

“Property Analysis and Investigation of Ethanol-Water Mixture: Implication to Use the Mixture as Safe Cooking Energy Source”

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Abstract- Among all the liquid fuels that can be produced locally and in a renewable manner, ethanol is the one and the best alternative. Thus, it is an excellent substitute for kerosene and burns better than kerosene without any particulate output or unpleasant smell of combustion and is renewable and its high flammability makes it very difficult to use it for cooking. Ethanol used for cooking in most areas with different concentration of water in order to reduce its flammability hazard. Therefore, the optimal flammable ethanol-water mixture is between inflammable water and flammability hazard of ethanol. This study is going to come-up with detail physical and chemical property (flammability, flame temperature, volumetric change of mixture and heat energy, combustion heat energy) of ethanol-water mixture determined analytically and experimentally.

The flash-point temperature, and flame height at different concentrations of ethanol-water mixture is experimentally determined. It found that flash-point is 23.7 °C, vertical flame height is 5.41 Cm, stoichiometric flammability limit is 89.55% air and maximum flame temperature is 1153.37 °C for 60% (v/v) ethanol water mixture and which is optimal flammable and optimal for cooking energy requirement from the mixture. Since its flash-point temperature is greater than that of the average atmospheric temperature of most cities of Ethiopia. Increasing the flash-point of ethanol is to make it safer for household hold cooking purpose.

Keywords-- Ethanol-water mixture, Flammability hazard, Flash-point, Heat energy

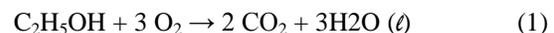
I. INTRODUCTION

Property of Ethanol

Ethanol under ordinary condition is a volatile, flammable, clear, colorless liquid. Its odour is pleasant, familiar, and characteristic, as is its taste when it is suitably dilute with water. Ethanol’s miscibility with water contrasts with that of longer-chain alcohols (five or more carbon atoms), whose water miscibility decreases sharply as the number of carbons increases.

The physical and chemical properties of ethanol are primarily dependent upon the hydroxyl group. This group imparts polarity to the molecule and also gives rise to intermolecular hydrogen bonding. In the liquid state, hydrogen bonds are formed by the attraction of the hydroxyl hydrogen of one molecule and the hydroxyl oxygen of a second molecule. It is completely miscible with water and organic solvents and due to its high hydroscopic readily absorbs water from air and this is due to having of weak hydrogen bonding. Ethanol has widespread use as a solvent of substances intended for human contact or consumption, including scents, flavorings, colorings, and medicines. In chemistry, it is both an essential solvent and a feedstock for the synthesis of other products. It has a long history as a fuel for heat Combustion. Ethanol has a boiling point 78.5 °C and specific density of 0.793 at 20 °C.

Complete combustion of ethanol forms carbon dioxide and water in pure case at STP:



Ethanol-water mixture for cooking

Now a day, number of design and models of ethanol-water mixture stoves are designed and in use most area of the world such as ‘Clean Cook’ of Gia project ethanol stove, which is designed and manufactured in Swedish company as shown figure 1-A, works in the concentration of 95 % ethanol, and 4.5 % water less of 0.5 % of other additives in volume ratio, ‘low-concentration’ ethanol stove in rural areas of India, as shown in figure 1-C, works in weight ratio of 50 % ethanol-water concentration and uses hand pump to pressurize the fuel from the separate fuel tank to the burner canister and has been developed at Nimbkar Agricultural Research Institute (NARI) the first time makes and the idea of its development is very novel. Nimbkar Agricultural Research Institute (NARI) also developed Ethanol stove for both cooking and lighting area where having deficiency of alternative lighting source.

The clear white yellowish color flame used in cooking gives light for the area near stove present as shown figure 1-B below. It is usually a low grade between 45-60 % (w/w) ethanol water concentrations [1 2 3].

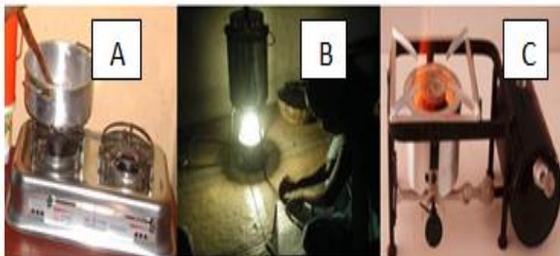


Figure-1: A- Clean Cook' ethanol stove, B-'low-concentration' ethanol stove for cooking and lighting, and C-'low-concentration' ethanol stove for cooking

Since, ethanol having of high flammability, pure ethanol can't use in domestic purpose. Ethanol is clean and nontoxic fuel that can use in wide range of applications, either as additives of automotive fuel, and domestic cooking purpose. The only hazard associated with ethanol is its high flammability in pure form. It has wide range of flammability, the upper flammability limit (UFL) 19 % and lower flammability limit (LFL) 3.3 % in volume ratio to air content [4]. When the content of water increases in a solution of ethanol and water mixture, the combustion stoichiometric air requirement is increase and hence the flammability to be reduced. Thus, mixing it with water is one alternative technique to use ethanol for cooking by reducing its hazardous flammability.

Ethanol- water mixture

Solution may be binary or tertiary and so on accordingly the number of substances to be contributed in mixture. In a solution, substance present in a large quantity is called solvent and the other to be solute in the arbitrary convention at known temperature and pressure. For the binary solution formed by ethanol and water, nomenclature of solvent and solute reverse depending on the relative amount one two. If the mixture is formed equal amount of two quantities, the nomenclature of solvent and solute left in the wish of experimentalists. Solution is physical bonding of molecules of two or more either solid or liquid soluble quantities mixing in one space of they occupy.

The solubility of mixture depends on either of molecular interaction force (attraction or repulsion) and/or thermodynamic functions. Ethanol and water are completely miscible in to each other in all proportion. The explanation for this is given by the fact that water-ethanol attraction force is stronger than that of water-water and ethanol-ethanol interaction. That is the interaction force between water and ethanol are predominantly dipole-dipole and hydrogen bonding. In thermodynamic relation of mixture, any dissolution processes the free energy change must be negative that is the process must be exoergonic. This implies that the free energy of solution must be less than the free energy of solute and solvent. All values of ethanol-water mixture the mixture enthalpy is negative, and the small mixing temperature and entropy, the free Gibbs energy of is always negative.

Therefore, the right dissolution of two mixtures, to get negative free energy of solution, there must be either higher negative or exothermic mixing or there to be higher positive randomness of solution.

The other principle for solubility is "like dissolves like" principle and usually based on phase similarity. This usually indicates that similar materials with similar property dissolved one by another. Since, the molecules of ethanol are much smaller than water molecules in the solution of ethanol-water mixture, so when the two liquids are mixed together the ethanol falls between the spaces left by the water thus reduction of volume than the sum volume of two quantities. It's similar to what happens when you mix a liter of sand and a liter of rocks. You get less than two liters total volume because the sand fell between the rocks, right? Intermolecular forces (hydrogen bonding, London dispersion forces, and dipole-dipole forces) also play their part in miscibility, but that's another story.

The great similarity of the two molecules and hygroscopic attractive property of ethanol, ethanol and water are complete miscible to each other solutions thus the water molecules (H_2O) and ethanol molecule (CH_3CH_2OH) are interchangeable arrangement in the solution. The molecules are in sense "dumb" and can't distinguish one from the other since both are colorless and there to be no possible limit for concentration of water in ethanol or ethanol in water.

The boiling point temperature of pure ethanol is 78.5 °C and the boiling point temperature of water is 100 °C, thus the boiling point temperature of ethanol-water mixture is between 78.5 °C and 100 °C. But from the experimental determination the boiling point temperature decrease linearly up to ethanol-water mixture of 95.6 % in volume ratio (at 78.2 °C), then increase again linearly to the boiling point temperature of pure ethanol. This is the unique property of ethanol in water solution. Since ethanol and water forms non-ideal mixture, the vapor pressure of vapor composition is large positive deviation from Raoult's Law between liquid compositions during boiling of ethanol water mixture. The occurrence of weak hydrogen bonding is responsible for large deviations in the random distribution of molecules that commonly used equations of state and liquid solution models are not able to describe.

Significance of the research

The object of this research is to conduct a paper of detail property analysis of ethanol-water mixture come to decision of best optimal flammable mixture for cooking purpose. To be achieved this through which;

- ✓ Experimentally flame height of different percentages of ethanol-water mixture and flash-point measured to determine optimal concentration in flammability and flame property to be observed
- ✓ Result discussion of tests of measurements for comparison of different concentration of ethanol-water mixture.

II. DETERMINATION OF ETHANOL–WATER MIXTURE IDEAL PROPERTY

The property of ethanol-water mixture is different from property of pure ethanol or pure water. Boiling point, density, flammability, flash point and freezing point changed accordingly the mole fraction of both quantities in the solution. To come-up with the correct numerical value of property of the mixture some correlations may use or in other case the experimental data values used.

Table 1:
Physical Properties of Ethanol And Water

Value	Units	Ethanol	Water
Liquid density	g/mL	0.789	1.000
Vapour density @ 95°C	g/mL	0.0015	0.001
Molecular weight	g/mol	46.0634	18.0152
Liquid Heat Capacity	J/gK	2.845	4.184
Heat of Vaporization	J/g	855	2260
Vapour Pressure @ 90°C	torr	1187	525

Knowing of both physical and chemical property of substance is the initial step to put the material as important and selective for the specific applications. The properties may be either in ideal or non-ideal property.

Boiling point pressure and temperature

Considering the ethanol-water mixture as ideal in its vapor pressure, total solution pressure is the sum of molar partial pressure of ethanol and water. The partial molar pressure of ethanol and water and it is a linear relation with vapor pressure in pure case of each. The relation is stated as the equations shown below;

$$P_{\text{water}} = P^{\circ}_{\text{water}} \times X_{\text{water}}$$

$$P_{\text{ethanol}} = P^{\circ}_{\text{ethanol}} \times X_{\text{ethanol}}$$

Therefore, the total pressure of mixture ethanol and water is to be the sum of partial molar pressure of both components.

$$P_{\text{mixture}} = P_{\text{water}} + P_{\text{ethanol}}$$

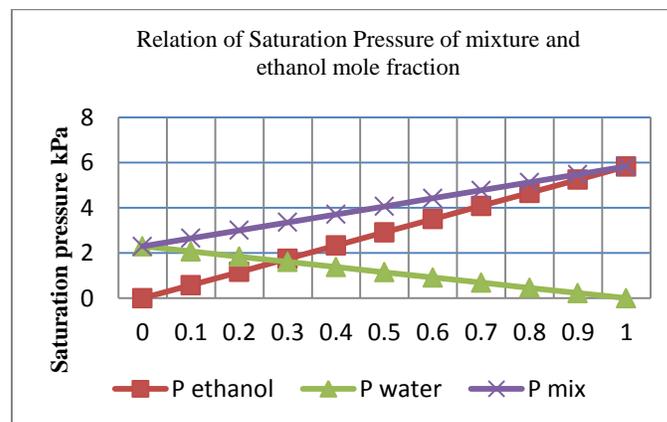


Figure 2: Ideal case partial pressure of ethanol, water and ethanol-water mixture

Antoine formula for the relation of temperature and saturation pressure

$$\ln(P_{\text{sat}}) = A - B/(T+C); P_{\text{sat}} \text{ (kPa)} \quad T \text{ (}^{\circ}\text{C)} \quad (2)$$

where: A, B, and C are Antoine constants and listed in table below.

Table 2:
Antoine Constants Of Water And Ethanol

<i>Species of solution</i>	<i>A</i>	<i>B</i>	<i>C</i>
<i>Ethanol</i>	<i>16.6758</i>	<i>3,674.49</i>	<i>226.45</i>
<i>Water</i>	<i>16.2620</i>	<i>3,799.89</i>	<i>226.35</i>

The relation of boiling point and ethanol mole fraction of ethanol-water solution by using of the data of the boiling point and mole fraction of ethanol-water mixture by using excel Microsoft ware the polynomial of order four relation equations developed.

Since the mole fraction of liquid, % liq is x, and it written as the boiling point temperature of ethanol-water mixture and ethanol mole fraction correlated at regression (R=0.999) and the relation of mole fraction of ethanol and the boiling point temperature of ethanol-water mixture is plotted by using MathCAD in figure-3 below. Therefore, the boiling point of every known concentration of ethanol-water is easily calculated by using equation 2.4 or it can easily read from the graph of figure below.

$$T \text{ (}^{\circ}\text{C)} = 60.526 * x^4 - 163.16 * x^3 + 163.96 * x^2 - 83.438 * x + 100 \quad (3)$$

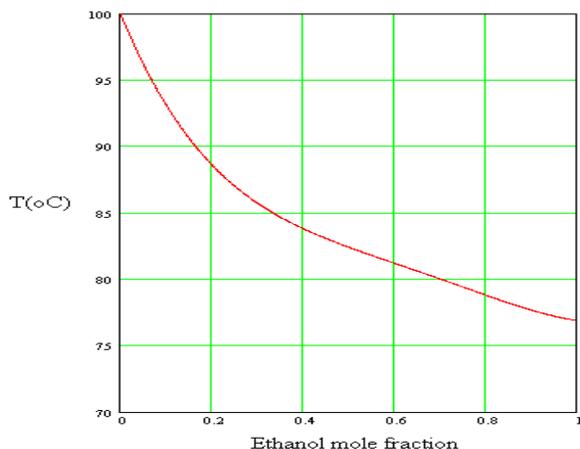


Figure-3: Boiling point temperature with ethanol mole fraction in water mixture

Fraction distillation of an azeotrope of ethanol-water mixture

Deviation of partial molar quantities of solution comparing with pure case of individual, solution may classify as either ideal or non-ideal solution. Ideal solution, there is no change of partial molar quantities (volume, internal energy and/or other quantities) of mixture and is completely satisfy the Raoult's Law with zero deviation in both liquid and vapor composition state in both pressure and temperature. In other case Non-ideal solution is there is quite positive or negative change of partial molar quantities (volume, internal energy and/or other quantities) of mixture compared with pure state. Changes of partial molar quantities of liquid and vapor composition during boiling and is not satisfied with Raoult's Law of solution.

The relation of vapor and liquid concentration with the boiling point temperature varies. It deals that at certain point temperature the composition of liquid phase and vapor escaped from the liquid surface except the azeotropic point. But at the azeotropic mixture of ethanol-water solution, the concentration of liquid and vapor escape from the liquid surface is identical (i.e. $x_1 = y_1 = x_2 = y_2$) and hence by method of fractional distillation is impossible to separate in to the individual mixture component.. That is we called liquid-vapor equilibrium (LVE) property of ethanol-water solution.

The minimum boiling point temperature (78.2°C) ethanol-water mixture attained at the concentration 95.6% by mass ratio. Fractional distillation used to reduce the water content after fermentation process produces 95.6% concentrated ethanol by mass which is an azeotrope mixture having boiling point of 78.2°C . If the solution with the azeotropic composition is heated then vaporization takes place in such a manner that the relative amount of two components are identical in the vapor and liquid phase.

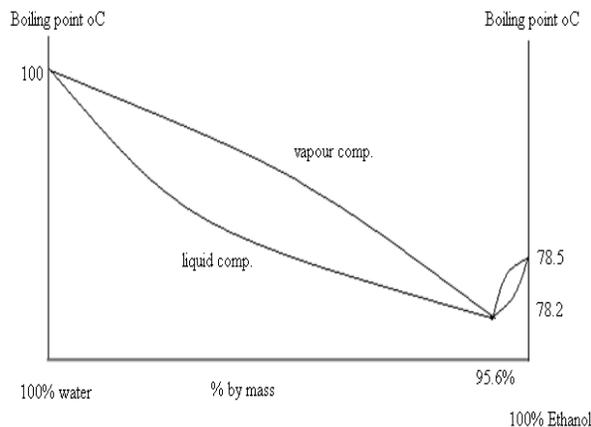


Figure 4: Boiling point phase diagram of ethanol-water mixture [5]

Similarly, the freezing point temperature of ethanol-water mixture is between the freezing point temperature of ethanol (-114.3°C) and the freezing point temperature of water (0 °C). Mixing ethanol and water to make it safe for household use the ratio above 50 % ethanol usually the freezing temperature below -32 °C and since there is very far of freezing point temperature than usual ambient condition, no usual freezing problem of mixture. However, the density of mixture varies with temperature, for all case its variation is only within the density of ethanol and water [5].

At the azeotropic concentration, the mole fraction of liquid and vapor in each quantity is equal. That means for example, the liquid and vapor mole fraction of ethanol or water is equal in ethanol-water mixture.

The azeotropic concentration of binary liquid solution of solute is determined by using the equation 4 below.

$$\frac{1}{x_{1az}} = 1 + \frac{\ln\left(\frac{P_{az}}{P_{1sat}}\right)}{\ln\left(\frac{P_{az}}{P_{2sat}}\right)} \quad (4)$$

Where:

- P_{1sat} is saturation pressure of solute
- P_{2sat} is saturation pressure of solvent
- P_{az} is pressure of mixture at azeotropic point

Enthalpy of mixing

Enthalpy of solution or enthalpy of mixture for a binary solution is measured using a suitable calorimeter.

Here it is not possible to determine the absolute value of total enthalpy of solution or the mean molar enthalpy rather we have to use the thermodynamic relation to calculate the change in partial molar enthalpy. The enthalpy change accompanying the formation of $(n_1 + n_2)$ mole mixture is calculated as follows;

$$\Delta H_{mix} = n_1 \Delta H_{1,m} + n_2 \Delta H_{2,m} \quad (5)$$

For a liquid-liquid solution of enthalpy of mixture per mole is:

$$\begin{aligned} \Delta H (n_1 + n_2)_{mix} &= x_1 \Delta H_{1,m} + x_2 \Delta H_{2,m} \\ &= x_1 \Delta H_{1,m} + (1 - x_1) \Delta H_{2,m} \end{aligned}$$

$$\Delta H (n_1 + n_2)_{mix} = x_1 (\Delta H_{1,m} - \Delta H_{2,m}) + \Delta H_{2,m} \quad (6)$$

Where:

$$\Delta H_m = \frac{\Delta H}{n}, \text{ mean mole enthalpy}$$

The Enthalpy of Solution is the heat change which takes place when one mole of a solute is completely dissolved in a solvent to form a solution of concentration measured under certain conditions. Enthalpy of Solution can be measured experimentally. It can also be calculated; it is the sum of two imaginary steps: the reverse of the lattice enthalpy plus the sum of the hydration enthalpies of the ions.

The mixing process of ethanol and water is exothermic process and energy released to form alternative bonding between ethanol and water. The relation of mixture enthalpy and mole fraction of ethanol and water shows that increasing mixture enthalpy up to 15 % ethanol in mixture and the decrease linearly. Therefore the maximum energy release (-780 J/mol) occurs at 15 % ethanol in water mixture.

Since ethanol-water mixture is non-ideal solution, the calculated value of equation 6 cannot match with the real data of mixture enthalpy. The excess Gibbs energy is as the correction factor between the experimental and analytical values. The real experimental data of mixture enthalpy of ethanol-water mixture at STP is plotted in figure 5 below [6]. When two miscible liquids are mixed, a positive or negative heat effect occurs, which is caused by the interactions between the molecules. This heat effect is dependent on the mixing ratio.

The integral mixing enthalpy and the differential molar mixing enthalpy can be determined by calorimetric measurements of the heat of reaction.

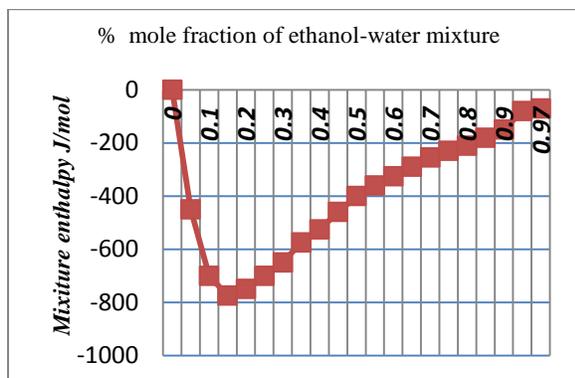


Figure 5: Mixing enthalpy of ethanol-water mixture [5]

The temperature change when known amounts of water and ethanol mixed was determined; this is the enthalpy change in an isothermal and isobaric environment. Agreeable data was found by analytically and compared to similar experiments. Since water's structure and unique properties affect many aspects of a solution, the solutions enthalpy's decreased at a certain time due to ethanol's non-electrolyte nature. All the values of ethanol-water mixture enthalpy are negative and which shows that Gibbs free energy to be negative for all temperature values and this indicates the miscibility of ethanol and water.

Partial molar volume

If you add 50 mL of water to 50 mL of water you get 100 mL of water. Similarly, if you add 50 mL of ethanol (alcohol) to 50 mL of ethanol you get 100 mL of ethanol. But, if you mix 50 mL of water and 50 mL of ethanol you get approximately 96 mL of liquid, not 100 mL why?

First, the molecules of ethanol are much smaller than water and thus they filled with the space left between water molecules just as mixing of fine sand and larger stone. In the other case, the intermolecular force of ethanol-ethanol or water-water is less than that of ethanol-water or water-ethanol. Mixing of known concentration is prepared by mixing calculated quantities of the two substances and the density of each mixture is accurately measured.

From Euler's theorem of homogeneous mixture is related as;

$$V = n_1 \left(\frac{\partial V}{\partial n_1} \right) + n_2 \left(\frac{\partial V}{\partial n_2} \right) \text{ is volume of mixture}$$

$$= n_1 V_{1,m} + n_2 V_{2,m}$$

$V_m = \frac{V}{n_1+n_2} = \frac{w_1+w_2}{\rho_{12}(n_1+n_2)}$ is the mean molar volume

$$V = \frac{V}{n_1+n_2} = \left(\frac{w_1+w_2}{X_1 M_1 + X_2 M_2} \right) (X_1 V_{1,m} + X_2 V_{2,m}) \quad (7)$$

Where:

- M- is the molar mass
- w-is the mass of the components

Therefore, by using of the simplified formula based on only known quantities, in equation 7 above, the volume of mixture is calculated and for the sum volume of two quantities there is little depression of volume. Thus, change of volume of sum volume of two quantities and mixture volume with the mole fraction of ethanol in the ethanol-water mixture relation shown in figure 6 below.

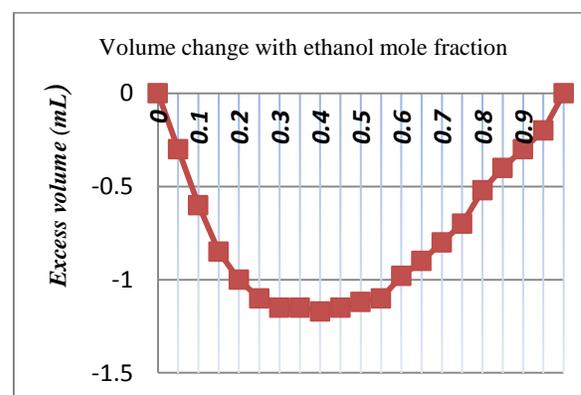


Figure 6: The calculated volume change of 10 mL sample

The maximum flame temperature

When fuel burns definite amount of products are formed and a definite quantity of heat is liberated by breaking down of molecules of the fuel. This quantity of heat may be utilized to rise a temperature of the products of combustion sufficiently to produce a flame. This temperature is called maximum flame temperature or calorific intensity.

In the case, experiment is performed at a constant pressure of combustion then heat liberated is denoted by (ΔH_c) and maximum temperature attained is the flame temperature or usually called adiabatic flame temperature. The measurement of adiabatic is the combustion is absolutely adiabatic with no loss of heat.

The fuel maximum flame temperature calculated by considering simple steady-state thermal energy balance can be constructed around a constant-pressure combustion system by using first law of thermodynamics. However, measuring and construction of adiabatic chamber to get maximum flame temperature is so difficult practically

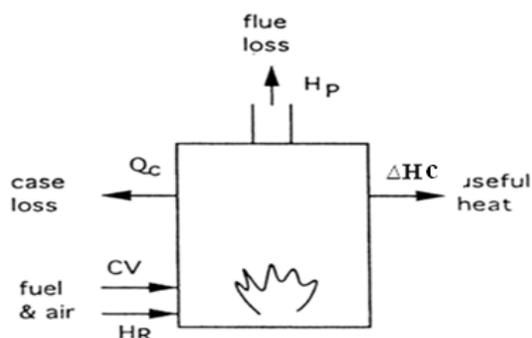


Figure 7: Combustion model of controlled system

The energy balance about the combustion of fuel in controlled system can be written as:

$$CV + HR = Qc + \Delta Hc + HP \quad (8)$$

Where:

- CV- calorific value of fuel
- HR-sensible heat of reactants
- Qc heat loss through the combustion chamber
- ΔHc useful heat or heat of total reaction or enthalpy of combustion
- HP Heat loss of flue gas

HR, the sensible heat in the air and fuel (ref. @ 25 °C) is very small since it is in equilibrium with the environment and often neglected. The case heat loss from the outside of the plant, QC is may be conduction, and convection loss through the combustion chamber and loss due to flue gas is to be zero for the adiabatic assumption case. So, by using heat of reaction or useful output heat by heat of combustion, we can determine the maximum flame temperature using equation 8 by rewriting of equation 9 below.

$$\Delta Hc = CV = \int_{T_1}^{T_2} \sum mCp, m dT \quad (9)$$

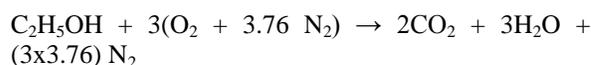
Where:

- o T1 is the initial reference temperature
- o Tf is maximum flame temperature

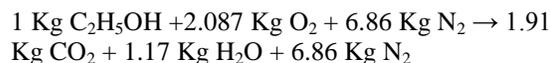
- o $\sum mCpm$ is sum of heat capacities of all species present in system after reaction complete

Based on the property, initial temperature and composition of the fuel, the maximum flame temperature to be determined accordingly equation 9.

For the reaction of pure ethanol (equation 1) is modified for mole balance and then in mass relation is as follows;



From this relation of balanced equation, again the mass balance is:



The procedure of calculating the adiabatic flame temperature of fuel by straightforward method is;

- 1) Evaluate the initial energy values of the fuel (CV and HR); But for this calculation, assuming the initial temperature change of reactants is zero i.e. HR=0.
- 2) Guess the value of Tf and use this value to find the specific heat of combustion products at the average between that value and the reference temperature i.e. $[(Tf + 25)/2]$ °C
- 3) Solve by using equation 9.
- 4) Compare the new value of Tf with the original estimated and if there substantial difference, use the new value to re-evaluate the specific heat, looping back to equation (2-8) until satisfactory convergence is achieved. This is for the calculation accuracy for that the specific heat of flue gases is change with temperature difference.

From the relation of equation 9 the right side is the high calorific value of ethanol at a standard temperature and pressure (298.15 K and 1atm) is 29,700 KJ/Kg and the left side is summation of heat capacities of all species present in combustion of ethanol. Simplified relation for maximum flame temperature is;

$$Tf = T1 + \frac{CV}{\sum mCpm}$$

For initial guess of Tf =700 °C, thus the specific heat Cp of products is;

- $CO_2 = 1.230 \text{ KJ/Kg } ^\circ\text{C}$

- $H_2O = 2.264 \text{ KJ/Kg } ^\circ\text{C}$
- $N_2O = 1.159 \text{ KJ/Kg } ^\circ\text{C}$

$$\sum mC_{pm} = 1.91 \times 1.230 + 1.17 \times 2.264 + 6.86 \times 1.159 = 12.949$$

$$T_f = 2591.8 \text{ K} = 2318.65 \text{ } ^\circ\text{C}$$

And the mean temperature of the flue gases to be $[(2318.65 + 25)/2] \text{ } ^\circ\text{C} = 1155.32 \text{ } ^\circ\text{C}$ and the specific heat at that temperature is;

- $CO_2 = 1.316 \text{ KJ/Kg } ^\circ\text{C}$
- $H_2O = 2.564 \text{ KJ/Kg } ^\circ\text{C}$
- $N_2O = 1.237 \text{ KJ/Kg } ^\circ\text{C}$

$$\sum mC_{pm} = 1.91 \times 1.316 + 1.17 \times 2.564 + 6.86 \times 1.237 = 14.009$$

$T_f = 2419.7 \text{ K} = 2146.6 \text{ } ^\circ\text{C}$ there is no more difference come in further iteration.

Therefore the adiabatic flame temperature of ethanol is $2146.6 \text{ } ^\circ\text{C}$. This value is more accurate and close to measured value or data, than the theoretical data it is best in my opinion.

Flammability of ethanol-water mixture fuel

In the chemical reaction of ethanol in air one mole of ethanol react with three moles of air, two moles of carbon dioxide and three moles of steam produced as equation 1 stated above. The stoichiometric air quantity is the minimum amount of air needed for the complete conversion of fuel to its product gases. But for most cases to achieve satisfactory complete combustion, some quantity of excess air is used. However, the excess air used for combustion may get as product in the product side that reduces the combustion heat and further reduces flame temperature.

Ethanol is very flammable with very low flash-point ($\sim 15 \text{ } ^\circ\text{C}$) and has been used in Brazil and South Africa as cooking fuel. However generally it is used (85 % v/v) and higher concentration and is a dangerous fuel and many fire deaths have been reported in its use at those concentrations. For the mixing of incombustible water to ethanol the water at the reactant side is converted to steam and as flue gas at the product side together with the product of ethanol combustion steam. Flash-point is clearly decreased with increasing water content in the mixture and this makes volatile ethanol safe for cooking.

Therefore, when the content of water in the mixture increase, the quantity of flue gas increase thus the quantity of heat liberated is reduced also the temperature of flame is again reduced.

To determine the stoichiometric air of the mixture of ethanol and water for example, 50 % ethanol-water solution fuel, since there is 50 % (v/v) ethanol in ethanol-water mixture and 21 % oxygen in air in the balanced equation of $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$: $1/0.50 = 2.0$ Volumes of ethanol-water mixture requires $3/0.21 = 14.285$ volumes of air, Or, one volume of ethanol-water mixture requires $14.285/2.0 = 7.1428$ volumes of air or in percentage relation $(1/(1+7.1428)) = 0.1228 = 12.28 \%$. This is ethanol-water mixture in air (stoichiometric air requirement of ethanol mixture).

Every fuel has its upper and lower flammability limit. The upper flammability limit (UFL) is the highest percentage limit of fuel in combustion air that is still flaming and the lowest flammability limit (LFL) is the lowest percentage of fuel in air that the flaming end. The similar calculation of above, flammability of pure ethanol is 6.54 % and shown the flammability of 50 % ethanol-water mixture is 12.28 %. That means the flammability is reduced by half. Ethanol will burn over wide range of flammability from the lower flammability level (LFL) of 3.3 % to the upper flammability level (UFL) is 19 % ethanol in air [7].

The flame temperature of different percentage ethanol-water mixture is depends on the percentage increase of Stoichiometric Volume of air for unit volume mixture of fuel and Stoichiometric volume percentage of air in constant pressure combustion process. Having of solution with the water content, the temperature is reduced due to in the reduction of generated heat to evaporate water content of mixture and increase of volume percentage of stoichiometric air. For that, the relation of maximum flame temperature for the volume percentage ethanol-water mixture is product of Volume % fuel, Volume % air, Peak Temperature ($^\circ\text{C}$), and Peak Pressure (atm) [8]. The peak temperature is the maximum temperature of ethanol-water solution in pure case which calculated in previous section. The calculated values of maximum flame temperature of ethanol-water mixture are summarized in table 3 below.

Table 3:
Maximum Flame Temperature And % Of Ethanol-Water Mixture

% of ethanol-water mixture (% v/v)	Stoichiometric Volume of air	Stoichiometric volume % of air	Max flame temperature (°C)
50%	7.1428	87.72	941.49
60%	8.571	89.55	1153.37
70%	9.9995	90.90	1365.88
80%	11.428	91.95	1579.04
90%	12.856	92.78	1792.45
95.0%	13.570	93.136	1899.29
100%	14.285	100	2146.6

Activity coefficient ethanol-water mixture

In chemical thermodynamics, activity (symbol a) is a measure of the effective concentration of a species in a mixture, and meaning that the species chemical potential depends on the activity of a non-ideal solution in the same way that it would depend on concentration for an ideal solution.

By convention, activity is treated as a dimensionless quantity, although its actual value depends on customary choices of standard state for the species. The activity of pure substances in condensed phases (solid or liquids) is normally taken as unity. A solute in dilute solution is more usual to express the composition of the solution of the solute which shows ideal behavior (also referred to as "infinite-dilution" behaviour). Activity depends on temperature, pressure, and composition of the mixture among other things [9]. The difference between activity and other measures of composition arises because molecules in non-ideal gases or solutions interact with each other, either to attract or to repel each other.

Activities should be used to define equilibrium constants but, in practice, concentrations are often used instead. The same is often true of equations for reaction rates. However, there are circumstances where the activity and the concentration are significantly different and, as such, it is not valid to approximate with concentrations where activities are required.

The chemical potential of i^{th} component in a liquid non-ideal solution is

$$\mu_i = \mu_o + RT \times \ln a_i \quad (10)$$

Where:

- μ_o -is chemical potential of i^{th} component in pure case of solution or it is standard value at temperature T ,
- R -Is gas constant, $R=8.31\text{J/K mol}$
- a_i -activity of i^{th} component
- $RT \times \ln a_i$ -is excess Gibbs energy (excess chemical potential)

We can find the activity of a component of a non-ideal solution from measurements of the vapor pressure of that component in the vapor in equilibrium with the solution. We know that the chemical potential of a component must be the same in the vapor as in the liquid.

$$\mu_{il} = \mu_{og}$$

$$\mu_i = \mu_{oi} + RT \times \ln a_i = \mu_{og} + RT \times \ln \left(\frac{P_i}{P_o} \right) \quad (11)$$

Therefore, $a_i = \frac{P_i}{P_o}$

Where:

- P_i is actual vapor pressure and
- P_o is the vapor pressure of the pure liquid

The ratio of activity a_i to mole fraction of i^{th} component in a solution is called activity coefficient:

$\gamma = a_i/x_i$ and for ideal solution $\gamma = 1$ (that means the activity each element contributes as equal as mole fraction) and for non-ideal solution γ may be either greater than one (positive deviation) or less than one (negative deviation) [10].

Sometimes it is convenient to write the activity as the product of an ideal part times a non-ideality correction part. For example, in a non-ideal solution we might write,

$$a_i = x_i \times \gamma_i$$

In the case of a non-ideal solution $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ when the solution going to the ideal approximation. That, and from which we can conclude that for a non-ideal solution,

$$\gamma_i = \frac{\text{actual vapor pressure}}{\text{Raoult's law vapor pressure}} = \frac{P_i}{x_i P_i}$$

Activity coefficient is a fundamental thermodynamic quantity which measures the solution non-ideality and is as a correction factor to the Raoult's law, governs dilute range fluid-phase equilibrium.

From the graph below, the activity coefficient of ethanol and water is equal at the mole fraction of $x=0.4$. Above the mole fraction of ethanol ($x=0.4$) the activity coefficient of ethanol is less than that of water is a dilution range of ethanol-water mixture.

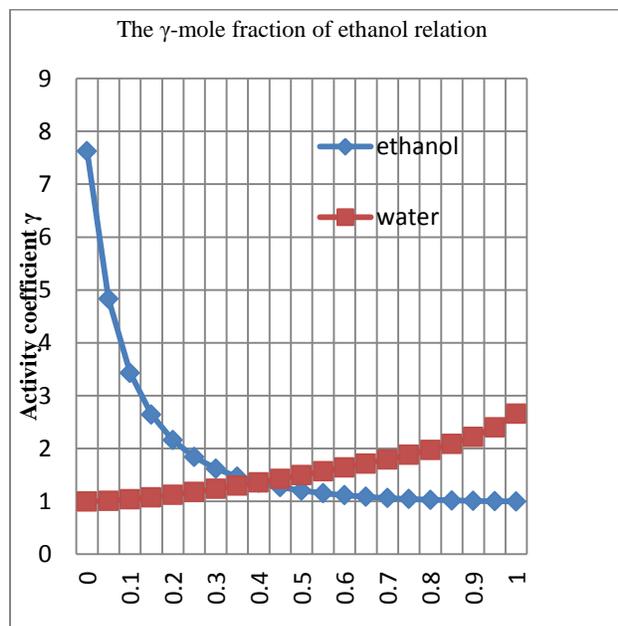


Figure 8: Activity coefficient of ethanol-water mixture

Flash point of ethanol-water mixture Analytical estimation

The flash-point of a given liquid is the experimentally determined temperature adjusted to standard sea-level atmospheric pressure of 760 mmHg (0.1 MPa) at which substance emits sufficient vapor to form combustible mixture with air.

Mathematically, flash-point is the temperature at which the vapor pressure is equivalent to the lower flammability limit in the air.

$$LFL = \frac{P_{sat}(T_{fl})}{P}$$

Where:

- $P_{sat}(T_{fl})$ is vapor pressure at the flash-point temperature (KPa)
- P is ambient pressure (KPa)

The flash-point of binary solution is determined by the formula developed by Liaw et.al. [11]

$$\sum_1 \frac{x_i \gamma_i P_{sat i}}{P_{sat}(T_{fl})} = 1 \quad (12)$$

Where:

- ✓ x_i is mole fraction of components of mixture
- ✓ γ_i is activity co-efficiency of components of mixture

The above equation is re-witted for the binary mixtures of ethanol and water mixture is as:

$$\frac{x_e \gamma_e P_{sat e}}{P_{sat}(T_{fl})e} + \frac{x_w \gamma_w P_{sat w}}{P_{sat}(T_{fl})w} = 1$$

A binary aqueous mixture contains water and flammable ethanol, water is non-flammable component and therefore has no flash-point (T_{fl}). The prediction is equation is reduced from the original Liaw model for the saturation pressure ethanol is:

$$P_{sat e} = \frac{P_{sat}(T_{fl})e}{x_e \gamma_e} \quad (13)$$

The saturation pressure of with the mole fraction of ethanol in water solution is estimated by using the Antoine's relation. Therefore, from the relation of equation 13, the saturation pressure of ethanol in the water solution at flash-point linearly related by the ethanol mole fraction and activity coefficient.

Flame height measurement set-up

The test canister construction is in the base of flammability favorable for ethanol-mixture and for easy caching of fire by it. The sequential procedures of all processes are as follows;

1. The single wick lit with ethanol mixture from the bottom of cylindrical can through the burner hole to the burner is prepared in similar manner for each six samples of testing
2. Careful measured volume ratio ethanol-water mixture is prepared for each testing samples
3. The fuel poured to the canister absorbed with the flame testing wick
4. The top of the canister burner small holes to evaporate the ethanol-water mixture ready to burn
5. Fire through the burner hole diameter observed
6. The flame height measured and data recorded for each test

Flame height is measured by careful observation of the clear blue colored ethanol-water mixture flame is measured by parallel aligning of the unit numbered ruler along the height of flame of single wick.

Bussmann .el al. introduced a theory for open air with the aim that an insight in to the process that are involved with open fires, will lead at least to first guesses on the ruler governing the dimensioning of combustion [12 13]. To avoid the wind blowing of flame problem, the time and the experiment area to should be atmospherically stable in wind speed.

The time and condition of experiment is carried in a closed door usually at night 3: 30 to 5: 00 and burner hole diameter is 6 mm². The ambient temperature is measure my hand glass mercury thermo meter is usually 24 ± 3 °C. I have used light switch off room for the clear observation of white-blue flame.

Flash-point measurement set-up

There are two methods of the measurement of flash-point value of liquid. These are closed-cup test and the open-cup device test. The open-cup flash-point value is typically a few degrees greater than closed-cup flash-point value and thus it is for heavy non-volatile fuels like asphalt grease. The closed-cup test is used for the small flash-point valued of the volatile fuels.

The flash-point of liquid mixture depends on the composition of a mixture and type of chemical involved. For the ethanol-water mixture the value of flash-point increase when the amount of water increase.

The flash-point is measured in the Petroleum quality testing lab of ‘Ethiopia petroleum corporation’ (EPE) by the well calibrated closed-cup device IP-170 (closed-cup) and well experienced operators. The ambient condition of measurement is at 21 °C and corresponding atmospheric pressure 583 mmHg (Addis Ababa) thus the observed measure value is corrected to the sea level normal atmospheric condition (760 mmHg).



Figure 9: Closed-cup IP-170 flash-point measuring device

Measured data analyzing

The mean flame height and flash-point of each sample of mixture is summarized in table 4 below. For the relation of each measure the standard deviation is done for each samples of ethanol-water mixture. The maximum uncertainty at 95 % confidence level is 0.62 for the flame height by Z-test and 0.34 for the flash-point by T-test. The values are little greater than the significance level of and shows that the external affection of the measurement.

Table 4:
The Measured Mean Flame Height And Flash-Point Of Ethanol-Water Mixture

mixture sample (%) v/v)	50	60	70	80	90	95
Mean flame height (cm)	5.0	5.4	6.2	7.5	9.0	9.3
Standard deviation	0.79	0.56	0.97	1.63	1.74	1.80
Uncertainty @ 95 % CI	0.28	0.2	0.34	0.58	0.62	0.6
Flash-point (°C)	24.45	23.7	22.01	20.28	18.64	16.4
Standard deviation	0.51	0.5	0.54	0.55	0.5	0.55
Uncertainty @ 95 % CI	0.316	0.34	0.34	0.34	0.34	0.34

III. ETHANOL-WATER MIXTURE PROPERTY RESULT AND DISCUSSION

The data are analyzed and measured is important to come up with optimal concentration of ethanol-water mixture that suitable for cooking in either energy content or flammability for cooking. The color of flame is from the blue to the yellowish-blue color when the content of water increased in the mixture and which little difficult to observe in ordinal light. The length of flame has been increasing with the percentage concentration of ethanol increase as data shown in table 4 above. At 50 % (v/v) ethanol-water mixture flame is weak and it may need some complex mechanism of stove design for the requirement of favorable cooking and sometime fire catching problem if the wick is not lit more by the fuel.

In the pure case, it catches the fire in a distance makes some sound of catching fire suddenly. This is the flammability hazardous of ethanol. It is clear that some content of water added the flammability is reduced in the same time temperature of flame reduce by expending its combustion heat energy to evaporate the added amount of water.

Based on the data's of flame height, flash-point, maximum flame temperature, over all property of flame, and flammability limit of ethanol-water mixture of different concentration is analyzed.

The 50 % (v/v) ethanol-water mixture flash-point is 24.45°C which is increased from 15°C (100 % ethanol) which around the average annual temperature of most regional cities of Ethiopia.

The flash-point of ethanol-water mixture is to be above 38 °C (the medium flammability hazard limit) at the concentration of above 85 % water but this is not flammable. The flash-point of flammable liquid is increased one by mixing it with inflammable liquid like water or tetra chloromethane and/or in other case blending of high flash-point liquid.

Table 5:
Property Summary Of 60 % (V/V) Ethanol-Water Mixture

<i>Parameters</i>	<i>Units</i>	<i>Values</i>
<i>Boiling point temp. & pre.</i>	<i>KPa and oC</i>	<i>4.42 KPa and 88.5 oC</i>
<i>Mixing enthalpy</i>	<i>J/mol</i>	<i>-650 J/mol</i>
<i>Mixture volume change (10 mL)</i>	<i>mL</i>	<i>-1.13 mL</i>
<i>Flammability</i>	<i>%</i>	<i>10.45 %</i>
<i>Stoichiometric volume of air for unit volume of fuel</i>		<i>8.571</i>
<i>Flame height (Measured)</i>	<i>Cm</i>	<i>5.40 Cm</i>
<i>Flash-point (Measured)</i>	<i>oC</i>	<i>23.7</i>
<i>Maximum flame temperature (calculated)</i>	<i>oC</i>	<i>1153.37 oC</i>

IV. CONCLUSIONS AND RECOMMENDATION

Conclusion

Ethiopia has enough ethanol production capacity, but is still no known best concentration of ethanol-water mixture in flammability energy content and no well-developed flexibility of design and models of ethanol stove except the 'clean cook' stove of GIA association in Ethiopia.

The experiment carried to determine the actual flame height, and flash-point measured for flame property observation, and fire catching property of each samples (50%, 60%, 70%, 80%, 90%, and 95% (v/v) of the 100 mL sample ethanol-water mixture). Accordingly, the mean flame height value, flash-point around the atmospheric temperature for more safety, and maximum flame temperature for enough energy content for cooking is determined. 60% (v/v) maximum flame temperature is calculated as 1153.37 °C and flash-point measured is 23.7 °C which greater than average atmospheric temperature of most cities of Ethiopia and the mean flame height is measured as 5.40 cm. It may be the lowest possible concentration of ethanol-water mixture for the best cooking fuel consumption and cooking house hold safety.

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The energy of ethanol-water mixture is determined by subtracting of the amount of energy utilized to evaporate water content by energy released by combustion of ethanol

Recommendation

The flash-point is still below the safe value. The flash-point of volatile solvent is increased by treating the solvent with the non-flammable liquids like water, tetrachloromethane etc. and/or blending with other high flash-point flammable solvents like terpenolic alcohols. For the further enhancement of flash-point of ethanol-water mixture to safe value it recommended blending with alpha-terpeneol at least 5 % (v/v) to make above flammability hazardous limit. For cooking energy requirement, fuel economy and lower flammability hazard 60 % ethanol, 10 % alpha-terpeneol and 30 % water recommendable.

Finally, anybody who is interested to continue this study, I would like to motivate to make base and recommend that one should improving the efficiency of stove in experimental based with manufacture optimal flammable stove.

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REFERENCE

- [1] World Energy Outlook, "Energy for Cooking in Developing Countries", 2006 pp 424 - 425. PDF found at <http://www.2.gtz/dokumente>
- [2] Stefan Heimann, "Renewable Energy in Ethiopia, 13 Months of Sunshine for a sustainable Development", Berlin 2009.
- [3] Nicolai Schlag and Fiona Zuzarte, "Market Barriers to Clean Cooking Fuels in Sub-Saharan Africa: A Review of Literature" Stockholm environment institute, April 2008
- [4] Flannery-Allen, Julie, "Vital, Ethanol brings an energy revolution to households in the developing world", Retrieved 30 May 2010.
- [5] Web-site: "The flame temperature of volume of mixture" found at <http://www.me.utexas.edu>
- [6] Vladimír Dohnal, Dana Fenclová and Pavel Vrbka, "Temperature Dependences of Limiting Activity Coefficients, Henry's Law Constants, and Alkanols in Water. Critical Compilation, Correlation, and Recommended Data", April 2005.
- [7] Chih-yung Huang, Pey-yu Chung, I-Min Tseng² and Liang-sun Lee, "Measurements and Correlations of Liquid-liquid-Equilibria of the Mixtures Consisting of Ethanol, Water, Pentane, Hexane, and Cyclohexane"
- [8] M. Hristova, D. Damgaliev, D. Popova, "Estimation of Water-Alcohol Mixture Flash-point", Journal of the University of Chemical Technology and Metallurgy, January 2010.
- [9] Meskir Tesfaye Asfaw, "Bio-fuels in Ethiopia". Presented on Eastern and Southern Africa Regional Workshop on Bio-fuels, Nairobi, Kenya, June 29, 2007.
- [10] N.A.Verhoeven, "Kerosene Stove and single wick fuel were burning", Eindhoven University of technology, February 1989.
- [11] Cahill, P., "Evaluation of fire Test Methods for Aircraft Thermal Acoustical Insulation" DOT/FAA/AR-97/58, September 1997
- [12] Audouin, L., Kolb, G., Torero, J.L., Most, J.M., "Average Centerline Temperatures of a Buoyant Pool Fire Obtained by Image Processing of Video Recordings, Fire Safety Journal", Volume 24, pp 167-187, September 1995.
- [13] Butler, B. W. and J. D. Cohen, "Firefighter safety zones: a theoretical model based on radiative heating", International Journal of Wildland Fire 8: 73-77, 1998
- [14] Amare G/Egziabher, James Murren and Cheryl O'Brien, "An Ethanol-fueled Household Energy Initiative in the Shimelba Refugee Camp, Tigray, Ethiopia: A Joint Study by the UNHCR and the Gaia Association", 20 January 2006.
- [15] Alemu Mekonnen and Gunnar Köhlin, "Determinants of Household Fuel Choice in Major Cities in Ethiopia", August 2008.
- [16] Christopher Walsh, "World Bank Enables Thousands of Africans to Access Modern Energy", Washington April 2008.
- [17] P. R. Rastogi, and R. R. misra, "Introduction to chemical thermodynamics", Fourth edition, April 2005.
- [18] Harry stokes, Gia project, "Alcohol fuels (ethanol and methanol): safety", pp 2, January 2005.
- [19] Franklin Chen, "Bartender's Conndrum: partial molar volume in ethanol-water mixtures" Wisconsin university. PDF at found at <http://www.uwgb> .
- [20] Eduardo P´erez, Yolanda S´anchez-Vicente, Albertina Caba˜nas, Concepci´on Pando, Juan A.R. Renuncio, "Excess molar enthalpies for mixtures of supercritical carbon dioxide and water + ethanol solutions", 23 March 2005. PDF found at <http://www.sciencedirect.com>

International Journal of Emerging Technology and Advanced Engineering

Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 7, Issue 5, May 2017)

- [21] Harry stokes, "Commercialization of a new stove and fuel system for household energy in Ethiopia using ethanol from sugar cane residue and methanol from natural gas", October 30, 2004.
- [22] Adrian Bejan, "Heat Transfer" John Wiley & Sons, Inc. 1993.
- [23] D. Rasbash, G. Rama Chandran, B. Kandola, "Evaluation of fire safety", June 1990. PDF found at <http://www.wileyurope.com>
- [24] G.D.RAI, "solar Energy utilization", 5th Edition, KHANNA, NEW DELHI, 2001
- [25] Baltasar, J. et al., "Flue Gas Recirculation in a Gas-fired Laboratory Furnace", Fuel, Vol. 76, pp. 919-929 1997. PDF found at <http://texasiof.ces.utexas.edu>