Advances in Bioresearch
Adv. Biores., Vol4 (2) June 2013: 77- 82
©2013 Society of Education, India
Print ISSN 0976-4585; Online ISSN 2277-1573
Journal's URL:http://www.soeagra.com/abr/abr.htm
CODEN: ABRDC3

ORIGINAL ARTICLE

Influence of the Composition in the Rheological Behavior of High Fructose Syrups

José Luis Montañez-Soto*[1], Martha Alicia Velázquez Machuca[1], José Venegas González[1], Aurea Bernardino Nicanor[2]and Leopoldo González-Cruz[2]

[1]Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional del Instituto Politécnico Nacional, Unidad Michoacán. Justo Sierra Nº28 Jiquilpan, Mich. México. C.P. 59510. Teléfono: 353-53-302-18. * E-mail: montasoto@yahoo.com.mx

[2]Instituto Tecnológico de Celaya. Av. Tecnológico y García Cubas s/n. C.P. 38010. Celaya, Guanajuato, México.

ABSTRACT

The objective of this work was to study the effect of fructose and glucose content in the rheological behavior of syrups.Initially high fructose syrups from the fructans present in leaves, bases and head of Agave tequilana Weber blue were obtained. Then was determined its contents of moisture, ash, fructose, glucose, direct reducing sugars and totals.Finally the physicochemical properties of the syrups were evaluated and compared with a commercial high fructose corn syrup (Frudex 55), and with other fructose, glucose and sucrose syrups; all of them at the same temperature and total solids concentration. All syrups behaved as Newtonian fluids and have no statistically significant differences (p <0.05) in its density, water activity, and in direct and total reducing sugars. The viscosity and surface tension of syrups depends on its fructose and glucose content. Also, greater fructose content produces syrups with lower viscosity and lower surface tension.

***Key words**: High Fructose Syrups, Viscosity, Rheological behavior, Newtonian fluids*

Received: 09/04/2013 Accepted: 12/05/2013

List of Non-Standard Abbreviations: High Pressure Liquid Chromatographic (HPLC) Average Degree of Polymerization (ADP)**;** High Fructose Syrup (HFS); High Fructose Corn Syrup (HFCS); Total Reducing Sugars (TRS); Direct Reducing Sugars (DRS); Glucose (G);Fructose (F); Dry Basis (DB);Water Activity (aw); Viscosity (η); Shear Stress (τ) Shear Rate (γ); Soluble Solids % (°Brix); Consistency Index (K);Flow Behavior Index (n)

INTRODUCTION

Nowadays, the high fructose syrups (HFS) have displaced sucrose and glucose and have become the sweeteners most demanded by the pharmaceutical,food and beverage industries due to its functional and technological advantages[1, 2].In the industry the HFS are obtained commercially from corn starch mainly,a process that utilizes various enzymes to hydrolyze starch into glucose and its subsequent conversion to fructose by the glucose isomeraseenzyme immobilized in columns on packedmatrices [3].The obtained product is a syrup with 42% fructose and the rest of glucose mainly, and for obtaining higher fructose syrup, adsorption columns packed with cationic exchange resins, or zeolites, in the Ca^{2+} form is frequently used within which diverse unitary operations like pumping, are performed [4, 5].

As a result of the chemical and structural changes which undergoes the substrate from the beginning of the process and to obtain the HFS with concentration and ratio of fructose/glucose desired, in each one of the stages of the elaboration process of these syrups, the rheological properties of the fluid are changing too, Because of this, in order to achieve an efficient and economic operation, and thus optimize the process, it is necessary to know how fructose and glucose content affects the rheological behavior of the syrups[6].

Knowledge of the rheological behavior of food in general, and of high fructose syrups in particular, is of utmost importance for the design in process engineering, quality control, as well as in the sensory evaluation and in determination of food structure [7, 8, 9].In process engineering, knowledge of the rheological behavior of a fluid is necessary for calculating pumping requirements, for establish the dimensions of pipes and valves, for carrying out mixtures and also for calculation basic operations related to heat transfer, mass and movement amount [6].In quality control, knowledge of the rheological behavior of a fluid is used for quality control of raw materials, as well as intermediary products during manufacturing and of course, of the final products.In sensory evaluation, knowledge of the rheological behavior of a fluid it helps to determine the preferred quality by the consumer through the correlations between rheological measurements and sensory evaluations [10].Also through knowledge of the rheological behavior of fluids, they help to elucidate the structure or composition of foods and to analyze the structural changes that occur during its process[11].

Fluid foods exhibit rheological behavior that range from simple Newtonian to a non-Newtonian [12, 13, 14],and these last can be time dependent or not [15].Many foods behave as a combination of elastic and viscous materials, and the rheological parameters which characterize them are; viscosity (η), in the case of Newtonian fluids,and the consistency index (K) and flow behavior index (n), in the case of non-Newtonian fluids [7].

The objective of this research project was to study the effect of fructose and glucose content in the rheological behavior of high fructose syrups obtained from different botanical sources such as *Agave tequilana* Weber blue fructans and maize starch.

MATERIALS AND METHODS

Ten eight years old *Agave tequilana* Weber blue plants grown in the municipality of Atotonilco el Alto, Jalisco, Mexico. Frudex 55®: high fructose corn syrup (HFCS) with 70% solids of which, 55% is fructose and 45% glucose (Arancia, Mexico).Mixture of exo-inulinase (EC 3.2.1.80) and endo-inulinase (EC 3.2.1.7) from *Aspergillusniger* in 5:1 ratio, with specific activity of 955 units/mg solid (Megazyme, Ireland).One unit of specific activity was defined as the required amount of enzyme to liberate one micromole of fructose per minute under determination standard conditions. Sucrose, β-D-(+)-glucose and D(-)-fructose, with 99%minimum purity (Sigma, USA).All other reagents were analytical grade.

Elaboration of high fructose syrups from fructans present in the leaves and head of the *Agave tequilana* Weber blue.

Initially were obtained the flours from each of the botanical fractions of the agave plant (tips of leaves, leaf bases and head), which were then used to extract the fructans contained in the same[16]. Later these extracts were used for the production of high fructose syrups by enzymatic way, which were concentrated to 70% total solids, packaged, labeled and stored in a dry, dark and at room temperature for later analysis [2]. By dissolving in distilled and deionizer water, were also prepared syrups of fructose, glucose and sucrose at 70% total solids.

Chemical characterization of syrups

Moisture and ash content was determined according AOAC methods [17]. Direct reducing sugars (ARD) and total reducing sugars (ART) were determined by the method of Miller [18]. Fructose and glucose content were determined with specific amperometric biosensors; for fructose [19], and for glucose [20].In both cases was used anamperometric detector model LC-4C (BAS, USA),provided with three electrodes: a working electrode (biosensor), a platinum auxiliary electrode (Ingold, Switzerland), and a doublejunction Ag/AgCl reference electrode (Orion, USA),whose external reference solution was 0.1 mol/l KCl. All determinations were done in triplicate.

Rheological behavior and viscosity of syrups

The rheological behavior of the syrups was evaluated at a temperature of 25°C, using a viscometer Rotovisco model Haake RV2 (Haake, Germany) using the sensor MV1 to a shear rate of 1000 s^{-1}.In this way it were determined the fluid type and viscosity (η) of syrups, applying the model of the power law of Newton ($\tau = \eta\ \gamma$),which relates the shear strength (τ) with the shear rate (γ), through the viscosity (η) of the fluid [7].

Physicochemical Characterization of syrups

The physicochemical parameters evaluated were: density, total solids (ºBrix), water activity (a_w), surface tension, color and viscosity.Density was determined at a temperature of 25°Cwith a pycnometerBrixco of 25mL. The total solids (°Brix) were determined at a temperature of 25°Cwith an ABBE Refractometer (American Optical Co., USA).Water activity was determined at a temperature of 25°C with a Thermoconstanter model RTD33 (Novasina, Switzerland).Surface tension was determined at a temperature of 25°C with a Surface Tensiometer model 2141 (Analyte, Australia).Color was determined using a Hunter Lab spectrophotometer with an illuminant D50 and D65 to 10° of the observer. It used the CIE-Lab system which involves the parameters L, a*, and b*. The parameter L refers to the brightness of the sample, that is, the degree to which the sample is able to reflect light. Positive values of the parameter a* indicated colorations toward the brownish tone,while negative values indicated colorations toward the green tone. Positive values of parameter b* indicated yellow colorations and negative values of this parameter indicated blue colorations.

Statistical analysis

The results correspond to the average value of three determinations ± standard deviation of the series. The data analysis was performed using SPSS version 12.0 for Windows®.An analysis of variance one-way was conducted and the test of Tukey's multiple comparison was done to determine statistical significance ($p < 0.05$) of the physicochemical properties of the different syrups studied, all of them at the same concentration of total solids and same temperature.

RESULTS AND DISCUSSION

No statistically significant difference ($p<0.05$) in moisture content in the syrup, because all they were prepared to the same total solids content (Table 1).As consequence of the addition of NaOH 1M for adjusts to 4.25 the pH of the agave syrups, its ash content was slightly higher than that contains corn syrup "Frudex 55®". Industrially these syrups are passed through ion exchange resins, to minimize its salt content and thus prevent them from interfering with the organoleptic properties of the syrups, or foods prepared with them[21].

Table1. Chemical characterization of syrups

Parameter		Agave syrups		Cornsyrup
	Leaves	Bases	Head	Frudex 55®
Humidity (%)	30.0 ± 0.12^a	30.0 ± 0.15^a	30.0 ± 0.01^a	30.0 ± 0.01^a
Ash ($\%_{DB}$)	0.31 ± 0.05^a	0.29 ± 0.05^a	0.27 ± 0.03^b	0.05 ± 0.01^c
DRS($\%_{DS}$)	99.05 ± 1.25^a	99.15 ± 1.15^a	99.55 ± 1.25^a	99.80 ± 1.30^a
TRS ($\%_{DB}$)	99.18 ± 1.50^a	99.30 ± 1.35^a	99.60 ± 1.10^a	99.87 ± 1.40^a
Fructose ($\%_{DB}$)	81.22 ± 0.43^a	84.54 ± 0.55^b	87.92 ± 0.28^c	53.12 ± 1.05^d
Glucose ($\%_{DB}$)	17.92 ± 0.58^a	15.20 ± 0.45^b	11.64 ± 0.36^c	46.86 ± 1.18^d

Different letters between columns of the same line indicate statisticallysignificant differences ($p < 0.05$)

Table 2: Physicochemical characterization of syrups

SYRUP	Density g/mL	Water activity (a_w)	Surface tension dinas/cm	Color a*/b*	Viscosity mPa-s
Glucose	1.51 ± 0.003^a	0.70±0.002^a	55 ± 0.6^a	Colorless	326 ± 4.9^a
Sucrose	1.50 ± 0.005^a	0.702±0.001^a	46 ± 0.4^b	Colorless	250 ± 4.5^b
Frudex 55®	1.50 ± 0.005^a	0.702±0.001^a	51 ± 0.4^c	0.01	212 ± 1.5^c
Leaves	1.50 ± 0.002^a	0.701±0.002^a	48 ± 0.5^b	0.18	203 ± 1.5^d
Bases	1.50 ± 0.003^a	0.699±0.002^a	47 ± 0.5^b	0.11	193 ± 1.3^e
Head	1.49 ± 0.003^{ab}	0.700±0.002^a	45 ± 0.6^{bd}	0.09	182 ± 1.2^f
Fructose	1.48 ± 0.003^b	0.700±0.001^a	43 ± 0.5^d	Colorless	169 ± 0.8^g

Different letters between lines of the same column indicate statistically significant difference ($p < 0.05$).

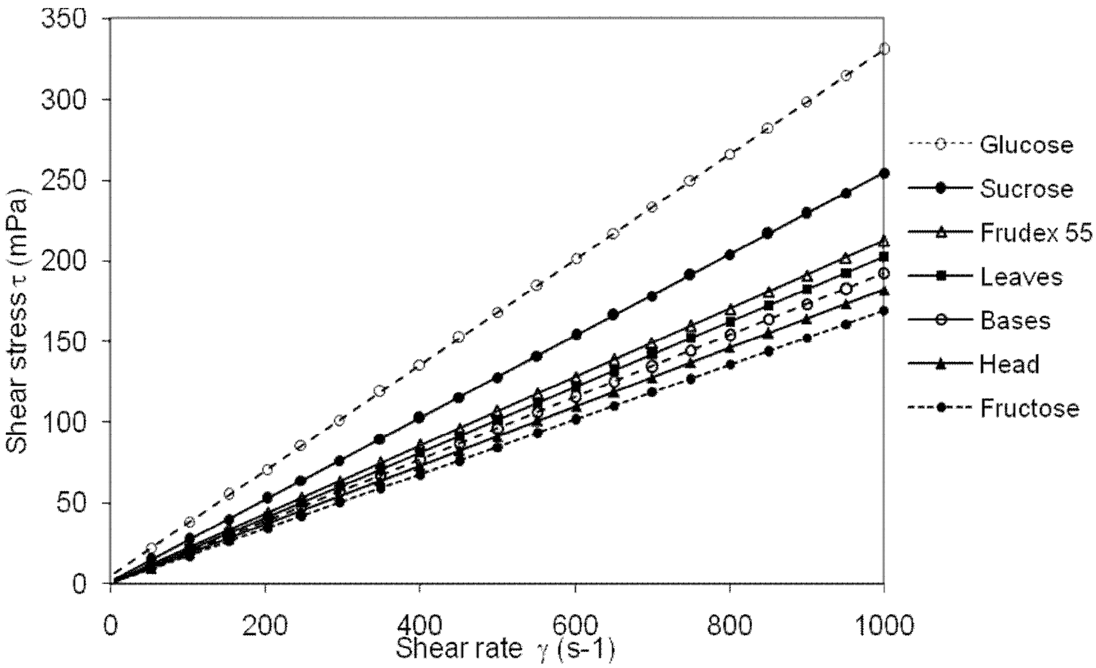

Figure 1.Shear stress vs. shear rate of the different syrupsat 70ºBrix and 25ºC.

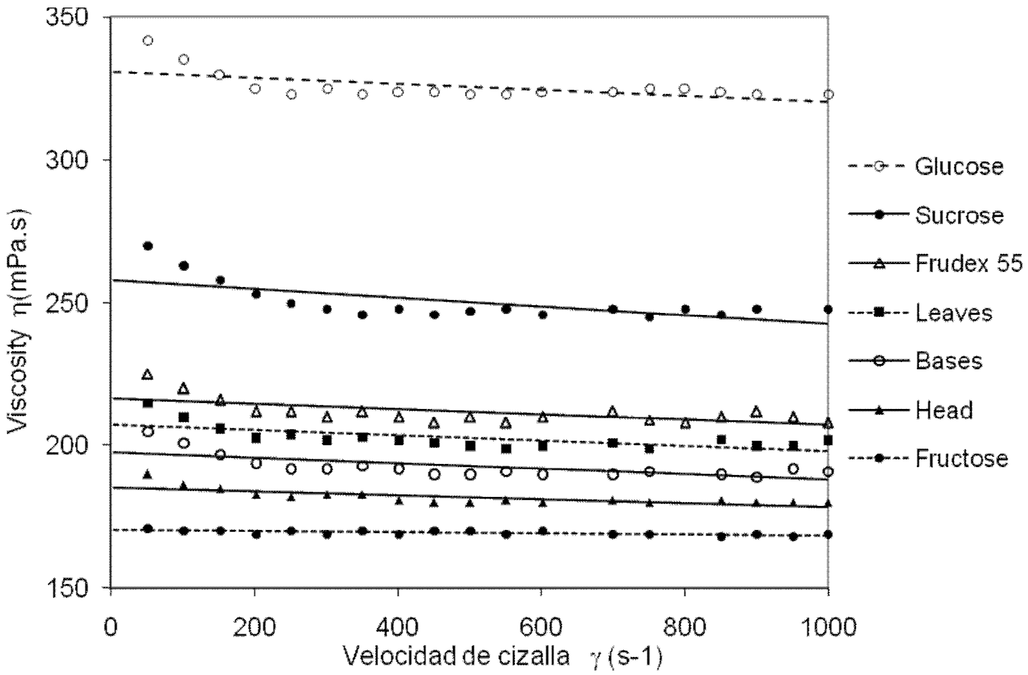

Figure 2.Viscosity vs. shear rate of the different syrups at 70ºBrix and 25ºC.

Because each fructan molecule contains only one glucose residue and the rest of fructose [22], the content of fructose in the syrups depends on the (ADP) of the fructans contained in the starting raw materials,fructans with higher ADP the content of fructose in the syrup will also be higher. The opposite occurs with the glucose content in the syrup, which decreases when increasing the ADP of the starting fructans. The fructose content in the different agave syrups obtained increases in the following order: leaves<bases<head, because in that order increases the content and the average degree of polymerization of inulin-type fructans present in each of the fractions agave plant[16].The fructose content in all agave syrups obtained is much higher than that containing commercial corn syrup "Frudex 55 ®", and it is similar to that containing the syrup obtained from fructans from Jerusalem artichoke (*Helianthus tuberosus*) [23, 24], the main botanical source proposal for the industrial production of HFS [5].

Rheological behavior of syrups

All syrups behave as Newtonian fluids, because the plot of shear strength (τ) vs. shear rate (γ), generates a straight line passing through the origin (Figure 1) and the viscosity coefficient (η) of the syrups is constant throughout the range of shear forces applied [15].

Another way to determine the flow behavior of a given fluid is to represent graphically the coefficient of viscosity (η) in function of the cutting speed or shear rate (γ), if this representation generate a straight line of slope equal to zero, this means that the coefficient of viscosity (η) of the fluid does not change and therefore, the liquid in question behaves like a Newtonian fluid type [7, 15].Over the whole range of applied shear rate, viscosity of the syrup is almost constant and zero slope, which means that the viscosity is independent of the applied shear rate (Figure 2), and confirms that the syrups presents a rheological behavior for Newtonian fluids. This graphical representation in addition to viewing the rheological behavior of syrups is also useful for determining the value of its viscosity (intercept).

Both the density and water activity are virtually identical in all syrups (Table 2), which is because both are intrinsic properties that are directly related to the moisture content and total solids in the syrup and since these are equals in all of them (humidity = 30%, total solids= 70°Brix), so are their density and water activity, which means that these properties are independent of the composition of syrups [25].The relatively low value of a_w and high concentration of sugars, it is very convenient for handling and storage of the syrup, because it prevents the growth of microorganisms therein, without resorting to cooling processes, cooling or addition of antimicrobial agents for its preservation, ensuring the physicochemical and organoleptic properties of the syrups [4].

Meanwhile, the surface tension of syrups depends on the composition thereof and in all cases it was less than the surface tension of pure water (72.75 dynes / cm) [25].Fructose causes a greater decrease in surface tension of the water, followed by sucrose and finally by glucose, which is due to intermolecular interactions between molecules of glucose are stronger than between molecules of sucrose and this in turn, molecules of fructose, and therefore also fructose is the most soluble of these sugars [26]. In other words, a higher concentration of fructose causes a greater lowering of the surface tension of pure water, which results in a lower surface tension of the syrup, as seen in the values of the surface tension of corn syrups (Frudex 55®), leaves, bases and the head of agave, in which the concentration of fructose in the same, increases in that order and in that order also decreases its surface tension of the syrups.

Syrups prepared with pure sugars such as fructose, glucose or sucrose, are colorless, meanwhile, the corn syrup Frudex 55® and the syrup obtained from the agave head appear yellow clear while the syrups obtained from the bases and agave leaves are orange. The syrup obtained from of the agave leafs develops a greater coloring due to higher content of chlorophyll in this portion of the plant, since this pigment is easily oxidized and imparts a brown color to the syrup during its elaboration.

In agave extracts have identified compounds derived from Maillard reactions as are some furans, pyrans, aldehydes and nitrogen and sulfur compounds such as 5-hydroxymethyl-furfural, methyl-2-furoate and 2.3-dihydroxy-3.5-dihydro-6-methyl-4-pyranone [27]. Likewise, Kim and Lee [28] report the formation of melanoidins as a result of Maillard reactions which occur during the heating of syrups. All these compounds give color to the syrup, which requires its refinement through columns of activated carbon to remove this coloration [4].

Fructose syrups have a lower viscosity than sucrose syrups and these in turn, the lower viscosity of glucose syrups (Table 2). For this reason, at the same concentration of total solids, viscosity of the syrup depends on the ratio of fructose and glucose in the same, a higher content of fructose reduces the viscosity of the syrup, while a higher content glucose increases viscosity of the syrup, as seen in the viscosity values of the syrups differents studied (Table 2), which decreases in the following order: Frudex 55®> syrup leaves> syrup base> pineapple syrup, since in this same order increases the content of fructose in the syrup.

These results agree with those previously reported by Doty and Vanniken[29], and more recently by Hernandez et al. [4], who found that at equal dry matter content and the same temperature, the viscosity of the syrup depends on the type of sugar, which was lower in fructose syrups, followed in ascending order by the invert sugar syrup, sucrose syrup, and finally by the glucose syrups, whose viscosity was much higher than all others.

The main factors affecting the viscosity of the solutions are: the nature of the continuous phase and the dispersed phase, particle-particle interactions and particle-solvent, concentration, shape, particle size, and temperature [15].The solubility of fructose in water is much higher than that exhibited by the sucrose and this in turn, greater than the solubility of glucose [26].The lower solubility of glucose is due to a greater degree of particle-particle interactions between its molecules, resulting in an increased viscosity of the solutionswhile the higher solubility of fructose is attributed to increased particle-solvent interaction, resulting in a lower viscosity of syrups.In other words, the higher viscosity of glucose syrups with respect to the fructose syrups, is attributed to an increased association of glucose molecules in the bulk solution, an association occurs through hydrogen bonding between them and providing an effect of highly branched polymer that increases the resistance of the syrup to flow freely and therefore, increases the viscosity of the system [15].

CONCLUSIONS

The density and the water activity of syrups are independent properties of its content of fructose and glucose, and therefore these parameters are equal in all syrups, since they all were prepared at equal content of moisture and solids total.

At the same total solids content and temperature, viscosity and surface tension of syrups depends on its content of fructose and glucose, both properties decrease with increasing content of fructose in the syrup or, both properties increase with increasing content glucose syrups.

Under working conditions established, regardless of their origin source and of its content of fructose and glucose, all studied syrups behave as Newtonian fluids, since the coefficient of viscosity (η) of the fluid is independent of the speed cutting or shear rate (γ).

ACKNOWLEDGEMENTS

The authors thank SIP-IPN, EDI-IPN and COFAA-IPN; by the financial support granted to carry out this research.

REFERENCES

1. Kovalenko, G.A., Perminova, L.V., Sapunova, L.I. (2010). Heterogeneous Biocatalysts for Production of Sweeteners-Starch Treacle and Syrups of Different Carbohydrate Composition. *Catalysis in Industry,* 2(2): 180-185.

2. Montañez, S.J.L., Venegas, G.J., Bernardino, N.A., Ramos, R.E.G. (2011b). Enzymatic production of high fructose syrup from *Agave tequilana*fructans and its physicochemical characterization. *Afr. J. Biotechnol.*,10(82): 19137-19143.
3. Palazzi, E., Converti,A. (2001) Evaluation of diffusional resistances in the process of glucose isomerization to fructose by immobilized glucose isomerase. *Enzyme Microb. Technol.,* 28: 246-252.
4. Hernández, U.J.P., Rodríguez, A.S.L., Bello, P.L.A. (2008). Obtention of fructose syrup from banana starch (*Musa paradisíaca* L). *Interciencia* 33(5): 372-376.
5. Jing, Y., Jiaxi, J., Wangming, J., Yuyang, L., Jianping, L. (2011). Glucose-free fructose production from Jerusalem artichoke using a recombinant inulinase-secreting *Saccharomyces cerevisiae* strain*. Biotechnol. Lett.*, 33: 147-152.
6. Corzo, O., Sanchez, M. (2008). Rheological study of the manufacturing of corn oil. *Basic Sci. Technol.,* 20(3): 329-333.
7. Rao, M.A.,Anatheswaran, R.C. (1982). Rheology of fluids in food processing. *Food Technol.*,36: 116-126.
8. Cancela, M.A., Álvarez, E., Maceiras, R. (2005). Effects of temperature and concentration on carboxymethylcellulose with sucrose rheology. *J. Food Eng*., 71: 419-424.
9. Dak, M., Verma,R.C., Jain, M.K. (2008). Mathematical Models for Prediction of Rheological Parameters of Pineapple Juice. *International J. Food Eng.,* 4(3): 20-30.
10. Tabilo, M.G., Barbosa, C.G.V. (2005). Rheology for the food industry. *J. Food Eng*.,67: 147-156.
11. Zuritz, C.A., Muñóz, P.E., Mathey, H.H., Pérez, E.H., Gascon, A., Rubio, L.A., Carullo, C.A., Chernikoff, R.E., Cabeza, M.S. (2005). Density, viscosity and coefficients of thermal expansion of clear grape juice at different solid concentrations and temperatures. *J. Food Eng.* 71(2): 143-149.
12. Ibanoglu, S., Ibanoglu, E. (1998). Rheological characterization of some traditional Turkish soups. *J. Food Eng*., 35: 251-256.
13. Velez, R.J.F., Barbosa, C.G.V. (1998). Rheological properties of concentrated milk as a function of concentration temperature and storage time. *J. Food Eng*., 35: 177-190.
14. Nindo, C.I., Tang, J., Powers. R.O., Singh, P. (2005). Viscosity of blueberry and raspberry juice for processing applications. *J. Food Eng.*, 69(3): 343-350.
15. Osorio, F.A. (2001). Rheological properties of food fluids. Methods for measuring physical properties in food industries. Publishing Acribia. Zaragoza, Spain, pp 10-60.
16. Montañez, S.J.L., Venegas, G.J., Vivar, V.M.A., Ramos, R.E.G. (2011a). Extraction, characterization and quantification of the fructans contained in head and leaves of *Agave tequilana* Weber azul. *Bioagro*, 23(3): 199-206.
17. AOAC (1997). Official Methods of Analysis. 16th Edition. Association of Official Analytical Chemists. AOAC International. Arlington, U. S. A., pp 95-105.
18. Miller, G.L. (1959). Use of dinitrosalicylic acid reagent for determination of reducing sugar. *Anal. Chem.*, 31: 426-428.
19. Montañez, S.J.L., Alegret, S., Salazar, M.J.A., Ramos, R.E.G. (2006). A new amperomeric biosensor for fructose determination based on epoxy-graphite-TTF-TCNQ-FDH-biocomposite*. Eur. Food Res. Technol.*, 223(3): 379-386.
20. Montañez, J.L., Ramos, E.G., Alegret, S., Delgado, R.J. (2011). Glucose Biosensor based on a Graphite-Epoxy-Platimum-Glucose Oxidase dispersed Biocomposite. *InformaciónTecnológica*, 22(1): 29-40.
21. Zhang, Y., Hidajat, K., Ray, A.K. (2004). Optimal design and operation of SMB bioreactor: production of high fructose syrup by isomerization of glucose. *Biochem. Eng. J.*, 21: 111-121.
22. López, G.M., Mancilla, M.N., Mendoza, D.G. (2003). Molecular structures of fructans from *Agave tequilana* Weber azul. *J. Agric. Food Chem*., 51: 7835-7840.
23. Manzoni, M., Cavazzoni, V. (1992). Hydrolysis of topinambur (Jerusalem artichoke) fructans by extracellular inulinase of *Kluyveromycesmarxianus* var. Bulgaricus. *J. Chem. Technol. Biotechnol.,* 54:311-315.
24. Wenling, W., Wuguang, W.,Shiyuan, W. (1999). Continuos preparation of fructose syrups from Jerusalem artichoke tuber using immobilized intracellular inulinase from Kluyveromyces sp.Y-85. *Process Biochem.,* 34:643-646.
25. Badui, D.S. (1997). Food Chemistry. 3rd Edition. 5th reprint. Mexico's Longman Publishers, S. A. of C. V. Mexicana Alhambra. Mexico, D.F., pp 65-94.
26. Charley, H. (1990). Food preparation: Sugars, sugar crystals and sweets.1st Edition, 3rd reprint. Orientation Editions S. A. of C. V. Mexico, D.F., 113-139.
27. Mancilla, M.N., López, G.M. (2002). Generation of maillard compounds from inulin during thermal processing of Agave tequilana Weber azul. *J. Agric. Food Chem.,*50: 806-812.
28. Kim, J.S., Lee, Y.S. (2009). Enolization and racemization reactions of glucose and fructose on heating with amino-acid enantiomers and the formation of melanoidins as a result of the Maillard reaction. *Amino Acids.,* 36: 465-474.
29. Doty, T.E., Vanniken, E. (1975). Cristaline fructose: use as food ingredient expected to increase. *Food Technol.*, 29(11): 34-38.

How to Cite This Article

José L. M., M. A. V. Machuca, J. V. González, A. B. Nicanor and L. González-Cruz.(2013). Influence of the Composition in the Rheological Behavior of High Fructose Syrups. Adv. Biores. 4 (2): 77-82.