JACS Hosting Innovations

Contents List available at JACS Directory

Journal of Advanced Chemical Sciences

journal homepage: www.jacsdirectory.com/jacs



Production of Bio-Ethanol From Cane Molasses: Energy Optimization Through Internal and External Heat Integration in Distillation Column

N.P. Patil^{1,*}, V.S. Patil¹, S.L. Bhole²

¹Division of Chemical Engineering, University Institute of Chemical Technology, North Maharashtra University, Jalgaon – 425 001, Maharashtra, India. ²Division of Chemical Engineering, Shivajirao Jondhale College of Engineering, Sonarpada, Dombivali (E), Thane – 421 203, Maharashtra, India.

ARTICLE DETAILS

Article history: Received 02 January 2016 Accepted 12 January 2016 Available online 25 January 2016

Keywords:
Bio-ethanol
Heat Integrated Distillation Column (HIDiC)
Multi-Pressure Distillation (MPRD)
Direct Vapor Recompression (DVR)
Energy Optimization

ABSTRACT

In past few years, world is facing the unexpected rise in the crude oil prices. On tracking the rise in these prices, it is observed that depletion in fossil fuel reserves is the main reason behind it. This fact motivated the scientist across the globe to find out the alternatives for the fossil fuels. The study in this field reveals that, alternative energy sources like solar, wind and hydrogen can serve the purpose to certain extent but surely they has not a potential to meet the global demands. Further research concluded that, biofuels especially ethanol has a great potential to serve as an alternative to conventional fossil fuels with minimal impact on the environment. It demands the high scale production of ethanol which is possible from renewable biomass. This paper in detail describes the production of ethanol from cane molasses in distillery. The major concern in distillery is the energy consumption in distillation arising through the low thermodynamic efficiency of columns. The paper in detail explains the implementation of different techniques like direct vapor recompression (DVR), heat integrated distillation column (HIDiC), multi-pressure distillation (MPRD) in order to reduce the energy consumption in a process. The paper significantly elaborates how the energy consumption in distillery could be reduced from 3.2 to 3.0 kg of steam/liter of ethanol produced through internal and external heat integration in columns. Heat integration achieves the reduction in steam consumption by applying MPRD.

1. Introduction

The unexpected rise in crude oil prices due to energy crises [1-4], demands the exploration of alternative energy sources ranging from wind, water and solar to hydrogen. Another factor that rigorously boosted the need for alternative energy sources is the environmental impacts caused due to emissions from the burning and production of fossil fuels [5]. The study in this field reveals that, the alternative energy sources like solar, wind and hydrogen can solve the problem to certain extent but surely they has not a potential to meet the global demands. In this context, biofuels especially ethanol has a great potential to come up as an environmentally clean fuel that can provide an alternative to conventional fossil fuels with minimal impact on the environment. Uthman et al conducted the experiment on production of fuel ethanol from variety of agricultural products and compares its performance with gasoline. The experimental results show close resemblance with gasoline making ethanol suitable to be used as a fuel in vehicles [6]. Sanchez et al further reported that, about 73% of the total ethanol produced worldwide corresponds to fuel ethanol, 17% to beverage ethanol and 10% to industrial ethanol [7]. In order to meet this global high demand of ethanol, large scale production of ethanol is necessary.

As far as production of ethanol is concerned, it can be manufactured in two ways, either by catalytic conversion of ethylene with steam or by microbial fermentation of sugar [8, 9] in the biomass. Christina et al reported that scarcity of petroleum feed stock and in abundance availability of renewable raw materials for fermentation, makes fermentation more attractive than catalytic conversion process [10]. The earlier one requires ethylene as a raw material, which ultimately comes from underground hydrocarbon based feedstock. Therefore employing catalytic conversion of ethylene to produce ethanol will no longer become an alternative to fossil fuels. But the microbial fermentation of biomass to produce ethanol is perhaps the best ideal and practical way, since the

reduction in energy consumption can be accomplished through internal and external heat integration in distillation columns.

2. Experimental Methods

The production of ethanol from cane molasses consists of microbial fermentation followed by distillation. The actual production of ethanol took place during fermentation only. Distillations merely separate the ethanol from fermented wash and concentrate/purify it to azeotropic point. The detailed fermentation and distillation processes are summarized here.

required biomass is available in abundance. Moreover the biomass is available at almost all the places across the world and at cheaper rate. The

Though the production of ethanol from biomass is proved to be ideal

and promising, the process particularly separation of ethanol from the

fermentation broth is highly energy-intensive [11]. It shares the large

fraction of the total energy requirement of the distillery. This paper in detail describes the production process of bioethanol from cane molasses.

The process consists of fermentation followed by distillation. The major

concern in distillery is the energy consumption in distillation arising through the low thermodynamic efficiency of columns. This low

thermodynamic efficiency ultimately results in the increased production

cost of bioethanol. The aim of this paper is to optimize the energy

consumption in the production of ethanol from cane molasses. The major

scope for the reduction in energy consumption is in distillation. This

renewability of biomass adds special feather to its cap.

2.1 Fermentation

Ethanol could be manufactured through the fermentation of various feedstocks like cane juice, cane syrup, molasses, cassava [12] and grains. As shown in Fig. 1, all the feedstocks except cane molasses require different pre-treatments.

Therefore production of bioethanol from molasses is quite easy and comparatively less energy consuming as compared to other feedstocks.

*Corresponding Author

Email Address: nileshppatil_21@yahoo.co.in (Nilesh P. Patil)

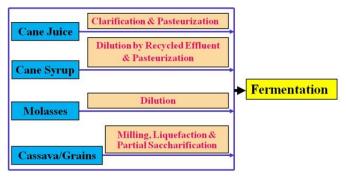


Fig. 1 Possible feedstocks and their pre-treatments before fermentation

In India, sugar cane molasses is a main feedstock for the production of bioethanol; cane juice is not presently used for this purpose [13]. As depicted in Fig. 2, cane molasses almost comprises of 70-80% solids and remaining 30-20% water. Table 1 represents the detail compositional analysis of different classes of cane molasses in India.

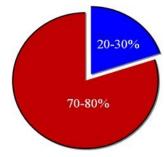


Fig. 2 Composition of cane molasses

Table 1 Composition of different classes of cane molasses in India

Parameters	Molasses		
	A Class	B Class	C Class
Dissolved Solids (%W/W)	74 - 76	72 - 74	70 - 72
Suspended Solids (%W/W)	0.2 - 0.5	1.0 - 1.5	2.0 - 2.5
Fermentable Sugar (%W/W)	62 - 64	47 - 49	40 – 45
Density (Kg/M³)	1.41	1.39	1.44
Viscosity (CP)	1600 - 1650	650 - 700	45000 - 46000
VA (PPM)	4000	4941	5000

During fermentation, initially molasses are cleaned up by screening it through wire mesh. Molasses are then transferred to the fermenter. Due to highly viscous nature of molasses, gear pump is use for the transfer of molasses. In fermenter, dilution of molasses takes place by adding the water in 1:5 (molasses: water) ratio by volume. Pre-prepared culture media from culture vessel is also transferred to fermenter. The residence time for fermenter is 24-36 hours depending on the concentration of ethanol produced. The residence time exceeding 36 hours is strictly avoided to control the side reactions in fermentation.

The concentration of ethanol in fermenter is regularly checked to ensure that the concentration of ethanol is within its inhibitory limit, since the higher concentration of ethanol inhibits the growth and reproduction of yeasts. Fermentation of molasses is a two-step process; in a first step sucrose is hydrolyzed to glucose and fructose whereas in second step glucose and fructose are converted to ethanol and carbon-dioxide. Ruhul et al reported that enzymes invertase and zymase present in the yeast *Saccharomyces cerevisiae* acts as a catalyst for the first and second reaction respectively [14]. They further simulated the production of bioethanol through the fermentation of molasses. Several microorganisms are available and can be employed for the fermentation of molasses, but yeasts *Saccharomyces Cerevisiae* [15-18] are employed on large scale. The fermentation of molasses can be carried out in batch, fed-batch or continuous mode [18-20]. The produced fermented wash with ethanol concentration of about 5-15% (w/w) is then sent for distillation.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
 (1)

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$
 (2)

2.2 Distillation

Distillation is carried out after fermentation, primarily for the separation of ethanol from fermented wash and then to concentrate the produced ethanol. Alone distillation can achieve the ethanol concentration of approximately 95% (w/w) but further concentration of ethanol using distillation is not possible since ethanol-water forms positive homogeneous azeotrope at this composition (95.63% ethanol and 4.37%water by weight). This azeotrope demands, azeotropic distillation for its separation. However, azeotropic distillation is not proved to be economical since the process demands double distillation of ethanol which is very energy intensive. Parkinson in his paper reported that the amount of energy required to enrich the ethanol from 95% to 99.80% requires about half the energy required in enriching ethanol from an initial 10% ethanol mixture to 95% at azeotropic point [21]. This process is also proved to be capital intensive because of the need for additional distillation columns. Additionally use of carcinogens like benzene as entrainer makes it a second choice.

To produce fuel grade ethanol of higher concentration the process must be capable of obviating azeotropic point [10], but since the paper is aiming in the production of potable grade ethanol (rectified spirit), distillation alone can serve the purpose. The paper rigorously gives due emphasis on production of potable grade rectified spirit (95% w/w) and energy consumption associated with it. The energy consumption in the process in analyzed in terms of steam consumption. De Koeijer et al reported that distillation offers a low thermodynamic efficiency of about 5-20% but it could not make this fact ever be decisive in application of distillation since low thermodynamic efficiency of distillation is not so much a result of the separation process [22]. Humphrey et al define the thermodynamic efficiency of a separation process as the ratio of the minimum amount of thermodynamic work required for the desired separation to the minimum amount of energy required for the separation [23]. He further introduce the mathematical formula for separation of an ideal binary mixture by distillation as,

$$E_{max} = \frac{W_{min}}{Q_{min}} = \left(\frac{-RT(xlnx + (1-x)\ln(1-x))}{\Delta H_{vap}(\frac{1}{(\alpha-1)} + x)}\right)$$
(3)

As far as technical and economic aspects are considered, high energy consumption is perhaps the only weakness in distillation. Over the years, lot of work was published on energy saving in distillation. Linnhoff et al broadly classified this work in following three categories as:

- 1. Energy saving within a single distillation column
- 2. Integration of individual column with other columns in the process
- 3. Better distillation sequences for the separation of a multicomponent mixture [24].

Since ethanol-water forms a binary system, the third category of the above is not applicable to it. Therefore the internal and external heat integration in a column can be achieved by implementing the first two categories of the above. Energy saving within a single distillation column is achieved by direct vapor recompression (DVR) system [25], in which vapors leaving the top of column are compressed to a desired pressure, temperature and are allowed to condense in a reboiler of the same column thereby providing the heat needed for the generation of the required vapour flow rate in the column. Pribic et al further reported that DVR is probably the best known arrangement for energy savings in distillation [26]. But this system appears to be capital intensive and economically justifiable only in some large capacity plants operating above atmospheric pressure where low boiling temperature difference exists.

Another viable option for DVR is HIDiC [27, 28] (Heat Integrated Distillation Column) in which vapors leaving the stripping section of the column are compressed to desired level. These compressed vapors are then sent to rectification section thereby implying a pressure variation within a column. In this technique, rectification section of the column operates at higher pressure than stripping section thereby allowing a continuous condensation of vapors. The heat released through the condensation of vapors is then transferred to the stripping section for the significant energy saving in its operation. The remarkable achievement of this technique is direct heat transfer from rectification to stripping section and significant reduction in compression ratio.

Years back, simple atmospheric distillation was used to effect the separation and purification of ethanol from fermented wash. Atmospheric distillation is a seven column system in which all the columns are operated at atmospheric pressure and almost all the columns are supplied with saturated steam. The highest ethanol concentration obtained by atmospheric distillation is approximately 95% (w/w) and steam

requirement of the process is 5.8 kg/liter of produced ethanol. In absence of heat integration, the energy consumption of the process is found to be quite high resulting in the increased capacities of boiler and cooling tower.

In order to overcome this deficiency, the new technique incorporating column to column (external) heat integration is developed. Cardona et further reported that process integration is the key for reducing production costs of ethanol and increasing relative competitiveness of bioethanol to gasoline [29]. This process is widely known as MPRD and gaining a prime interest across the globe. The developed MPRD process is depicted in Fig. 3. MPRD is a seven column system in which two columns are operated at pressure, three at vacuum and the remaining two are at atmospheric pressure.

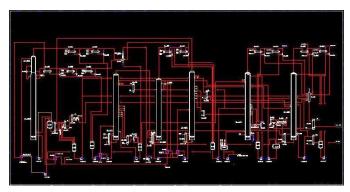


Fig. 3 Process flow diagram (PFD) for newly developed scheme with heat integration

The operation details of the MPRD scheme are tabularized in Table 2.

Table 2 Temperature and pressure variation in MPRD

Columns	Operating Pressure		Operating Temperature	
Columns	Top	Bottom	Top	Bottom
Analyzer Column	0.47	0.55	73.0	82.0
Degassifying Column	0.45	0.47	72.0	73.0
Pre-Rectifier Column	2.20	2.42	98.0	125.0
Extractive D Column	0.50	0.68	81.0	82.0
Rectifier Column	2.20	2.49	98.0	127.0
Recovery Column	1.013	1.213	78.0	105.0
Simmering Column	1.013	1.213	78.0	83.0

In this technique, columns are operated on the basis of pressure difference. More precisely the vapors leaving the top of pressurized columns are used as a heat source (instead of steam) for the reboiler of column operating at vacuum. If the columns are operating at same temperature then in order to implement the terminology, intentionally a pressure difference is created between two columns. Particularly in case of bioethanol production, two columns operating at pressure are supplied with saturated steam while the remaining column runs on the vapors coming from the top of two pressurized columns. It results in the significant reduction in steam consumption and cooling water requirement as compared to atmospheric distillation. In addition to this, application of newly designed trays brings significant contribution to the reduction in energy consumption. Patil et al discussed the comparative performance of various trays types [30].

 Table 3 Steam consumption in MPRD

Name of the Distillation Column	Steam Consumption (Approximate) (Kg/Liter of TS)	
Analyzer Column	1.575	
Degasifying Column	0.175	
Pre-Rectifier Column	1.40	
Extractive Distillation Column	0.60	
Rectifier Column	1.80	
Simmering Column	0.60	
Recovery Column	0.20	
Total Steam Requirement	3.20	

Table 3 represents the individual steam consumption of each column in a process whereas comparative reduction in steam and utility consumption is tabularized in Table 4. From Table 4 it is observed that, due to implementation of MPRD with HIDiC, overall steam requirement of the process is remarkably reduced from 3.2 to 3.0 kg/L of ethanol. It can also be commented that, overall requirement of cooling water must also be reduced, but it cannot be exactly figure out.

3. Result and Discussion

It is observed that, bioethanol could be produced from the fermentation of various feedstocks. Some of them need different pretreatments before fermentation. Particularly in India, molasses are considered as a most suitable feedstock for the production of bioethanol since it is the cheapest feedstock available in abundance and round the year. Moreover, molasses requires no pretreatments before its fermentation thereby making the process significantly easy and comparatively less energy consuming.

Table 4 Comparison of operating parameters

S. No.	Parameter	AD	MPRD	MPRD [HIDiC]
1	Product	ENA	ENA	ENA
2	Distillation Column	07	07	07
3	No. of Distillation	07	02	02
	Column Supplied by			
	Steam			
4	Enrichment of	10 - 96.5	10 - 96.5	10 - 96.5
	Ethanol			
	[From - To] %			
5	Steam Requirement	5.8 kg	3.20 kg	3.00 kg
	kg/liter Ethanol			
6	Steam Properties	1.5 +/- 0.05	3.5 +/- 0.05	3.5 +/- 0.05
	Requirement	kg/cm2(g) at	kg/cm2(g) at	kg/cm2(g) at
		128 °C	148 °C	148 °C
7	Heat Integration	NO	YES	YES
8	Cooling Water	X* m3/hr	0.55X* m3/hr	Not Calculated
	Requirement			

Besides its high energy consumption, distillation is found to be the most reliable operation for the separation of ethanol from spent wash and to concentrate it to azeotropic point. Azeotropic distillation is not proved to be economical because of various limitations associated with it. Atmospheric distillation is also found to be more energy intensive. The effort to reduce the energy consumption of the process leads to internal and external heat integration in a column. The internal heat integration within a single distillation column can be achieved by DVR but the same can be applicable only in some large capacity plants operating above atmospheric pressure and having low temperature difference in their boiling points.

HIDIC brings the significant energy saving in its operation allowing direct heat transfer from rectification to stripping section of the column and significant reduction in compression ratio. The external heat integration can be achieved through the application of MPRD and is found to have great potential to reduce the energy consumption in the process. The energy consumption in the process is analyzed in terms of steam consumption. Steam requirement in atmospheric distillation is $5.8 \, \text{kg/L}$ of produced ethanol. Application of MPRD lowers the energy (steam) consumption to $3.2 \, \text{kg/L}$ whereas HIDiC lowers the steam consumption to $3.0 \, \text{kg/L}$ of produced ethanol.

4. Conclusion

Considering all the facts, it is concluded that cane molasses are the most suitable feedstocks for bioethanol production. Distillation remains the most reliable operation for the separation and concentration of ethanol from spent wash. Azeotropic distillation can be used, but various economic and environmental limitations associated with it, make it a second choice. Though atmospheric distillation is found to be capable, it offers more energy intensive operation. The significant reduction in energy consumption could be possible by internal and external heat integration in a column. DVR is found to have potential in energy saving but it also has its limitations. HIDiC offers a viable option for energy saving in its operation thereby reducing compression ratio in a column.

Application of MPRD can bring the external heat integration. Steam requirement in atmospheric distillation is $5.8\,\mathrm{kg/liter}$ of produced ethanol. Application of MPRD lowers the energy (steam) consumption to $3.2\,\mathrm{kg/liter}$. Further combination of MPRD with HIDiC lowers the steam consumption to $3.0\,\mathrm{kg/liter}$ of ethanol and emerges as a most reliable, convenient and economically optimized choice. This hybrid technology significantly brings down the energy consumption in the process.

Abbreviation

DVR : Direct vapor recompression MPRD : Multi-Pressure Distillation

HIDiC : Heat Integrated Distillation Column

Notation

- Maximum thermodynamic efficiency E_{max}

 W_{min} - Minimum work consumed per kmol of feed

- Minimum amount of energy required for separation per kmol Q_{min} of feed

R -Ideal gas constant T- Temperature

Χ - Mole fraction of the more volatile component in the feed (0 < x < 1)

 ΔH_{vap} - Molar heat of the vaporization of bottom product

- Relative volatility. α

References

- N. Anderton, R. Kingwell, Spatial and temporal aspects of grain accumulation costs for ethanol production; an Australian case study, I. Biomass Bioenergy, 32 (2008) 109-119.
- M. Balat, H, Balat, Recent trends in global production and utilization of bio-[2] ethanol fuel, Appl. Energy 86 (2009) 2273-2282.
- X. Du, D. Hayes, the impact of ethanol production on US and regional gasoline markets, Energy Policy 37 (2009) 3227-3234.
- K.D. Lambert, J. Middleton, Logistical design of a regional herbaceous crop residue based ethanol production complex, Biomass Bioenergy 34 (2010) 91-100.
- A.H. Fushcia, J. Abraham, A comparison of corn-based ethanol with cellulosic ethanol as replacements for petroleum-based fuels: A review, Int. Jour. Sustain. Energy 28:4 (2009) 171-182.
- H. Uthman, A. Jimoh, The production and characterization of ethanol fuel from agricultural products as an alternative fuel for gasoline, Energy Sour. A 34(22) (2012) 2041-2047.
- O.J. Sanchez, C.A. Cardona, Trends in biotechnological production of fuel [7] ethanol from different feed stocks, Biores. Technol. 99 (2008) 5270-5295.
- C.LF. Pereira, E. Ortega, Sustainability assessment of large-scale ethanol [8] production from sugarcane, J. Cleaner Prod. 18 (2010) 77-82.
- T. Silalertruksa, H.S. Gheewala, Environmental sustainability assessment of bio-ethanol production in thailand, Energy 34 (2009) 1933-1946.
- $[10] \quad B.\ Christina,\ D.\ Faitakis,\ K.T.\ Chuang,\ Simulation\ studies\ of\ the\ removal\ of\ water$ from ethanol by a catalytic distillation process, Chem. Eng. Comm. 192(11) (2005) 1541-1557.
- [11] H.J. Huang, S. Ramaswamy, U.W. Tschirner, B.V. Ramarao, A review of separation technologies in current and future biorefineries, Sep. Purif. Technol. 62 (2008) 1-21
- [12] O.D. Adeniyi, A.S. Kovo, A.S. Abdulkareem, C. Chukwudozie, Ethanol fuel production from cassava as a substitute for gasoline, J. Dispersion Sci. Technol. 28:4 (2007) 501-504.

- [13] P. Ghosh, T.K. Ghose, Bioethanol in India: Recent, past and emerging future, Adv. Biochem. Eng. Biotechnol. 85 (2003) 1-27.
- A.M. Ruhul, H.M. Saquib, M. Sarker, Simulation of Ethanol Production by Fermentation of Molasses, Jour. Eng. 1(4) (2013) 69-73.
- N. Kiransree, M. Sridhar, L. Venkateswar Rao, Characterization of thermo tolerant, ethanol tolerant fermentative Saccharomyces cerevisiae for ethanol production, Bioprocess Eng. 22 (2000) 243-246.
- [16] S.S. Win, A. Impoolsup, A. Noomhorm, Growth kinetics of Saccharomyces cerevisiae in batch and fed batch cultivation using sugarcane molasses and glucose syrup from cassava starch, Jour. Indus. Microbial. 16 (1996) 117-123.
- O.F. Echegaray, J.C.M. Carvalho, A.N.R. Fernandes, S. Sato, E. Aquarone, M. Vitolo, Fed-batch culture of Saccharomyces cerevisiae in sugarcane blackstrap molasses: invertase activity of intact cells in ethanol fermentation, Biomass Bioener. 19 (2000) 39-50.
- F. Ghorbani, H. Younesi, The kinetics of ethanol production from cane molasses by Saccharomyces cerevisiae in a batch bioreactor, Energy Sour. A 35(11) (2013) 1073-1083.
- R. Gabriela, P. Elena, B. Camelia, V. Constanta, B. Gabriela, Investigation of yeast performances in the fermentation of beet and cane molasses to ethanol production, Ovidius Univ. Annal. Chem. 20(2) (2009) 199-204.
- M. Rebros, M. Rosenberg, Z. Grosova, L.U. Kristofíkova, M. Paluch, M. Sipocz, Ethanol production from starch hydrolyzates using Zymomonas mobilis and glucoamylase entrapped in polyvinyl alcohol hydrogel, Appl. Biochem. Biotechnol. 158 (2009) 561-570.
- G. Parkinson, Battelle maps ways to pare ethanol costs, Chem. Eng. 88(11) (1981) 29-31.
- G.M. De Koeijer, S. Kjelstrup, Minimizing entropy production rate in binary tray distillation, Int. J. Appl. Thermodyn. 3 (2000) 105-110.
- $J.L.\ Humphrey, G.E.II.\ Keller, Separation\ Process\ Technology, McGraw-Hill, New$ York 1997
- B. Linnhoff, H. Dunford, R. Smith, Heat integration of distillation columns into overall processes, Chem. Eng. Sci. 38(8) (1983) 1175-1188.
- Z. Olujic, F. Fakhri, A. De Rijke, J. De Graauw, P.J. Jansens, Internal heat integration - the key to an energy conserving distillation column, Jour. Chem. Technol. Biotechnol. 78(2-3) (2003) 241-248.
- [26] P. Pribic, M. Roza, L. Zuber, How to improve the energy savings in distillation and hybrid distillation-pervaporation systems, Sep. Sci. Technol., 41(11) (2006) 2581-2602.
- M. Nakaiwa, K. Huang, M. Owa, T. Akiya, T. Nakane, M. Sato, et al, Energy savings in heat-integrated distillation columns, Energy 22 (1997) 621-625.
- M. Nakaiwa, K. Huang, K. Naito, A. Endo, M. Owa, T. Akiya, et al, A new configuration of ideal heat integrated distillation columns, Comp. Chem. Eng. 24 (2000) 239-245
- C.A. Cardona, O.J. Sanchez, Fuel ethanol production: process design trends and integration opportunities, Biores. Technol. 98 (2007) 2415-2457.
- N.P. Patil, V.S. Patil, Operational and economic assessment of distillation column from the performance of tray, Int. J. Eng. Trend. Technol. 4 (2016) 500-