0.00	20.21±0.05	6.41±0.01	1233.5±9.3					
70	75.4	0.79±0.00	20.05±0.23	6.41±0.01	1225.2±15.9	10^6	(-) 0.5	(+) 2×10^6	0.9992	I
	90.4	0.80±0.00	20.07±0.06	6.42±0.01	1229.7±6.4					
	105.5	0.80±0.01	19.99±0.18	6.42±0.01	1236.2±4.0					
	120.6	0.80±0.01	20.11±0.10	6.41±0.00	1233.6±7.8					
80	75.4	0.80±0.00	19.96±0.19	6.41±0.01	1244.4±16.8	10^6	(+) 0.8	(+) 1.3×10^6	0.9998	I
	90.4	0.80±0.00	19.96±0.15	6.42±0.02	1244.4±3.7					
	105.5	0.80±0.00	19.94±0.11	6.41±0.01	1253.9±5.5					
	120.6	0.80±0.00	19.94±0.11	6.41±0.01	1253.9±5.5					
90	75.4	0.80±0.00	19.87±0.03	6.42±0.00	1247.4±1.5	10^6	(-) 0.1	(+)1×10^7	0.9994	I
	90.4	0.80±0.01	19.78±0.28	6.41±0.00	1254.9±7.9					
	105.5	0.81±0.00	19.88±0.27	6.42±0.00	1263.5±11.3					
	120.6	0.79±0.01	19.74±0.07	6.37±0.02	1243.6±7.7					
Bulk density of Canola meal (ρ_b)					737.6±9.8					
Particle density of canola meal (ρ_t)					1387.1±5.4					

$^@$ Classification based on the initial rearrangement (Nordström et al., 2009)

The calculated Kawakita parameter ‘a’ represents the maximal engineering strain ‘C_∞’ of the canola meal and was found to be 10^6, at all temperatures. Mathematically, the parameter ‘b^{-1}’ is equal to the pressure ‘P’ when the value of ‘C’ reaches one-half of the limiting value (C = C/2) (Klevan et al., 2010). The value of parameter ‘b^{-1}’ for canola meal was different at different temperatures and ranges from 0.8 to 2. Nordstrom et al. (2009) has previously proposed that the value of index ‘ab_I’ can be used as an indication of the occurrence of particle rearrangement during the compression process. In case of canola meal, a high ‘ab_I’ value at a temperature of 70-90 ºC indicates a high degree of particle rearrangement during compression, where a material is considered by a high value of the parameter ‘a’ combined with a low ‘b^{-1}’.

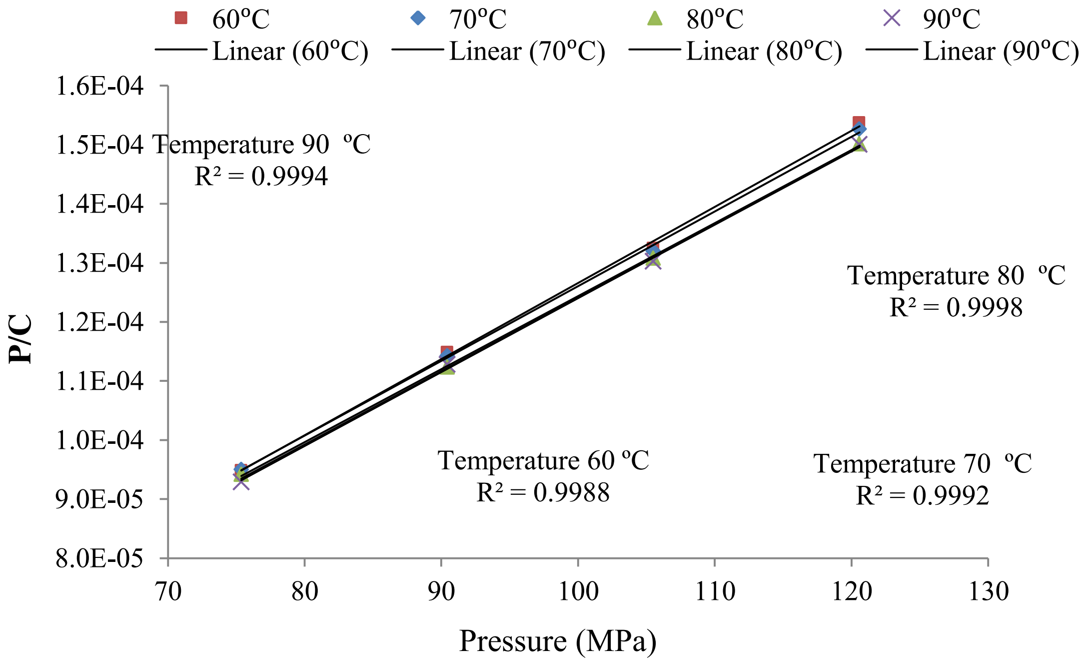


Fig. 3.17: Kawakita-Ludde model experimental data for densification of canola meal

Further, it was found that, the canola meal feed shows different behavior of particle rearrangement during compression at different temperatures. The value of index ‘ab_I’ > 0.1 for the temperature 70-90 ºC (see **Table 3.16**) falls under Class I type of powder, where particles show significant compression behaviour due to primary rearrangement of the original particles followed by fragmentation and deformation dependent on their fragmentation pattern. However, very low value of index ‘ab_I’ ≤ 0.1 in case of temperature of 60 ºC, falls under Class II type of powders showing limited compression due to secondary particle rearrangement and particle deformation (Nordstrom et al., 2009). In all cases, the value of R^2 was found to be ≥ 0.999 illustrating the perfect fit for the Kawakita and Ludde (1971) model (**Fig. 3.17**).

3.4.4. Pellet coating and storage study

The moisture content, durability and hardness of the canola meal coated pellets against the exposure time was presented in **Fig. 3.18**. It was clearly seen that, the coated canola meal pellets retain the original pellet quality characteristics up to eight weeks. The rapid drop in moisture content from 8.0 to 0.7 % (w/w) may be due to the fact that evaporation of residual isopropyl alcohol takes out the bound moisture from the pellet during storage, whereas retaining the durability up to ~98 % and hardness ~168N. In case of control pellets (without coating), moisture content of pellets increases from 6.82 to 7.85 % (w/w), making pellets less durable. Exposure to ambient temperature has decreased the durability and hardness of controlled pellets from 99 to 48% and 189.6 to 117.6 N, respectively. In comparison to the controlled canola meal pellets, moisture resistant canola meal pellets have obviously shown improved stability in an ambient environment. Thus, the coating of pellets made it as a one of the alternatives to make moisture resistant quality pellets with the high durability and hardness value.

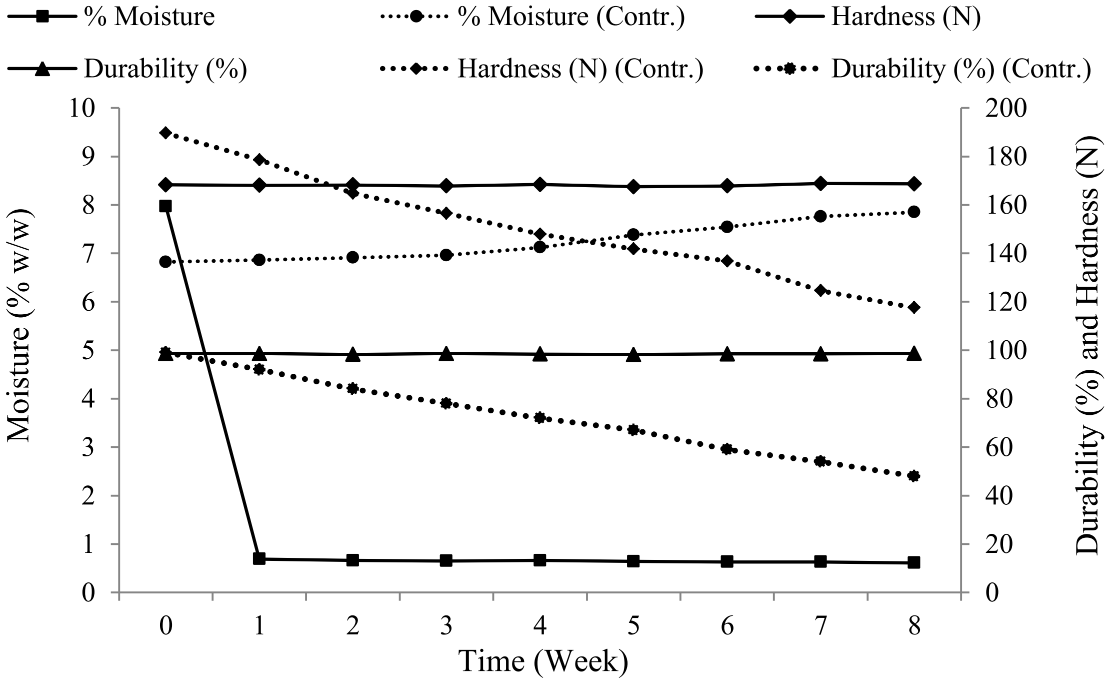


Fig. 3.18: Storage study of canola meal coated pellets

3.5 Gasification of pellets in fixed bed reactor

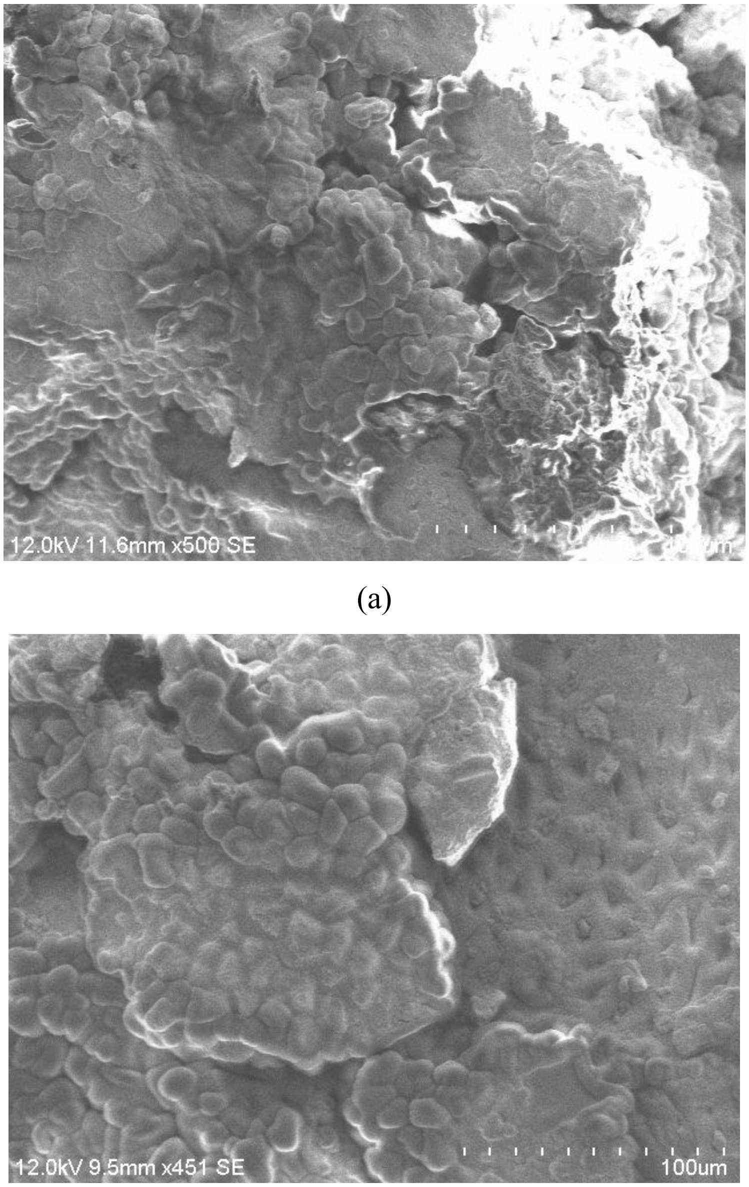
The non catalytic gasification of canola meal pellets using different gasifying agents has shown that, canola meal pellets can be successfully utilized as fuel pellet for the production of biogas with high LHV. From **Table 3.17**, it can be seen that gasification of canola meal pellet using CO_2 as a gasifying agent has produced a maximum gas yield (40.0 moles/kg daf-pellet) and syngas yield (16.6 moles/kg daf-pellet) with maximum carbon conversion efficiency about 82.7%. The LHV of product gas using all three gasifying agents was in the range of 40-50 MJ/m^3. The char produced as a by-product was in the range of 19-25 %wt for steam and CO_2 gasifying agent, whereas in case of O_2, it is the lowest as O_2 is strong gasifying agent and burns maximum amount of carbon in the feed (Tilay et al., 2014). Similarly, tar produced was found to be maximum in the case of the CO_2 gasifying agent which is due to the introduction of carbon into the system producing more tar (Tilay et al., 2014).

Table 3.17: Gasification of canola meal pellet using different gasifying agents

Gasifying agent	Steam	O_2	CO_2
Equivalence Ratio (ER)	0.2	0.4	0.2
Temperature (ºC)	650	650	750
Gas yield (moles/kg daf-pellet)	13.7	29.8	40.0
Syngas yield (moles/kg daf-pellet)	5.8	6.4	16.6
Carbon Efficiency (%)	27.4	66.5	82.7
LHV (MJ/m^3)	40.8	44.7	50.7
Total hydrocarbon produced (moles/kg daf-pellet)	2.7	2.8	1.9
Char produced (% (w/w))	24.9	6.8	19.8
Tar produced (% (w/w))	31.7	25.8	45.8

3.6 Scanning electron microscope (SEM)

The SEM images show that tight bonding occurred in between different particles. Images taken at higher magnification have provided a deeper insight into the bonding mechanisms of the canola meal pellet (**Fig. 3.19**). The proteins and biomass polymer particles are stuck to each other, allowing very few void spaces. This showed that binder and biomass polymers (lignin and hemicelluloses) have exceeded the glass transition temperatures during the pelletization process, allowing them to form solid bridges between adjacent particles. The globular portion of the images might be due to the denaturation of globular protein particles. Denaturation at high temperature made it to adhere to the adjacent particles.



(a)

(b)

Fig. 3.19: SEM images of a fracture surface for canola meal pellet

4. CONCLUSIONS

The energy consumption is increasing and limited fossil fuels are depleting with increasing populations and economic developments. Renewable energy such as canola meal was widely explored in this study to consider as the energy source, which has sustainable supply in Canada and safe to use. Canola meal can be used for energy production in the form of either direct canola meal waste or as pellets made from canola meal, canola meal with crude glycerol using various techniques. The conclusions obtained from this work are summarized below:

Characterization and pelletization of canola meal using crude glycerol as binding agent

- Crude glycerol was found to be an effective binding agent in the concentration range of 5-10 % (w/w). Pellets made with 5 % (w/w) crude glycerol demonstrated the best handling characteristics with a survival rate of ~ 92 %. Heating value of pellets made using 5 and 10 % (w/w) of glycerol was found to increase slightly from the original canola meal pellet.

Oxygen gasification of canola meal after protein extraction for synthesis gas production in a fixed-bed reactor

- Canola meal after protein extraction can be effectively used as a feedstock for syngas production. A maximum H_2 content of 72.2 mole% and highest H_2/CO ratio were obtained at 735 °C and ER of 0.27 using oxygen as gasifying agent. The overall yield of H_2 and CO was found to increase with temperature and ER and was maximum at ER of 0.40 and temperature of 900 °C. The carbon conversion efficiency for product gas increased from 22.1 % at 650 °C and ER of 0.20 to 60.3 % at 900°C and 0.4 ER.
- The optimum conditions for highest amount of LHV of 11.4 MJ/Nm^3 were obtained at 815 °C and ER of 0.20 using oxygen as gasifying agent. For all operating conditions, LHV of product gas varied between 9-12 MJ/Nm^3 which makes it suitable for methanol production.
- Use of dolomite as catalyst for tar cracking reduced tar formation by 50 % and the total syngas production was observed as high as 1.14 Nm^3/kg.

Gasification of canola meal and factors affecting gasification process

- Non catalytic gasification of canola meal was studied in fixed bed and fluidized bed gasifier using three different gasifying agents (steam, O_2 and CO_2).

- In steam gasification, highest H_2/CO ratio (2.73) and LHV (19.3 MJ/Nm^3) was reached at temperature 750 ºC and ER 0.4 with H_2: 49.9 mol%; CH4: 6.6 mol%; CO: 25 mol% and CO_2: 11.8 mol% in product gas. CO_2 as gasifying agent was found to have a strong effect on the gas yield and syngas yield with high concentration of CO in syngas.
- Maximum gas yield of 82.8 moles/kg biomass was observed with CO_2 gasification as compared to steam (46.4 moles/kg biomass) and O_2 (39.4 moles/kg biomass) gasification at highest operating parameters (850 ºC, 0.4 ER).
- Oxygen had a very strong effect on carbon efficiency (65.5%) converting maximum carbon from biomass/ char and formed tar from product gas to other components as compared to steam (44.6%) and CO_2 (41.3%).
- These outcomes will heighten the understanding behind non-catalytic gasification of canola meal using of different gasifying agents for designing process for different applications.
- The results from pilot scale gasification system indicated that, the higher syngas yield and the total percentage of H_2 and CO in the synthesis gas were obtained from steam gasification. CO_2 gasification promotes maximum gas yield and O_2 gasification gave maximum carbon efficiency.

Production of moisture-resistant canola meal fuel pellets

- The work includes study of the effects of moisture content, additives, applied load and temperature on the mechanical properties of canola meal pellets. It was found that, all these parameters significantly affected the pellet quality. Optimized pellets with 99 % durability and 189 N hardness were produced at an applied load of 3500 N and a temperature of 90 ºC with the 5 % (w/w) binder, 2 % (w/w) lubricant and 12 % (w/w) moisture content.
- A linear Kawakita and Ludde model was developed to determine the effect of compressive pressure on the feed and thus the feed material was classified based on the Kawakita parameters. It was found that the canola meal particles undergo extensive rearrangement followed by fragmentation and deformation during the compression process.
- Further work was focused on the effect of coating agent (moisture resistant pellets) on pellet durability and hardness upon storage. The coated pellets exposed to the ambient temperature could sustain its durability (~98 %) and hardness (~168 N) up to eight weeks without any

moisture uptake, whereas control pellets (uncoated) lose its durability (~48 %) and hardness (~117 N) due to moisture uptake.

- ❖ The SEM images of pellets exhibited effective bonding characteristics between different particles in the canola meal feed.
- ❖ The gasification of canola meal pellets using different gasifying agents showed that canola meal pellets can be used as a substitute for other biomass solid fuels. The product gas produced using steam, O_2 and CO_2 gasifying agent were found to have LHV in the range of 40-50 MJ/m^3. Therefore, canola meal pellets provide an alternative for biofuel production from waste biomass feedstocks in the form of moisture-resistant quality fuel pellets.

5. OUTCOMES

The research work from this study is published as follows:

1. Tilay A, Azargohar R, Gerspacher R, Dalai A, Kozinski J (Feb, 2014) Gasification of canola meal and factors affecting gasification process. Bioenerg. Res. DOI 10.1007/s12155-014-9437-5.
2. Canola meal moisture-resistant fuel pellets: Study on variables, effects of additives on the pellet quality and compression characteristics. Tilay A., Azargohar R., Drisdelle M., Dalai A., Kozinski J. (To be communicated for publication)

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