INFLUENCE OF LIQUEFACTION TEMPERATURE UPON RHEOLOGICAL PROPERTIES OF CORN STARCHY MASHES

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Abstract: *In this paper we studied the effect of liquefaction temperature of the corn starchy mashes upon their rheological properties. For the study two types of corn grind starchy mashes respectively one of fine grind with particles of <0.5 mm and one of rougher grind with particles of > 0.5 mm have been made. The enzymatic package, used in obtaining the two types of starchy mashes, consists of three enzyme types: Spezyme® (liquefaction enzyme), Stargen 001 (α-amylase and amiloglucosydase for the starch hydrolysis) and Fermgen (protease). For the two types of starchy mashes we tested different liquefaction temperatures of 40ºC, 50ºC, 60ºC and 70ºC. The rheological properties of starchy mashes have been analyzed by the viscometer Brookfield RV Pro II+ during their obtaining in two phases: before and after the starchy mashes liquefaction. From the study carried out we observed that the mashes obtained from fine corn grind, the liquefaction temperature of 60ºC is more efficient whereas more reduced viscosity being obtained in comparison with the other liquefaction temperature of 40ºC, 50ºC and 70ºC. For the mashes obtained from rough corn grind we observed the fact that the liquefaction temperature of 50ºC is more efficient, more reduced viscosity being obtained in comparison with the other liquefaction temperatures of 40ºC, 60ºC and 70ºC.*

Keywords: *viscosity, enzyme, fine grind, rougher grind.*

Introduction

The utilization of biomass as the starting material for the production of biofuels has received considerable interest in recent years. Starchy and cellulosic materials of plant origin are the most abundant utilizable biomass resources. Starchy biomass has to be hydrolyzed either by enzymatic or acid hydrolysis to release fermentable sugars.

The enzymatic hydrolysis of starchy material for ethanol production via fermentation consists of two or three steps and requires improvement if it is to make efficient production at low cost [1].

Besides the particular traits, the fermentation processes have specific rheological behaviours and rheological characteristics modification in time. Knowing the way of flowing of these liquids as well as its evolution during the fermentation time represents an essential condition for obtaining the optimum parameters of the process. The rheological characteristics of the fermentation liquids have a decisive influence upon the biosynthesis process performances by controlling mass and heat transfer, the conditions under which the mixing is made as well as the further separation operations [2].

Experimental

Starch biomass

In the fuel bioethanol industry, starch is mainly provided by grains (corn, wheat, or barley). Corn, which is the dominant feedstock in the starch-to-ethanol industry worldwide, is composed of 60 to 70% starch. [1] Starch, by its two components, has four types of bonds in its structure: α-1.4 glycosidic inside amylose and amylopectin macro-molecules, α-1.4 marginal glycosidic, α-1.3 glycosidic and α-1.6 glycosidic [3]. Starch complete hydrolysis into glucose requires enzymes for all four types of bonds [4].

The raw material used for this study is the starchy biomass made from corn mash.

Enzymes and microorganisms

The hydrolysis of starchy raw materials can be done by acids or enzymes, but due to several advantages of enzymatic hydrolysis, it is the preferred choice for industrial applications [5].

Enzyme hydrolysis is carried out in two stages [6]:

- the first stage is called "liquefaction";
- the second stage is called "saccharification"

The liquefaction enzymes are represented by α-amilase which divides the α-1.4 cross links from the amylose and the amylopectin. The α-amylase is an endohydrolase which acts randomly in the inner side of the amylose chains having as result linear dextrins and even small glucose quantities. In the case of amylopectin the α-amylase forms linear dextrins and branched dextrins with medium and small molecular mass [7].

SPEZYME® enzyme contains a thermostable starch hydrolyzing α-amylase that is produced by a genetically modified strain of *Bacillus licheniformis*. The endo-amylase in SPEZYME® enzyme hydrolyzes α-1.4 glycosidic bonds to quickly reduce the viscosity of gelatinized starch, producing soluble dextrins and oligosaccharides under a variety of process conditions [8].

Recommended conditions [8]:

- Solids 30 to 36%
- Optimal pH 5.7 to 5.8
- Optimal temperature 83 to 85ºC
- Liquefaction time 90 to 140 minutes
- Dosage recommendation 0.20 to 0.24 kg/MT DS.

SPEZYME® enzyme provides the following benefits to ethanol producers [8]:

- Quick viscosity reduction allowing for higher solids
- Liquefaction pH's as low as 5.2
- Process flexibility
- Improved performance at low slurry temperatures

For the saccharifying of liquefied mashes, glucoamylase is utilized and this is an endohydrolase which devides the α-1.4, α-1.6 and α-1.3 glucosidic cross links from the amylose and the amylopectin [7].

STARGEN™ 001 enzyme contains Aspergillus Kawachi alpha amylase expressed in Trichoderma reesei and glucoamylase from Aspergillus niger that word synergistically to hydrolyze granular starch substrate to glucose [9].

The endo-activity, alpha amylase and exo-activity, glucoamylase, in STARGEN™ 001 enzyme catalyzes the complete hydrolysis of granular starch under a variety of alcohol fermentation conditions.

Recommended conditions [9]:

- Solids 12 to 38%
- Optimal pH 3.0 to 4.5
- Dosage recommendation 1.0 to 2.5 kg /MT DS.

FERMGEN™ is an acid proteolytic enzyme characterized by its ability to hydrolyze proteins under low pH conditions. The fungal protease is obtained by controlled fermentation of a genetically modified selected strain of *Trichoderma reesei* [10].

Recommended conditions:

- Solids 26 to 38%
- Optimal pH 3.5 to 5.0
- Optimal temperature 28 to 35ºC
- Dosage recommendation 0.1 kg/MT

Study on corn mash viscosity

To study the influence of liquefaction temperature upon the rheological properties of corn starchy mashes we used two types of grind. For the first type we used fine corn grind with particles of < 0.5 mm and for the second type we used rougher corn grind with particles of > 0.5 mm.

The rheological properties of starchy mashes have been analyzed by the viscometer Brookfield RV Pro II+ during their obtaining in two phases: before and after the starchy mashes liquefaction.

The two types of mashes were obtained by mixing the grind with water in 1:3 ratio. The mixture obtained was treated by enzymes in two stages: liquefaction and saccharifying. The liquefaction was performed at different temperatures of 40ºC, 50ºC, 60ºC and 70ºC, at a pH of 5.8 for 120 minutes by adding 0.22 kg/MT DS Spezyme enzyme.

The liquefied mash was saccharified at 34°C, at a pH of 4.5 for 60 minutes by adding 2 kg/MT DS Stargen 001enzyme.

The saccharified mash was treated at a pH of 4.5 with 0.1 kg/MT Fermgen enzyme, to which was added yeast at a ratio of 3 g/l and it was than subjected to fermentation for obtaining bio ethanol fuel.

The study was carried out at two different rotation speeds, both 50 RPM and 100 RPM, using HA4 spindle and specific temperature phase.

The mashes obtained after previous described method were fermented in BlueSens bioreactors with a capacity of one liter which monitoring free oxygen, of leaven ethanol content from mash and free carbon dioxide.

The mashes fermented were distilled with a rotoevaporator volume of 500 ml.

The analysis of obtained distillate was made by a Shimadzu gas chromatograph with flame ionization detector.

Results and discussion

The experimental results obtained for the fine grind mash are presented in table 1.

The experimental results obtained for the rougher grind mash are presented in table 2.

Table 1.
The fine grind mashes viscosity according to the liquefaction temperature

Nr. Crt.	Temperature, °C	Viscosity before liquefaction, cP		Viscosity after liquefaction, cP	
		50 RPM	100 RPM	50 RPM	100 RPM
1.	40	4.97	5.66	4.77	5.48
2.	50	4.97	5.66	4.07	4.4
3.	60	4.97	5.66	3.14	3.88
4.	70	4.97	5.66	3.2	4.01

Table 2.
The rougher grind mashes viscosity according to the liquefaction temperature

Nr. Crt.	Temperature, °C	Viscosity before liquefaction, cP		Viscosity after liquefaction, cP	
		50 RPM	100 RPM	50 RPM	100 RPM
1.	40	5.4	6.35	3.85	4.6
2.	50	5.4	6.35	3.97	4.54
3.	60	5.4	6.35	5.28	5.49
4.	70	5.4	6.35	5.41	5.28

In figure 1 and 2 the viscosity values obtained for the two types of mashes at the four liquefaction temperatures, at the two rotation speeds are compared. Figure 3 shows the content of ethanol at the end of fermentation for the two types of mashes. The content of ethanol determined by chromatography of the distillate obtained from fermented mashes is shown in figure 4.

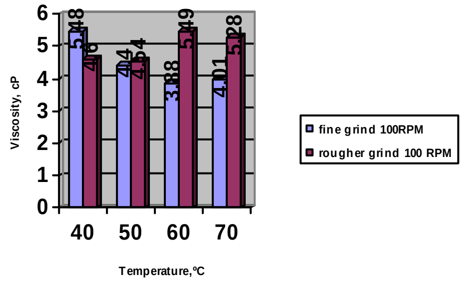

Figure 1. The corn mashes viscosity variation according to the liquefaction temperature at 100 RPM

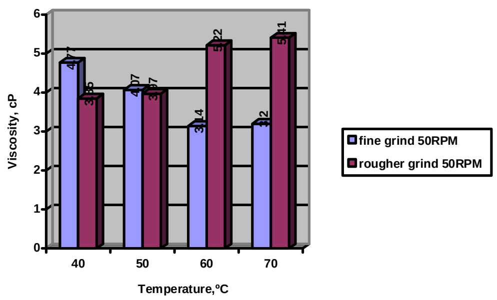

Figure 2. The corn mashes viscosity variation according to the liquefaction temperature at 50 RPM

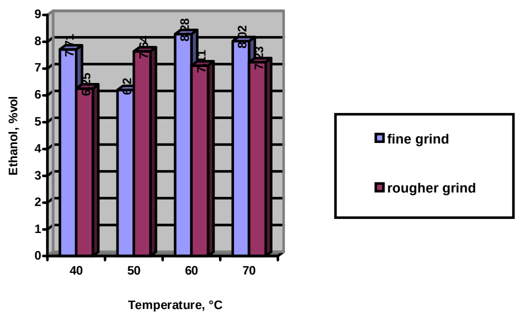

Figure 3. Ethanol content of mashes at the end of the fermentation

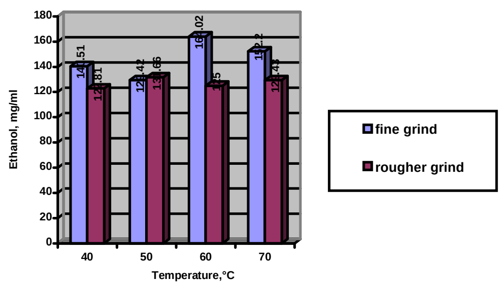

Figure 4. Ethanol content of the distillate obtained from fermented mashe

Conclusions

From the study carried out we observed that the mashes obtained from fine corn grind at the liquefaction temperature of 60ºC is more efficient and a more reduced viscosity resulted in comparison with the other liquefaction temperature of 40ºC, 50ºC and 70ºC. For the mashes obtained from rough corn grind we observed the fact that the liquefaction temperature of 50ºC is more efficient and more reduced viscosity resulted in comparison with the other liquefaction temperatures of 40ºC, 60ºC and 70ºC. From figures 3 and 4 one may notice that a higher content in ethanol at 60ºC for the mashes obtained from fine grind and at 50ºC for mashes obtained from rougher grind is registered.

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