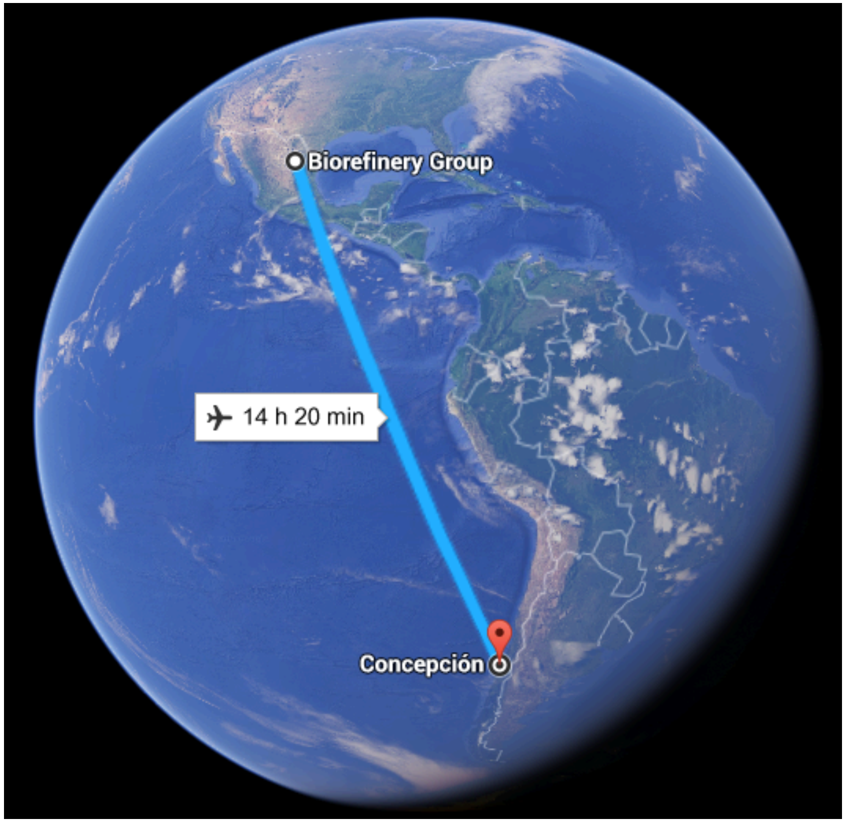
Comparison between microwave and conduction convection heating for autohydrolysis processing in the production of high added value compounds and substrates for biofuel under the biorefinery concept

Anely A. Lara-Flores, Jesus Velazquez-Lucio, Elisa Zanuso,
Rosa M. Rodríguez-Jasso, Cristóbal N. Aguilar, Héctor A. Ruiz

Biorefinery Group
Food Research Department, School of Chemistry
Autonomous University of Coahuila
Saltillo, Coahuila, Mexico

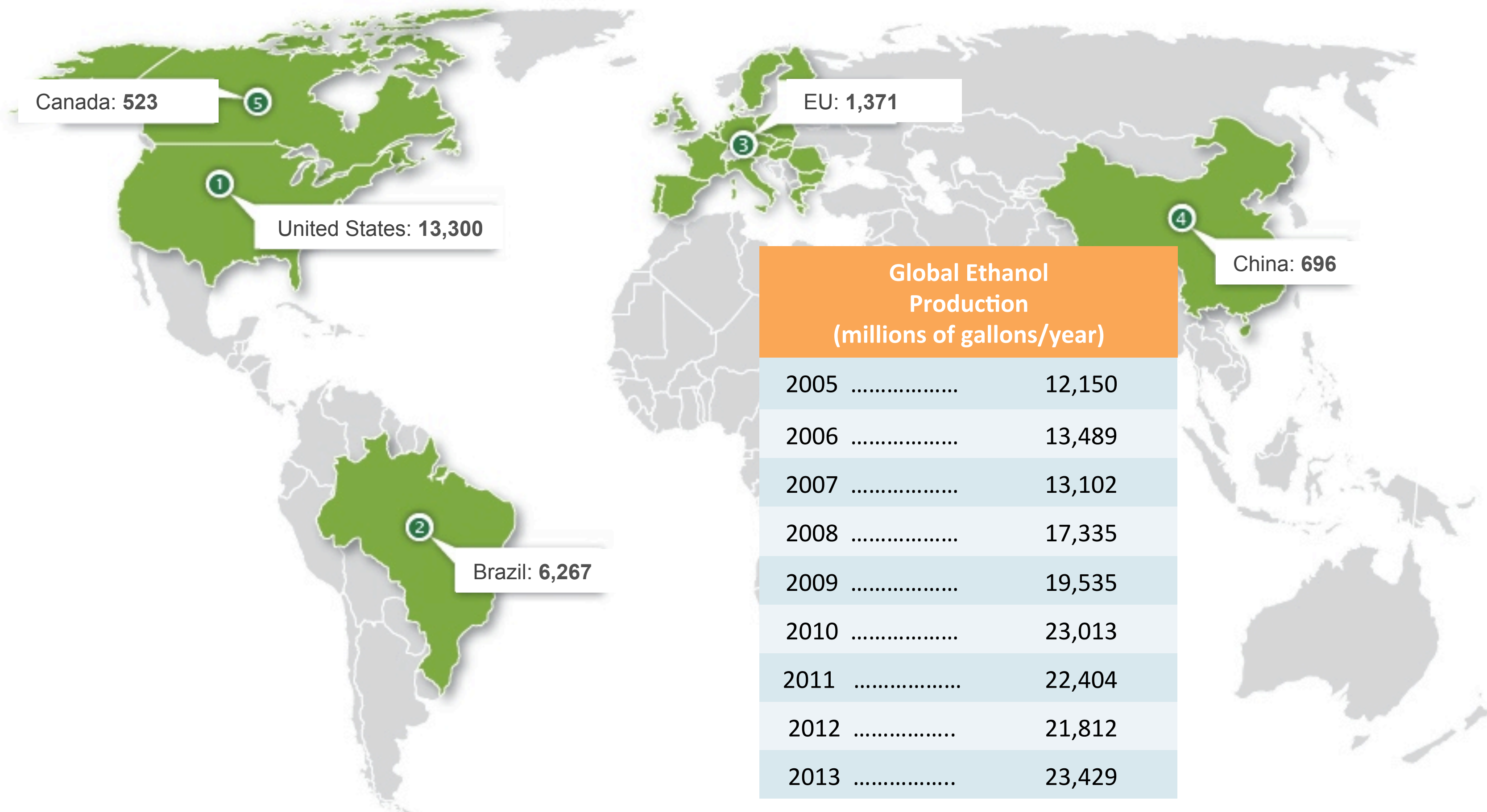
BIOREFINERYGROUP



Ethanol as Fuel ?

Global Ethanol Production

Top Five Countries (2013) **Ethanol Production** (millions of gallons/year)   1 Gal = 3.78 L

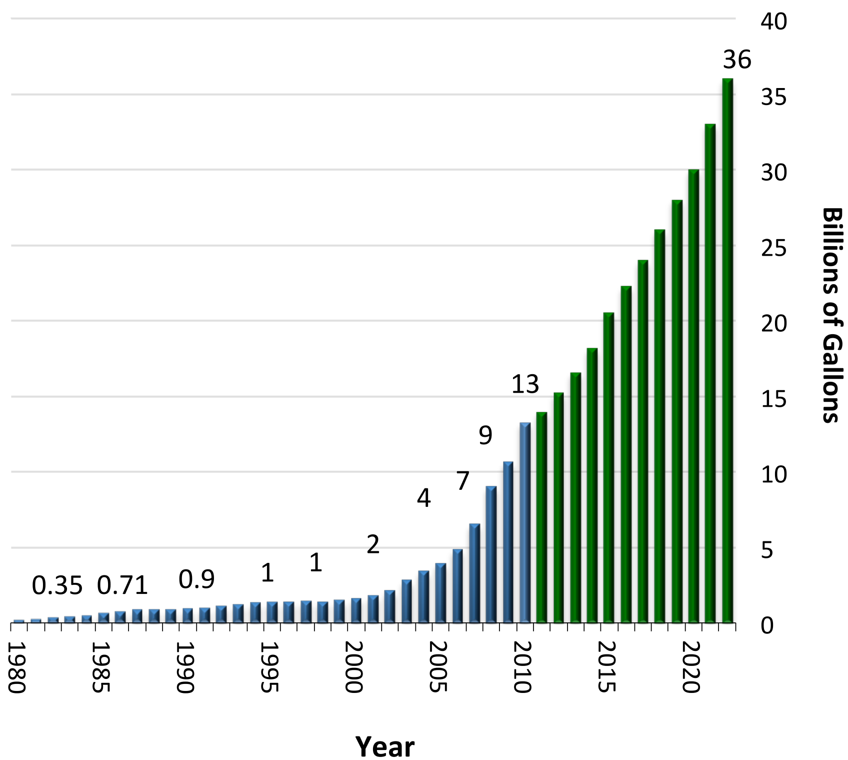


Global Ethanol Production (millions of gallons/year)	
2005	12,150
2006	13,489
2007	13,102
2008	17,335
2009	19,535
2010	23,013
2011	22,404
2012	21,812
2013	23,429

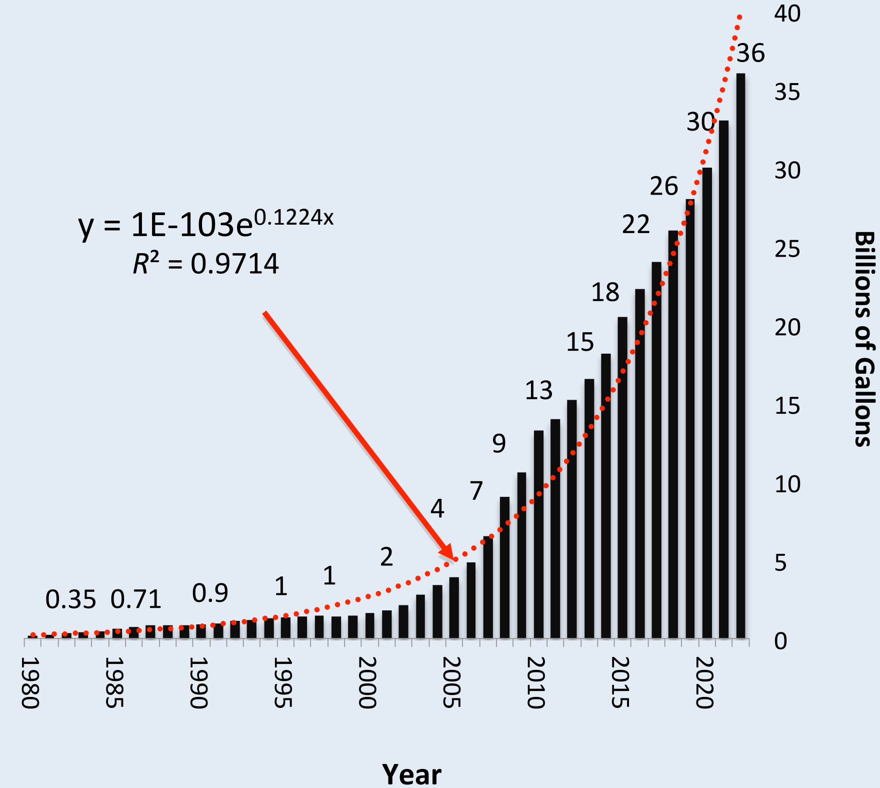
Source: RFA, F.O. Licht's 2013 Estimates

BIOREFINERYGROUP

Market in USA



Non-linear Regression Analysis



Héctor A. Ruiz et al. (2012). *Fuel*, 95 528-536

Source: U.S. Department of Energy/Energy Information Administration and RFA

Fossil Resources

Crude oil

Natural gas

Classical Petroleum-refinery

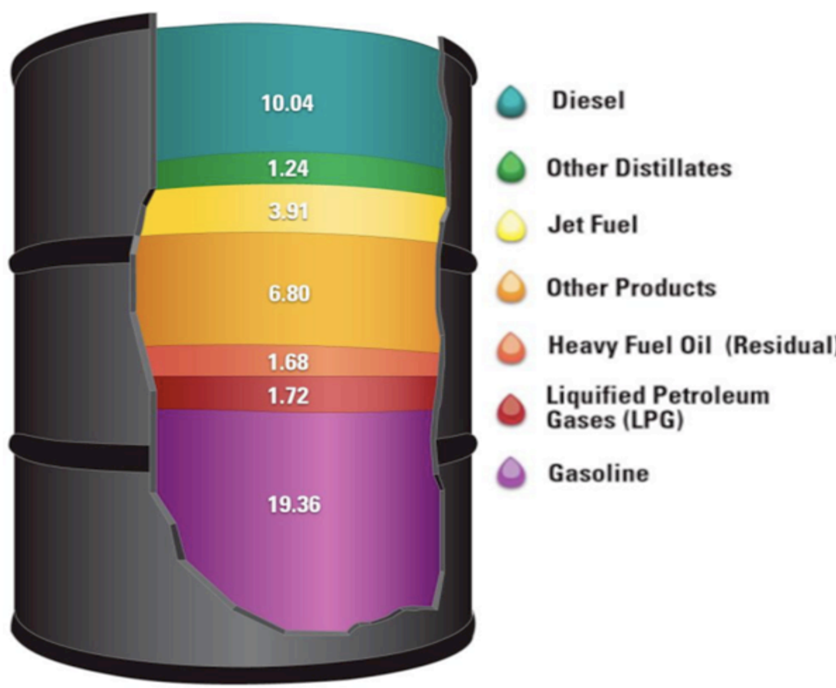
Products

Energy (fuel, etc)

Chemicals

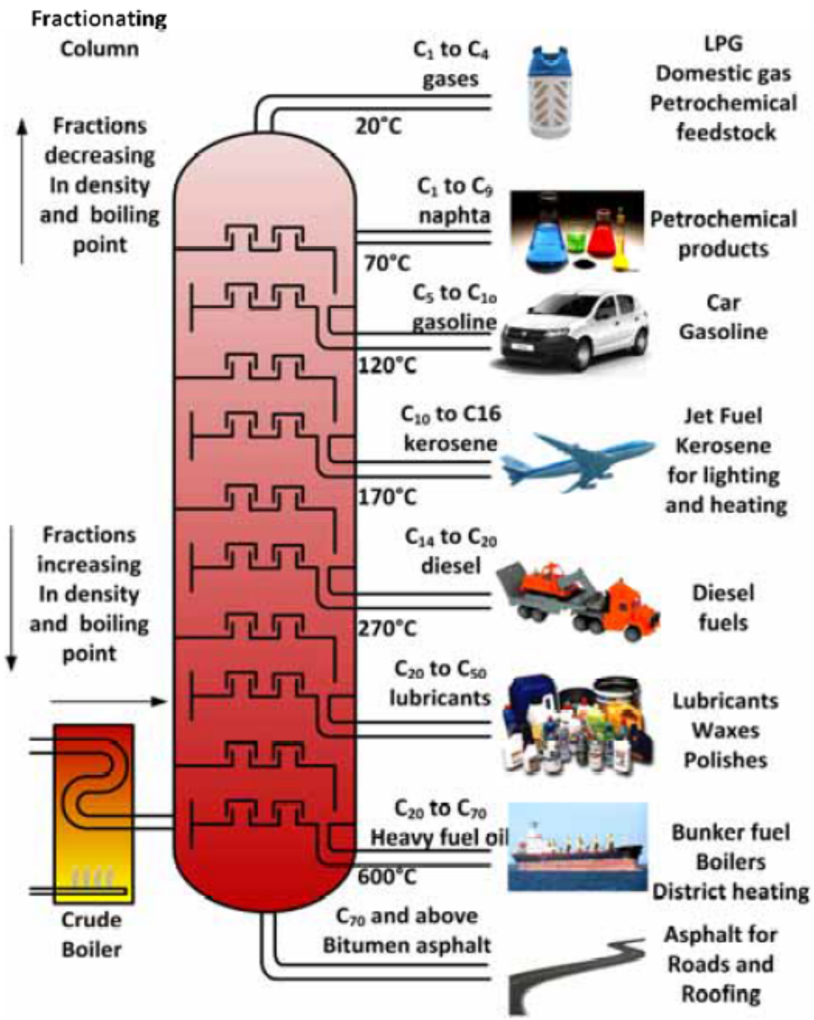
Materials (plastic, etc)

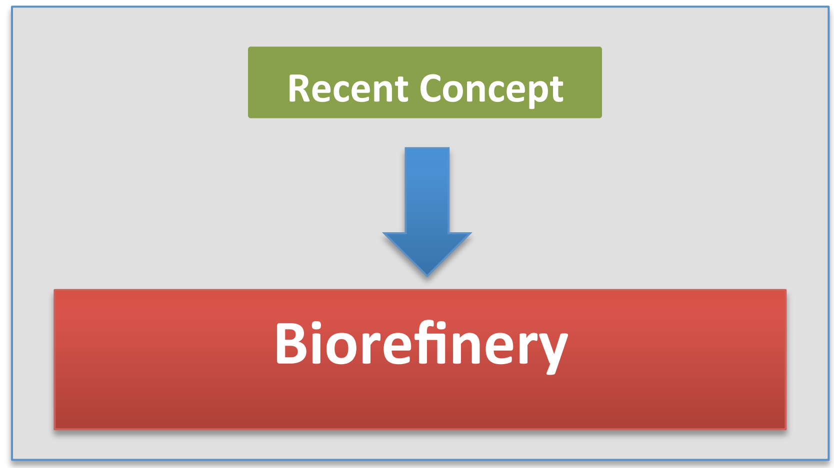
Products Made from a Barrel of Crude Oil (Gallons)



BIOREFINERYGROUP

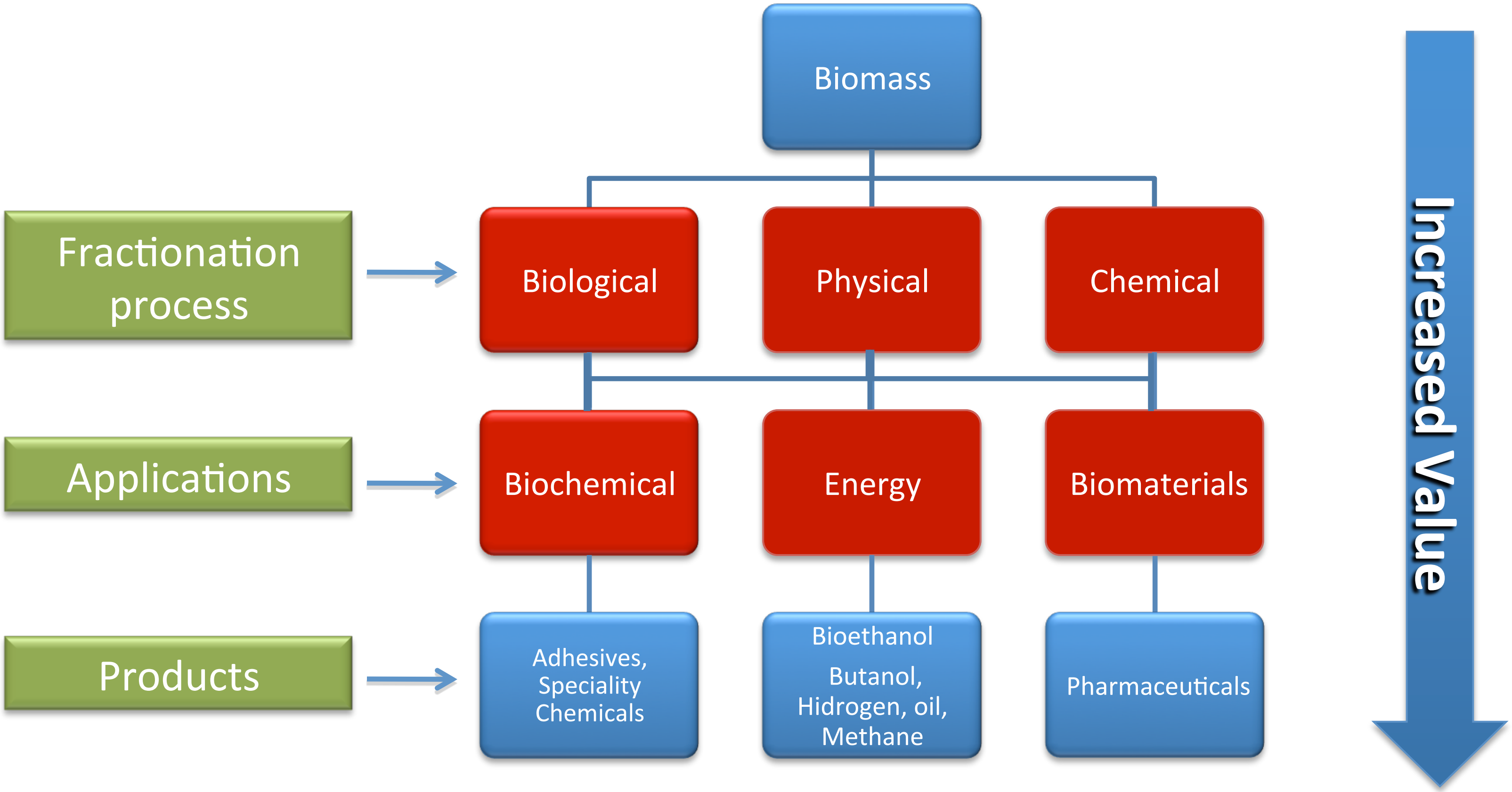
Fractional Distillation





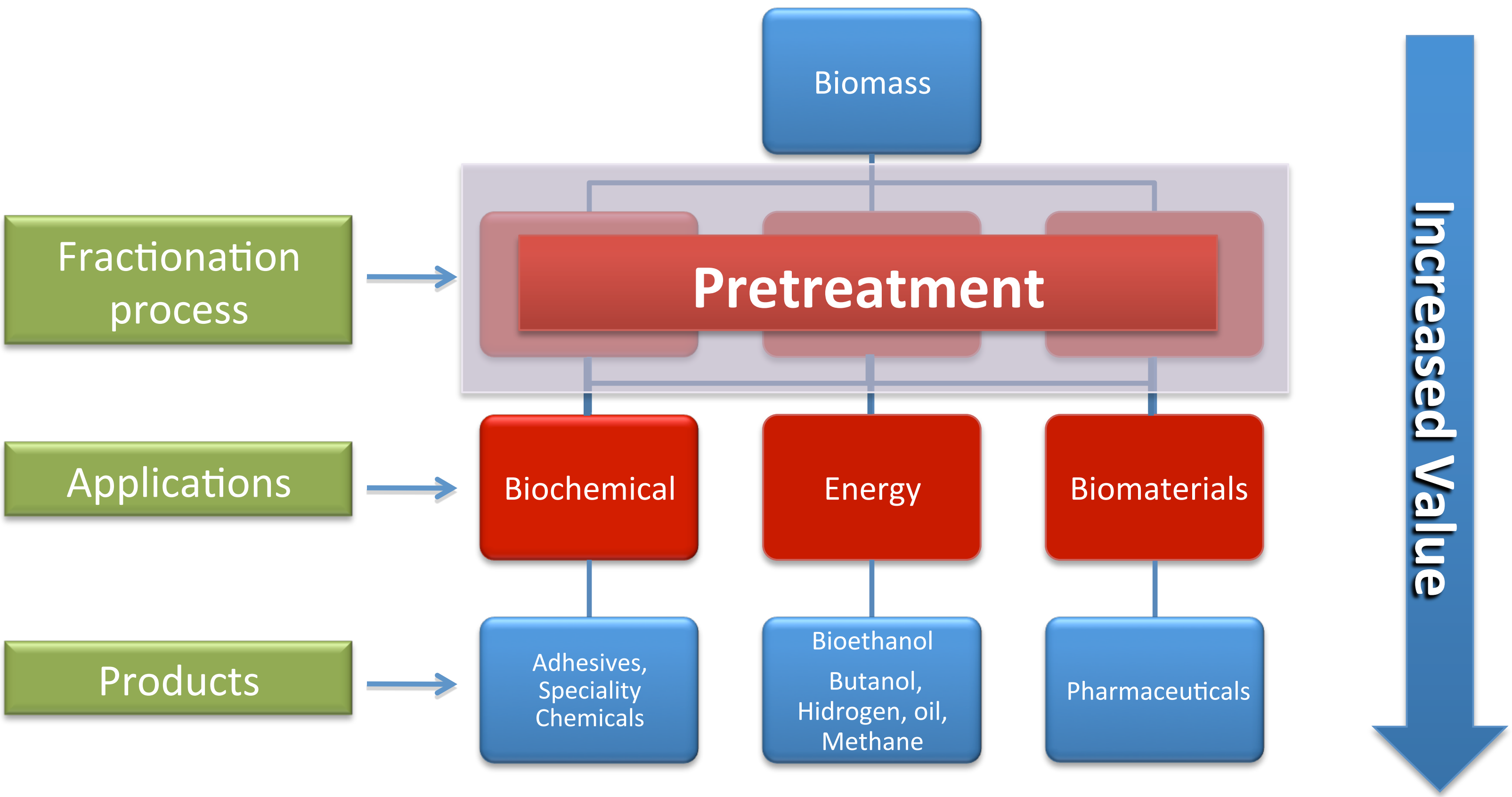
Source: Oil and Gas Production Handbook

Integrating of second and third generation biorefineries



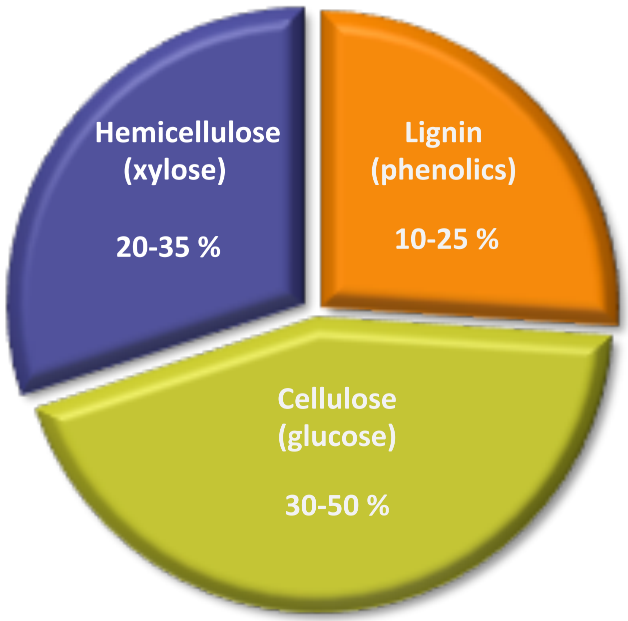
BIOREFINERYGROUP

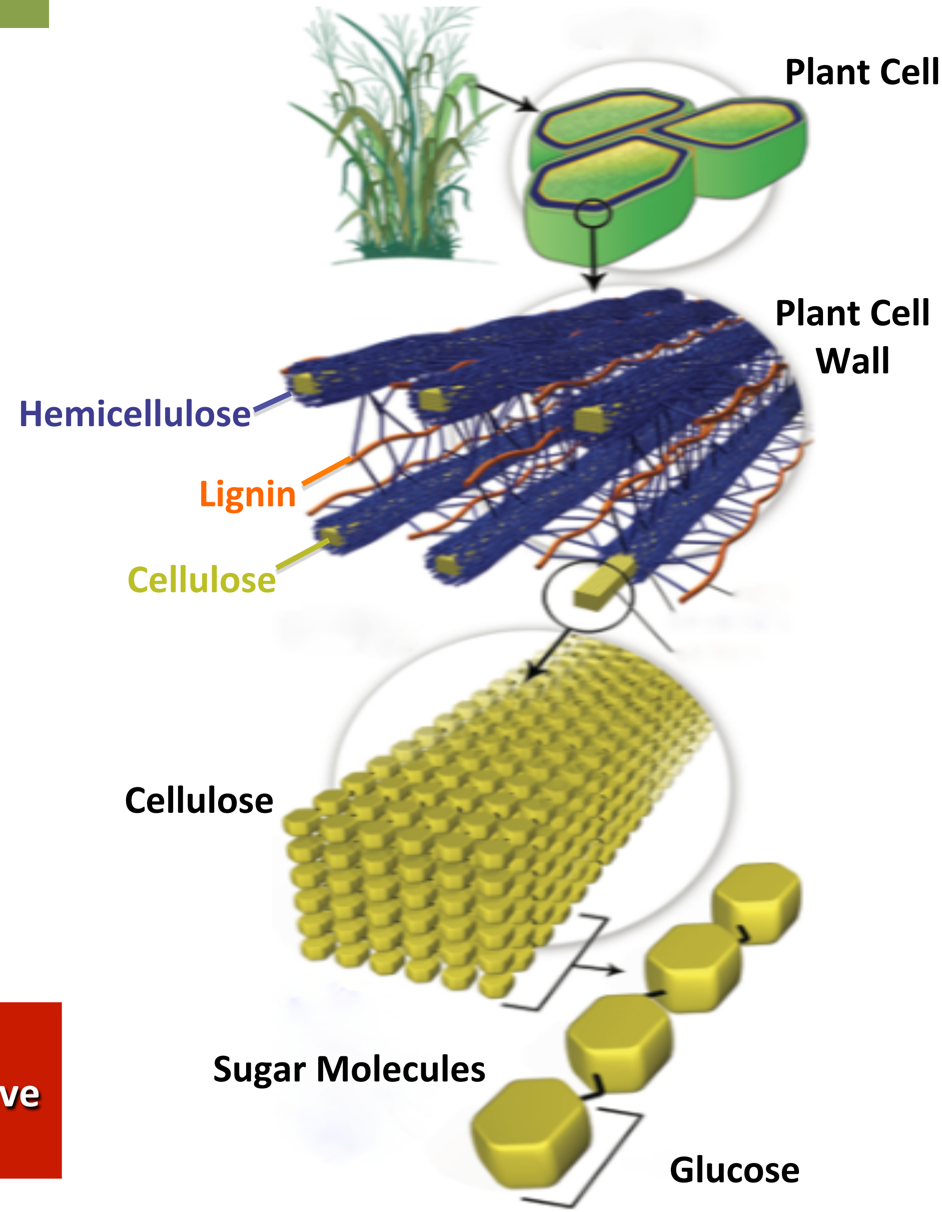
Integrating of second and third generation biorefineries



Second Generation of Bioethanol

Lignocellulosic Materials (LCM)
(Agricultural Residues)

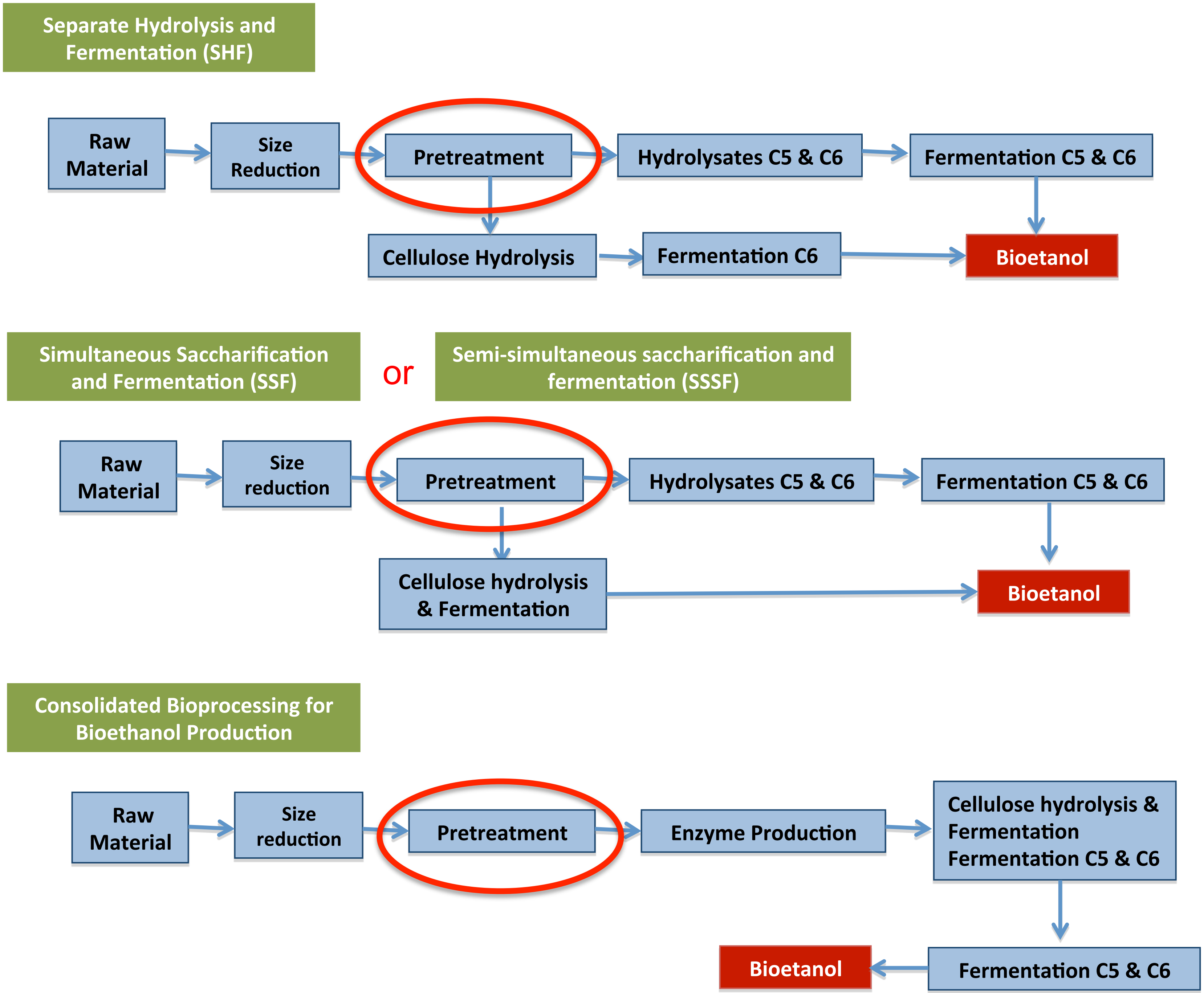




Substrates
(wheat straw, corncobs, sugarcane bagasse, Agave bagasse, etc.)

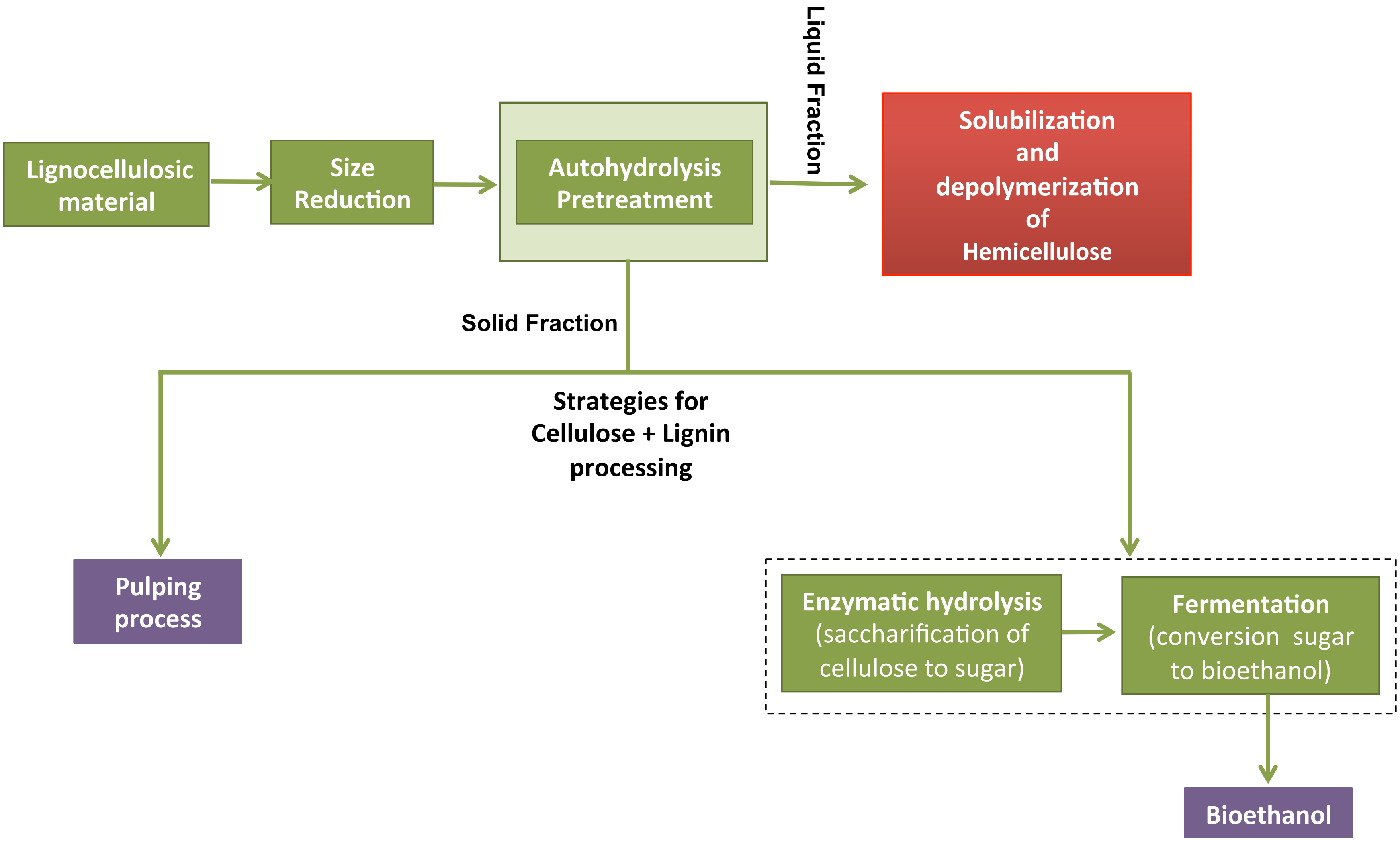
Source: U.S Department of Energy, 2011

BIOREFINERYGROUP


Separate Hydrolysis and Fermentation (SHF)
Raw Material
Size Reduction
Pretreatment
Hydrolysates C5 & C6
Fermentation C5 & C6
Cellulose Hydrolysis
Fermentation C6
Bioetanol
Simultaneous Saccharification and Fermentation (SSF)
or
Semi-simultaneous saccharification and fermentation (SSSF)
Raw Material
Size reduction
Pretreatment
Hydrolysates C5 & C6
Fermentation C5 & C6
Cellulose hydrolysis & Fermentation
Bioetanol
Consolidated Bioprocessing for Bioethanol Production
Raw Material
Size reduction
Pretreatment
Enzyme Production
Cellulose hydrolysis & Fermentation Fermentation C5 & C6
Fermentation C5 & C6
Bioetanol

Fractionation of lignocellulosic material using hydrothermal processing

Our Work According to Integrated Biorefineries



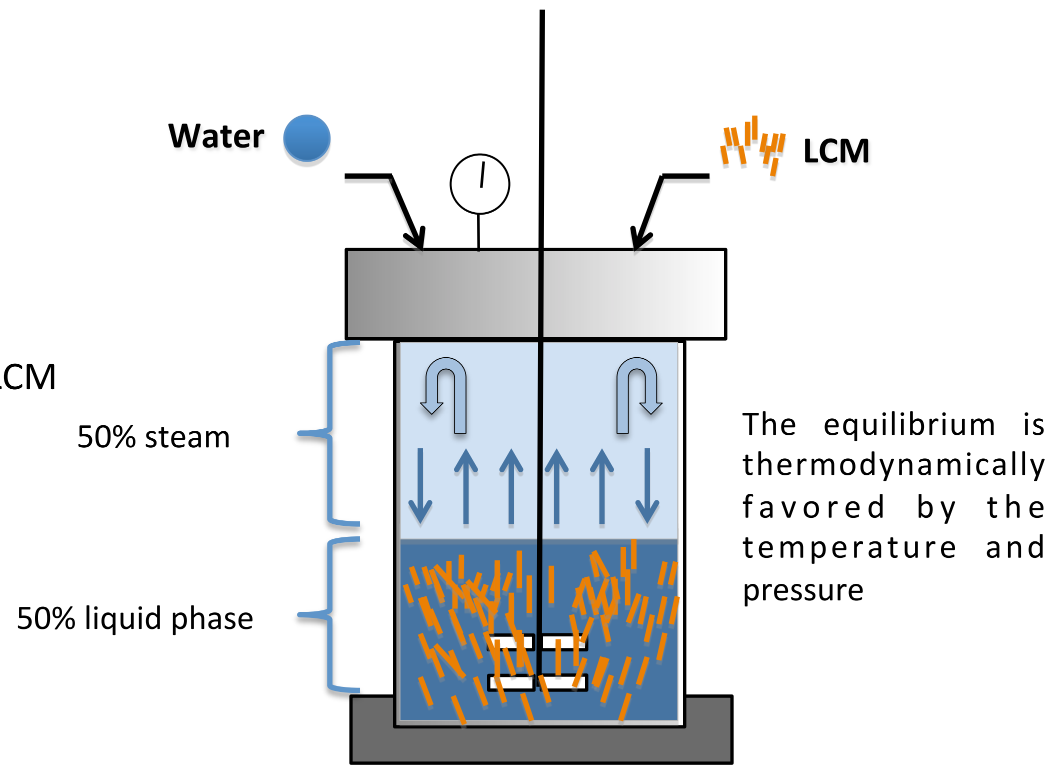
BIOREFINERYGROUP

Fundamentals of Autohydrolysis Pretreatment

In this technology, water at high temperatures and pressures is applied on lignocellulosic materials for hydrolysis, extraction and structural modification: autohydrolysis, hydrothermal treatment, hot compressed water (HCW), hydrothermolysis, liquid-hot water (LHW), aqua solve process, aqueous processing and pressure-cooking in water.

Advantages

- Environmentally friendly process
- Hemicellulose is solubilized and depolymerized
- Low by-product generation (inhibitors as furans)
- No chemicals other than water are necessary
- Caused relocalization of lignin on the surface of LCM

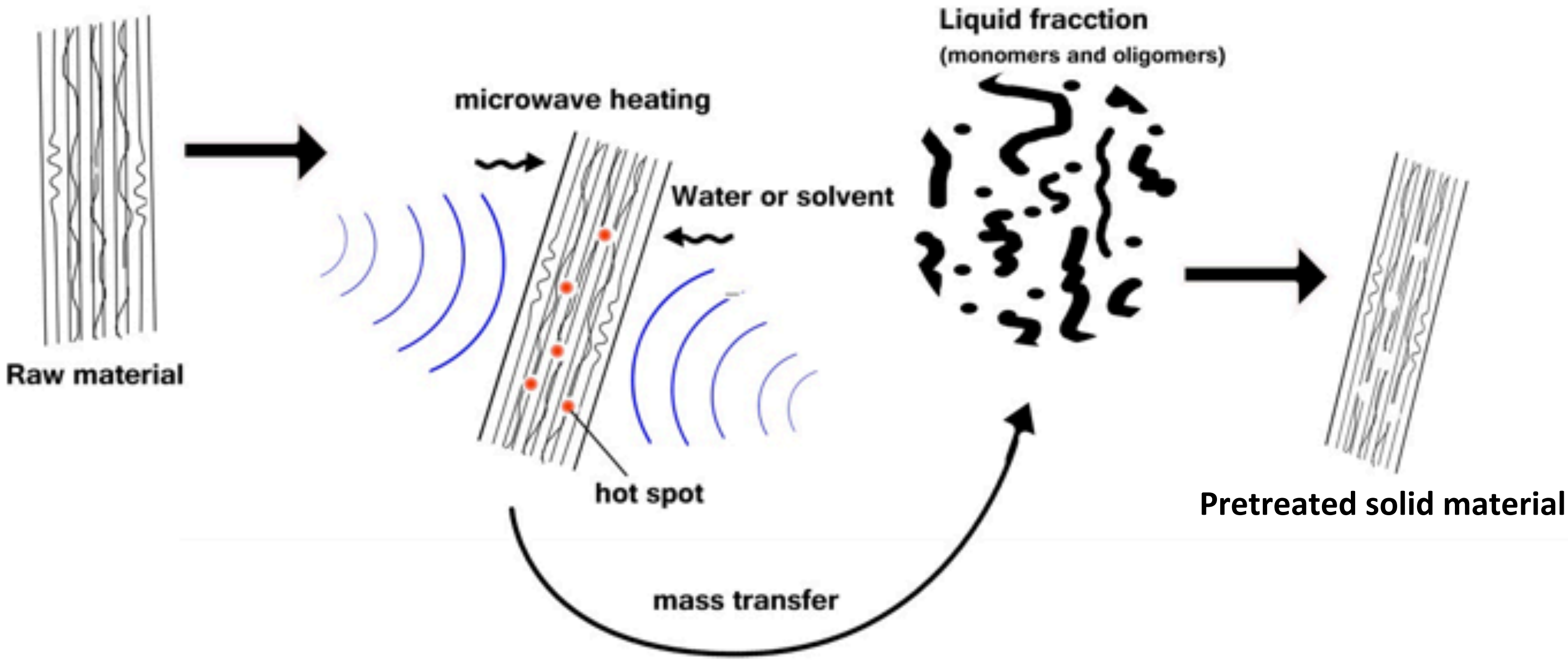


Héctor A. Ruiz et al. (2013). *Renew. Sus. Energ. Rev.*, 21, 35-51

BIOREFINERYGROUP

Microwave Pretreatment

Microwave radiation causes breakdown of the LCM via the collision molecular due to dielectric polarization, by increasing of the temperature selectively and non-homogenously in the more polar parts. Then some hot spots are created within the materials which generate their explosion due to the heat increase. The blast effect created between the particles by the method of heating improves relocation of crystalline structures of LCMs.



Alejandra Aguilar *et al. Manuscript in preparation*

Heating (conduction, convection or radiation) in Autohydrolysis Pretreatment

The heating (conduction, convection or radiation) in the reactors can be performed by steam, fluidized sand baths, oil baths, electric heating jackets and microwave radiation to achieve fairly uniform heating as well as fast heat-up

Renewable and Sustainable Energy Reviews 21 (2013) 35–51

ELSEVIER

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

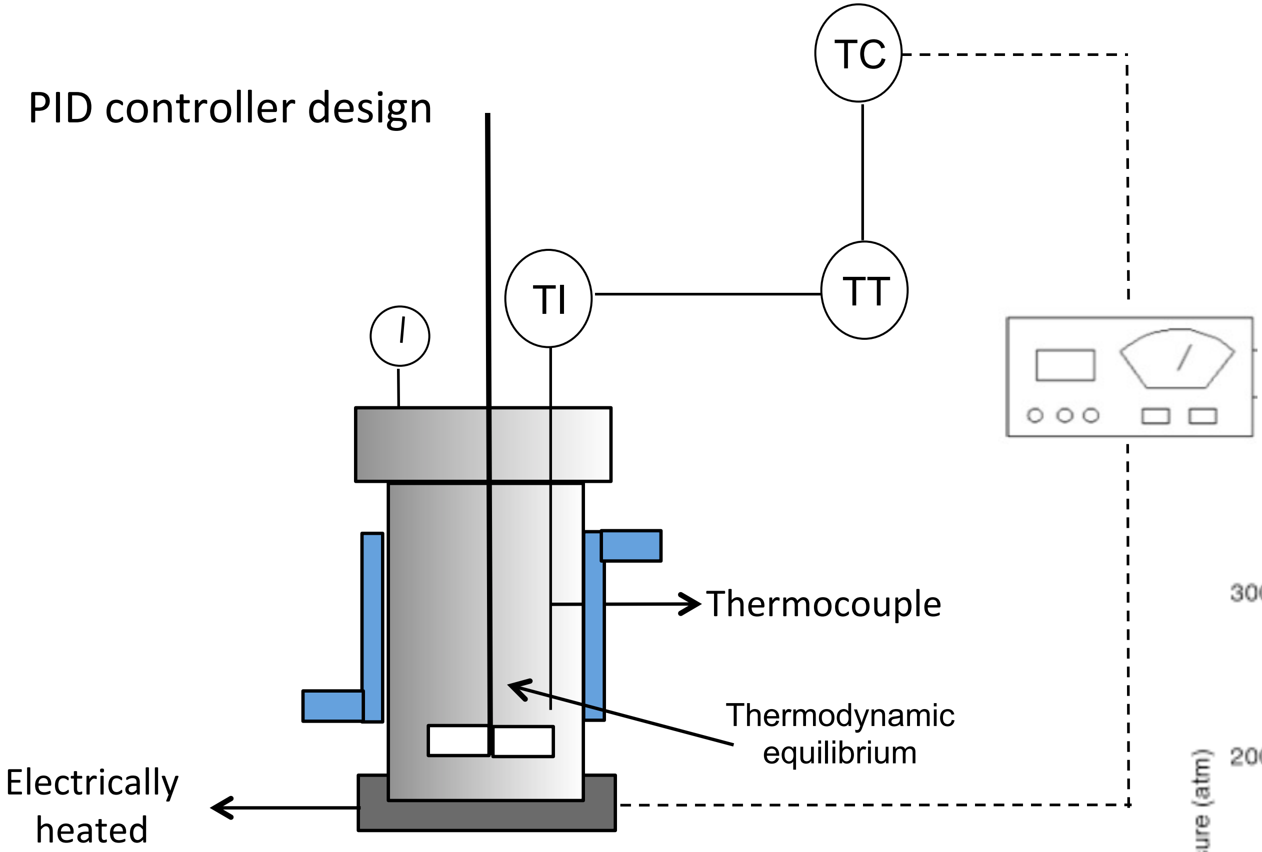
journal homepage: www.elsevier.com/locate/rser

Hydrothermal processing, as an alternative for upgrading agriculture residues and marine biomass according to the biorefinery concept: A review

Héctor A. Ruiz*, Rosa M. Rodríguez-Jasso, Bruno D. Fernandes, António A. Vicente, José A. Teixeira

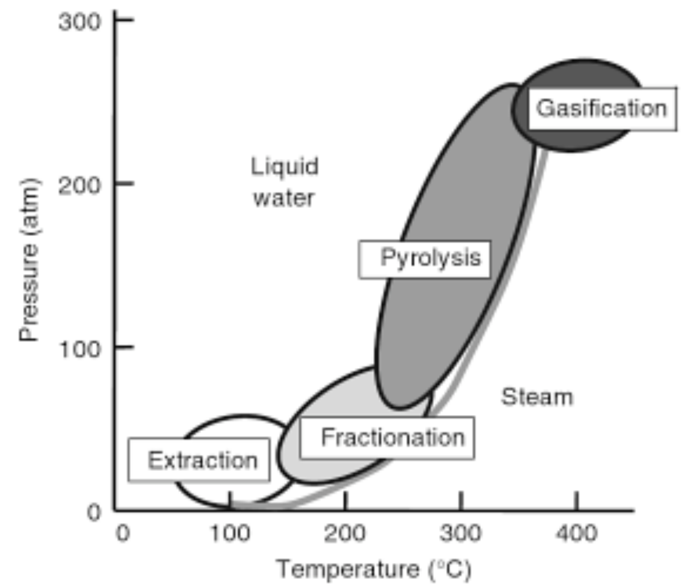
Fundamentals of Autohydrolysis Pretreatment

PID controller design



Other heating sources

- Steam
- Microwave Radiation



- Autoionization of water into hydronium ions H_3O^+ as catalyst
- Acetic acid from acetyl groups of hemicellulose

Robert C. Brown (2011). *Thermochemical processing of biomass: conversion into fuels chemicals and power*

Heating and Cooling Temperature Profiles in Autohydrolysis Process

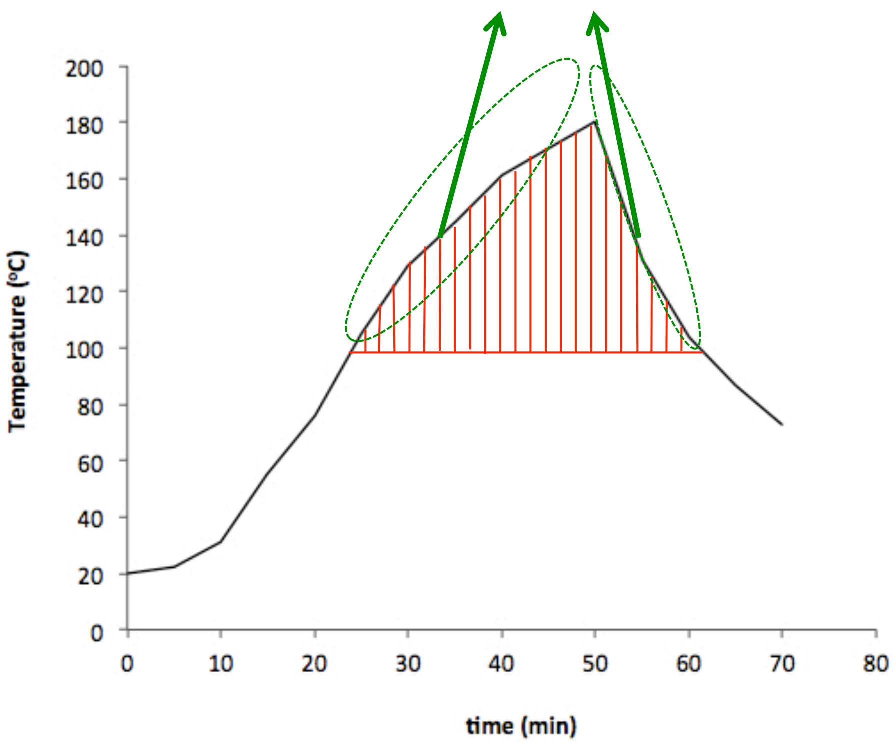
$$logR_0 = log[R_{0\,Heating} + R_{0\,Cooling}]$$

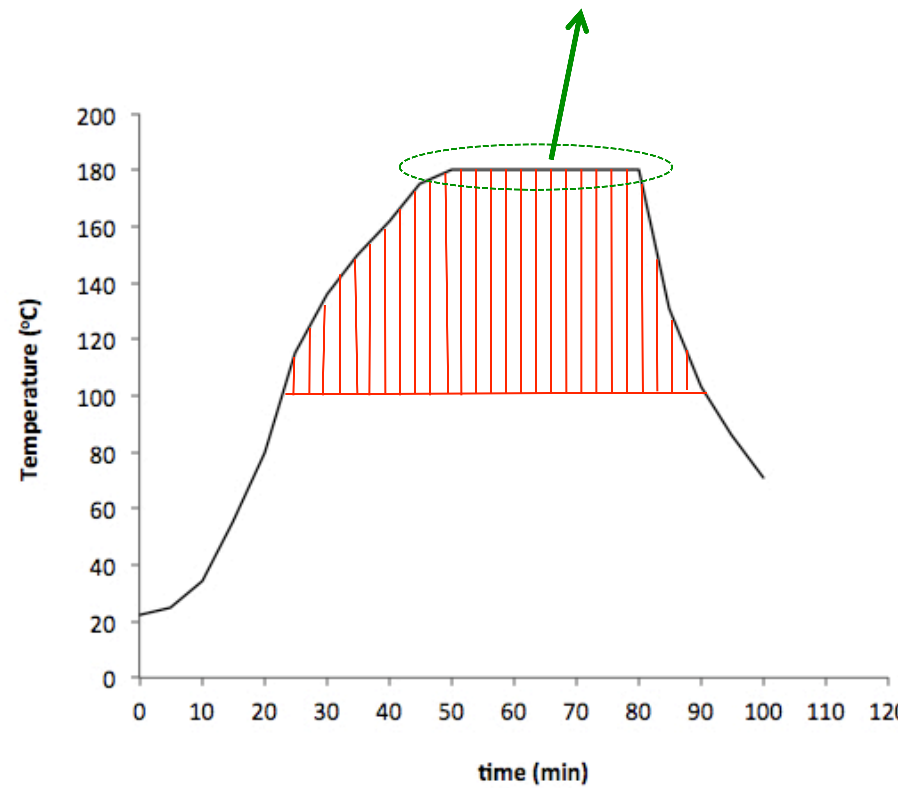
$$logR_0 = \left[\int_0^{t_{MAX}} \frac{T(t)-100}{\omega}dt + \int_{t_{MAX}}^{t_F} \frac{T'(t)-100}{\omega}dt\right]$$

non-isothermal heating regimen section

$$Log\,(R_0) = \int_0^t exp\left[\frac{T-100}{14.75}\right]dt$$

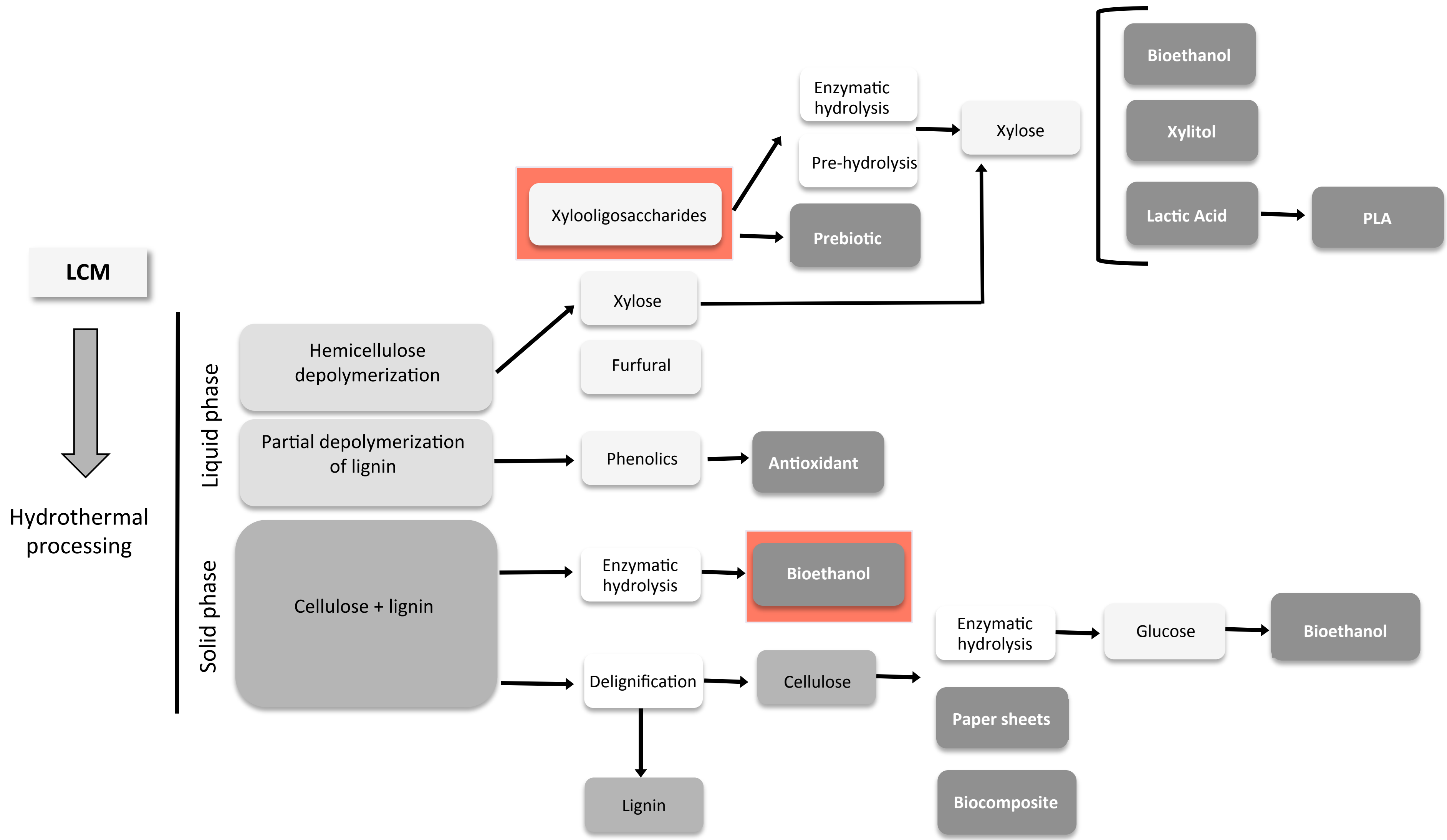
isothermal heating regimen section





Héctor A. Ruiz et al. (2015). *Algal Biorefineries Vol. 2: Products and Refinery Design*, 467-491

Integrated Biorefineries Platform Using Hydrothermal Process

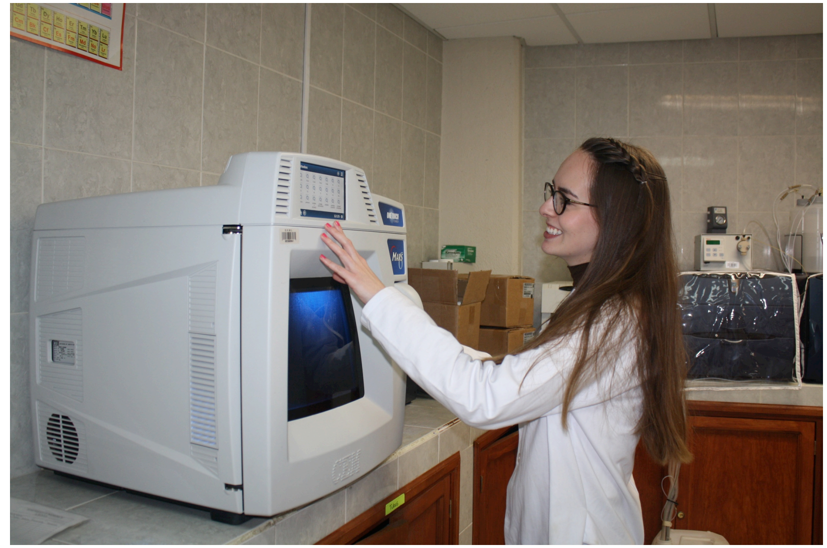


Héctor A. Ruiz et al. (2013). *Renew. Sus. Energ. Rev.*, 21, 35-51

BIOREFINERYGROUP

Our Work According to Integrated Biorefineries using using Corn residues

conduction- convection



microwave radiation

Corn residues
(cobs and stover)

BIOREFINERYGROUP

Autohydrolysis Pretreatment: Conduction- Convection and microwave radiation on corn residues

1,200 W

Conduction-Convection

microwave radiation

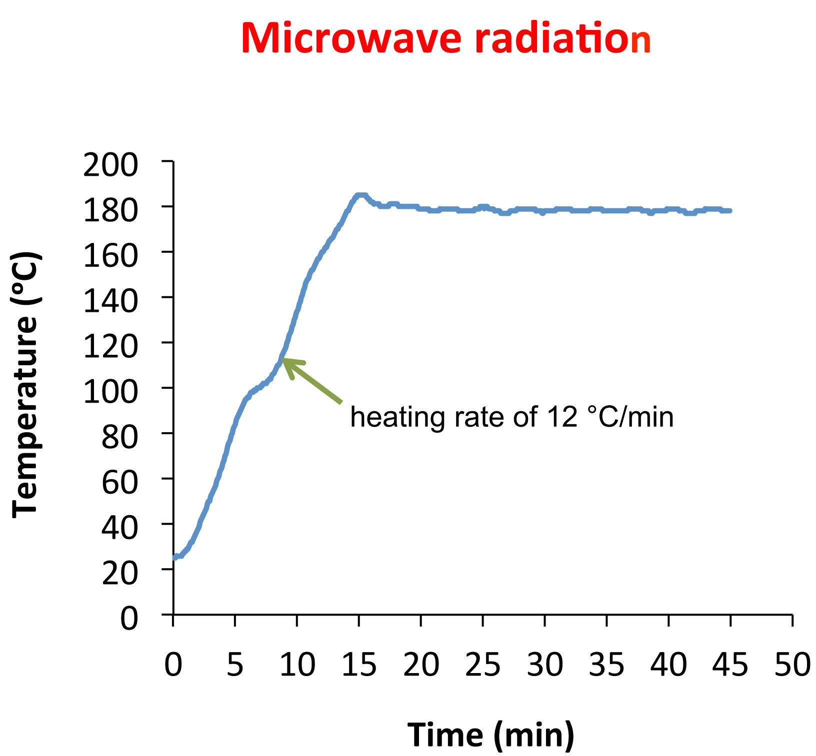
Experimental design

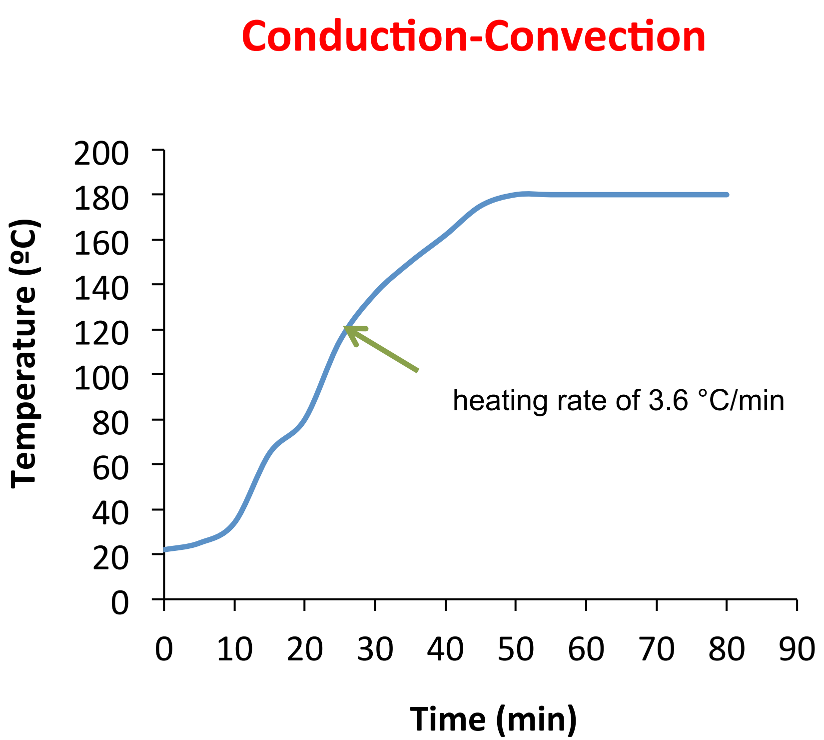
Assay	time (min)	Temperature (ºC)
1	20	160
2	20	200
3	60	160
4	60	200
5	40	180
6	40	180
7	20	180
8	60	180
9	40	160
10	40	200

Oligomers from hemicellulose (g/ 100 g r.m) in dry basis

BIOREFINERYGROUP

Heating profiles



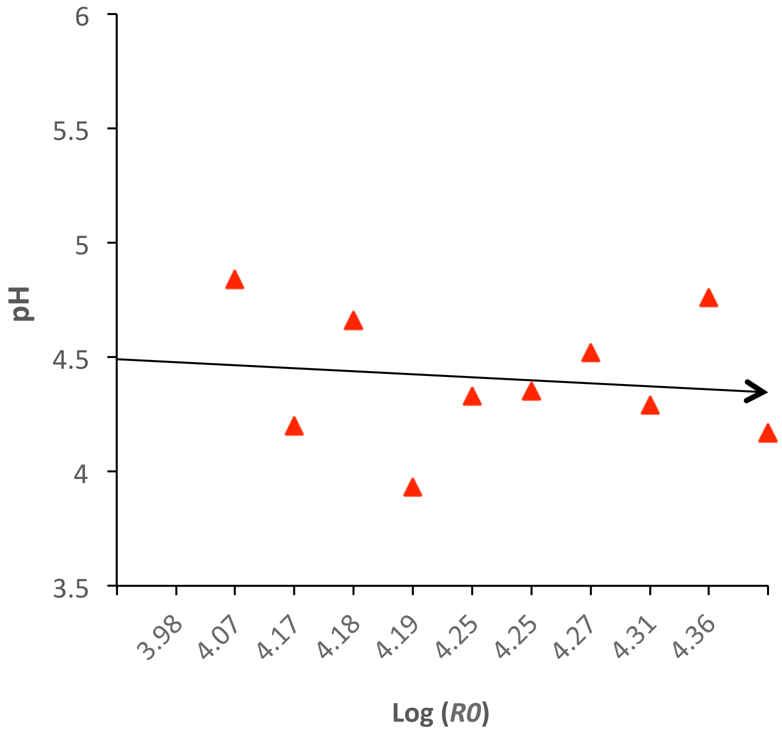


BIOREFINERYGROUP

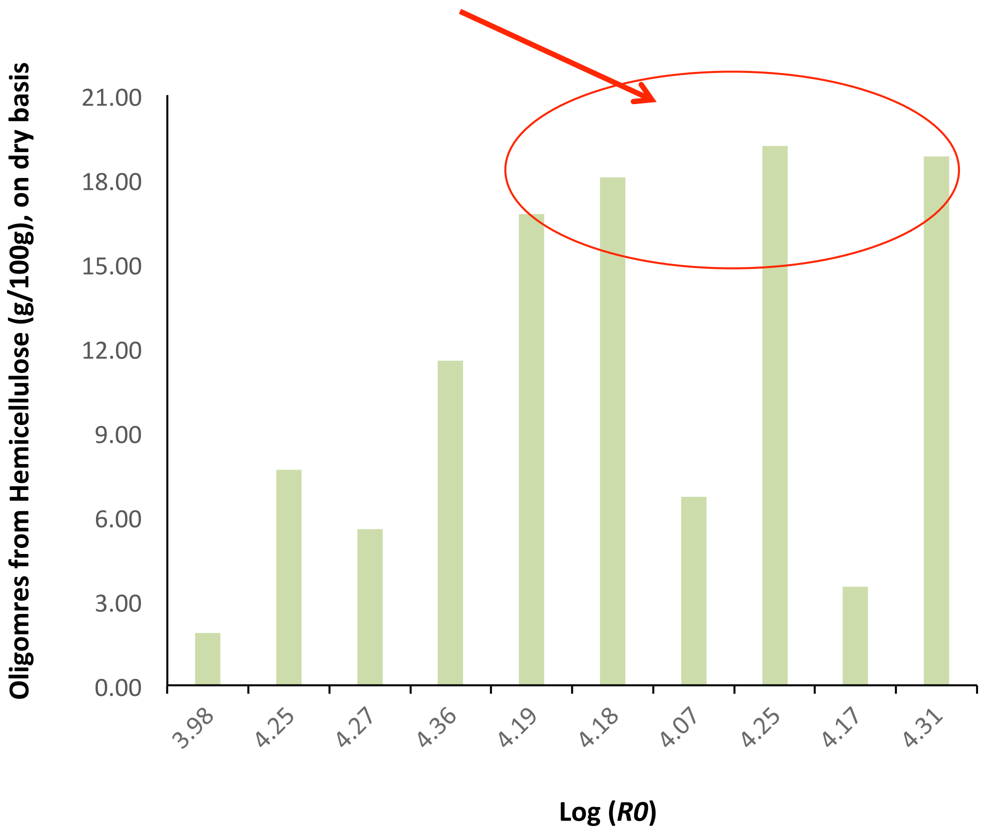
Chemical Characterization (g/100 g), on dry basis

R_0 (Factor de severidad)	CELULOSA		HEMICELULOSA		LIGNINA KLASON	
	MH	CH	MH	CH	MH	CH
3.98 (150/10)	36.43±1.34	38.72±0.32	20.55±0.88	23.49±0.67	19.09±0.67	15.69±0.12
4.31 (150/30)	42.16±0.50	42.84±0.57	17.06±0.68	20.17±0.65	20.26±0.65	16.89±0.42
4.17 (150/50)	47.17±1.01	45.16±1.13	9.93±0.21	18.07±0.23	23.02±0.23	18.01±0.75
4.19 (165/10)	45.09±0.03	43.38±1.58	11.97±0.31	18.49±0.75	21.75±0.75	19.04±0.64
4.25 (165/30)	56.77±0.35	59.70±0.79	6.02±0.40	8.89±0.16	23.82±0.16	24.65±0.41
4.27 (165/50)	61.49±1.21	61.75±1.27	2.78±0.10	3.52±0.12	24.71±0.12	27.42±0.68
4.07 (180/10)	59.48±0.15	61.45±0.25	2.63±0.39	4.11±0.13	26.91±0.13	25.45±0.40
4.18 (180/30)	64.67±0.24	62.60±0.02	0.84±0.15	1.81±0.09	30.40±0.09	31.81±0.13
4.36(180/50)	61.74±1.23	63.04±0.94	0.27±0.02	0.00±0.0	33.23±0.00	34.95±0.03

Results of Autohydrolysis: Conduction- Convection



Optimum point



BIOREFINERYGROUP

Optimization of Autohydrolysis for oligomers from Hemicellulose

This optimum point was determined using the Hessian matrix method

Oligomers=-1038+12.3t-0.04t^2+1.2T-0.012t^2-0.0028tT

$$\frac{\partial z}{\partial x} = 12.31225264 - 0.0027284y - 0.07284911x$$

$$\frac{\partial z}{\partial y} = 1.24011046 - 0.02301808y - 0.0027284x$$

$$\frac{\partial^2 z}{\partial x^2} = -0.07284911 \qquad \frac{\partial^2 z}{\partial y^2} = -0.02301808$$

$$\frac{\partial^2 z}{\partial x \partial y} = -0.0027284 \qquad \frac{\partial^2 z}{\partial y \partial x} = -0.0027284$$

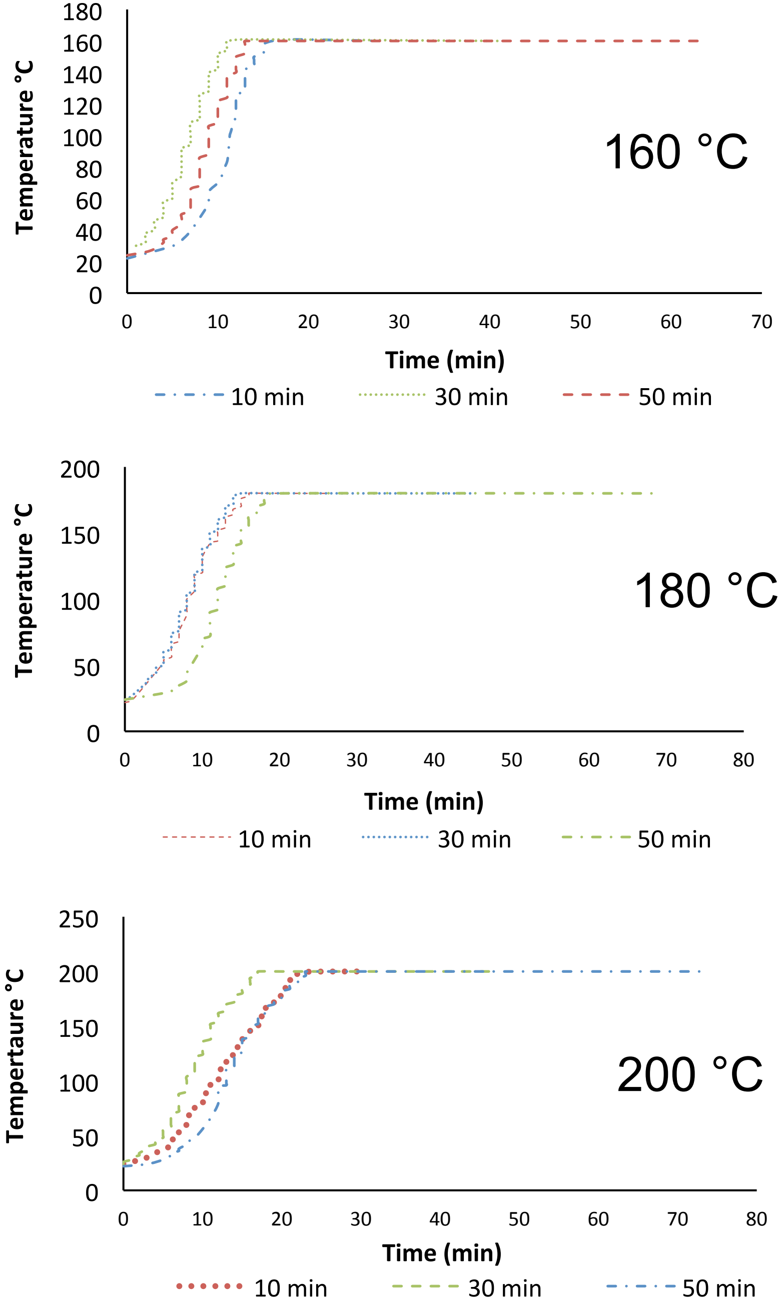
$$H(x,y) = \begin{bmatrix} \frac{\partial^2 z}{\partial x^2} & \frac{\partial^2 z}{\partial x \partial y} \\ \frac{\partial^2 z}{\partial y \partial x} & \frac{\partial^2 z}{\partial y^2} \end{bmatrix} = \begin{bmatrix} -0.07284911 & -0.0027284 \\ -0.0027284 & -0.02301808 \end{bmatrix}$$

$$H(x,y) = (-0.07284911)(-0.02301808) - (-0.0027284)(-0.0027284) = 0.0016694$$

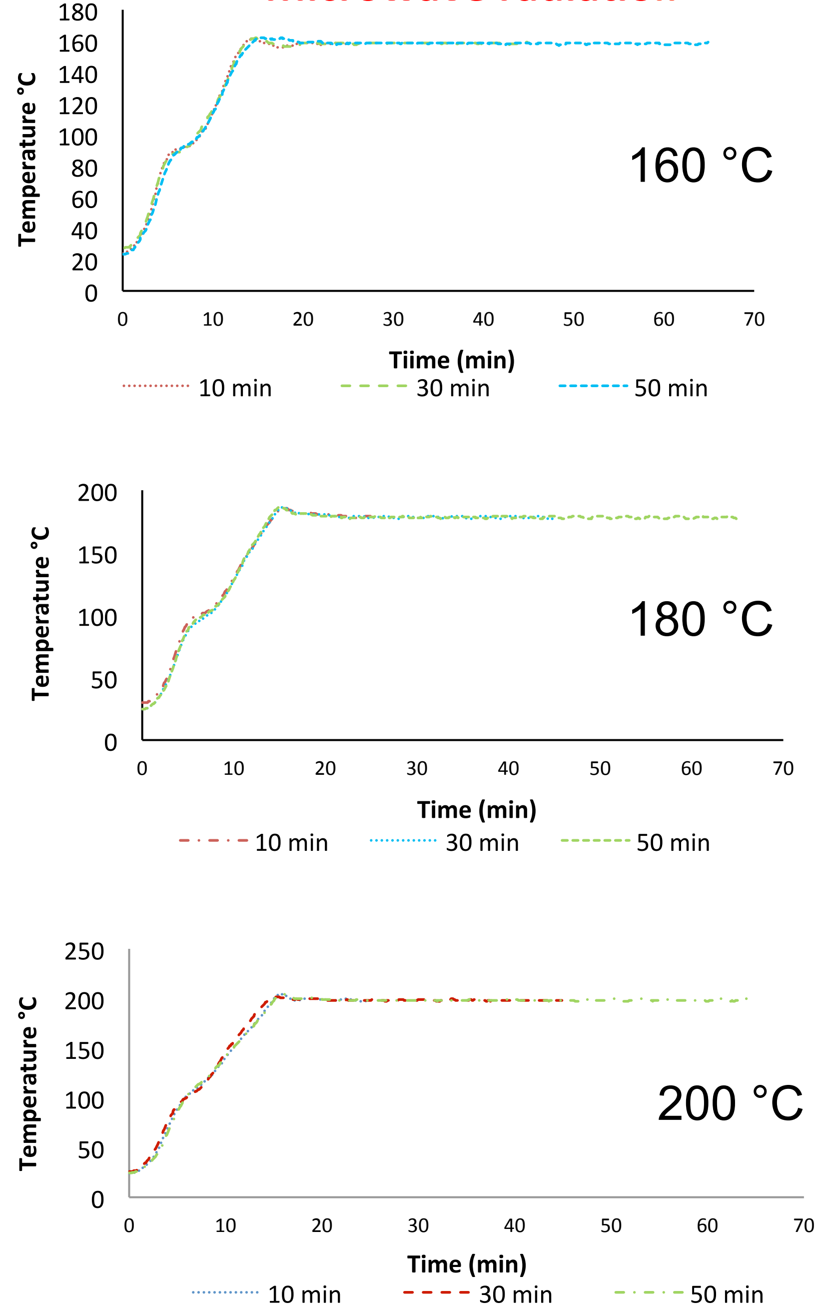
(1) Optimum point for Conduction- Convection = 18.98 g /100 g

(2) Optimum point for Microwave radiation = 16.96 g /100 g

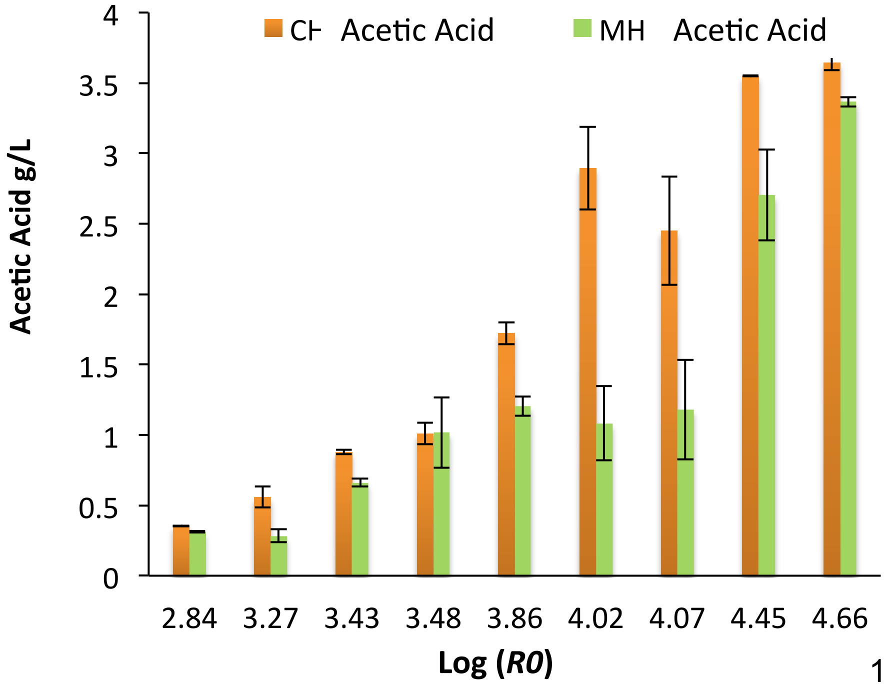
Conduction- Convection



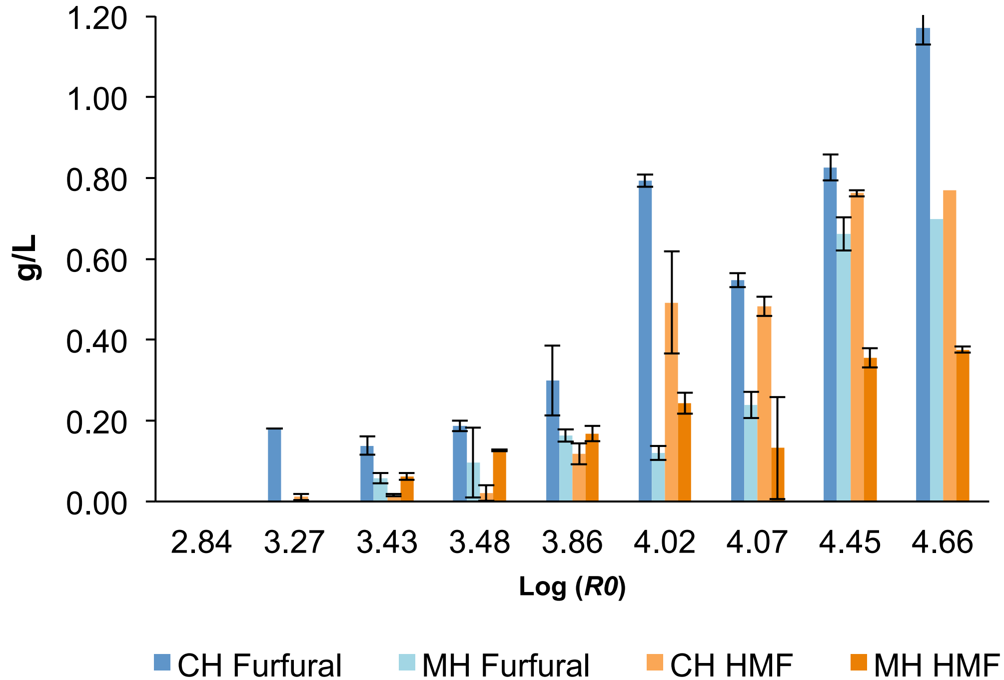
Microwave radiation



Alejandra Aguilar *et al. Manuscript in preparation*



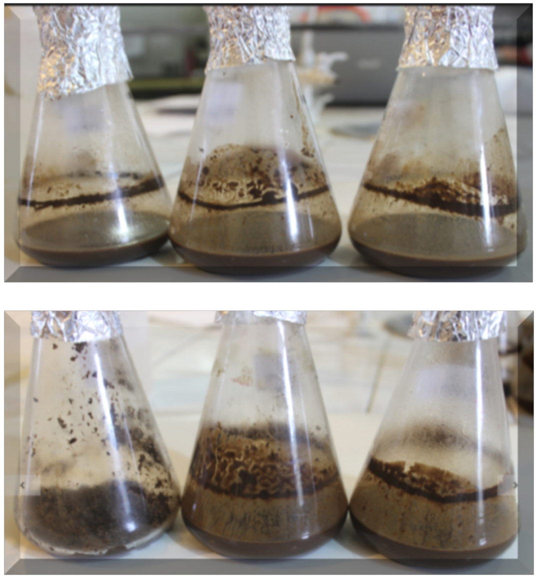
CH Acetic Acid
MH Acetic Acid
Acetic Acid g/L
0
0.5
1
1.5
2
2.5
3
3.5
4
2.84
3.27
3.43
3.48
3.86
4.02
4.07
4.45
4.66
Log (R0)

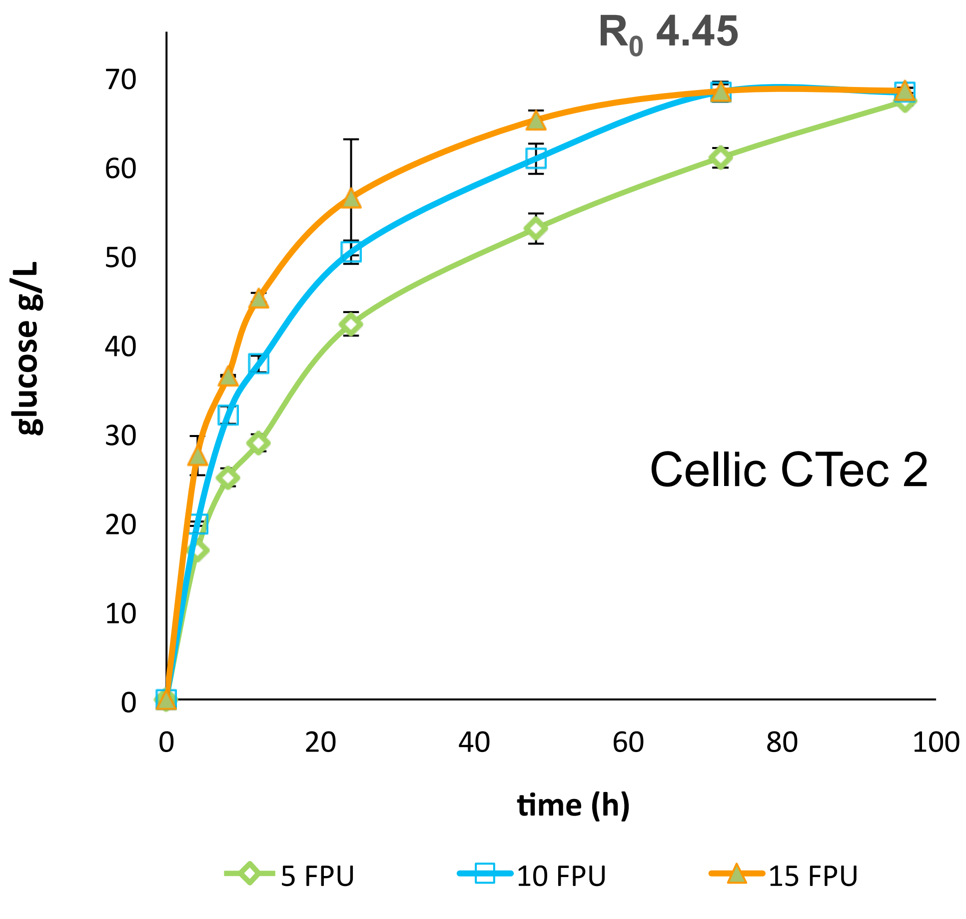


g/L
0.00
0.20
0.40
0.60
0.80
1.00
1.20
2.84
3.27
3.43
3.48
3.86
4.02
4.07
4.45
4.66
Log (R0)
CH Furfural
MH Furfural
CH HMF
MH HMF

Enzymatic hydrolysis – Microwave Radiation

Cellic CTec 2



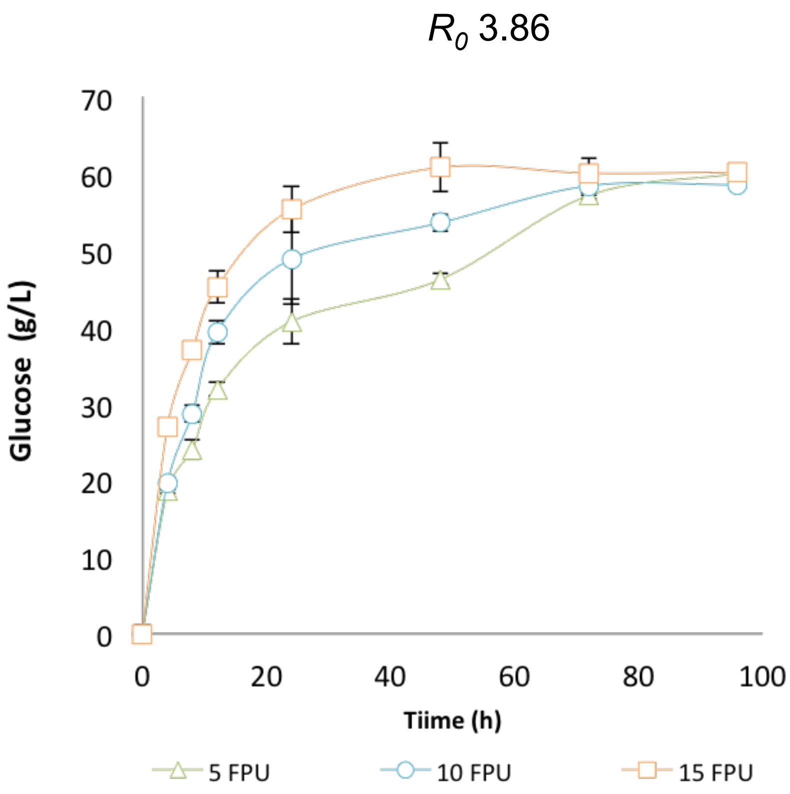


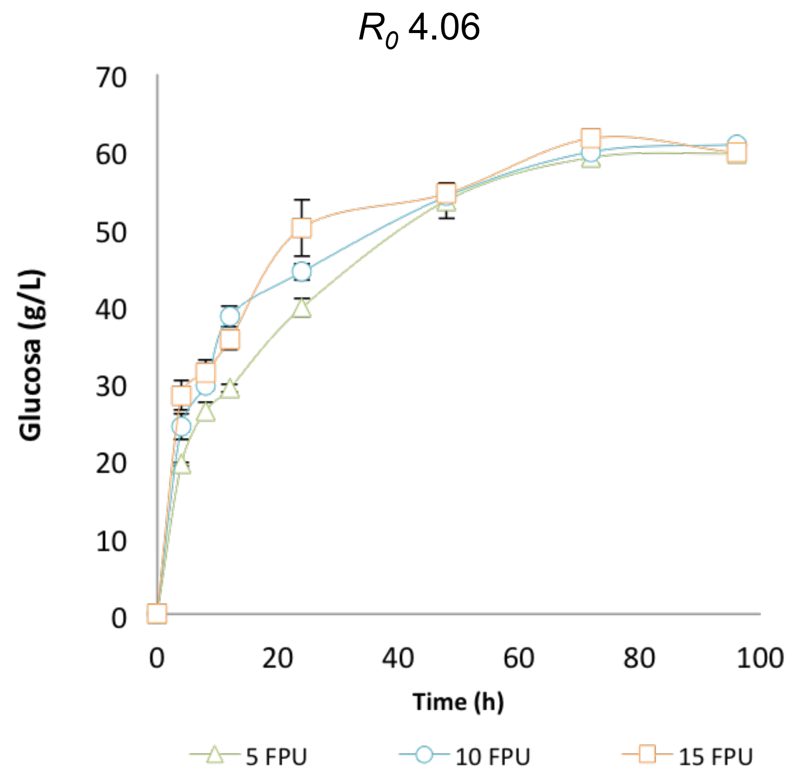
Alejandra Aguilar et al. Manuscript in preparation

BIOREFINERYGROUP

Enzymatic hydrolysis – Conduction-Convection

Cellic CTec 2





Alejandra Aguilar et al. Manuscript in preparation

BIOREFINERYGROUP

Application of Biorefinery Concept using Hydrothermal Processing

Carbohydrate Polymers 92 (2013) 2154–2162

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

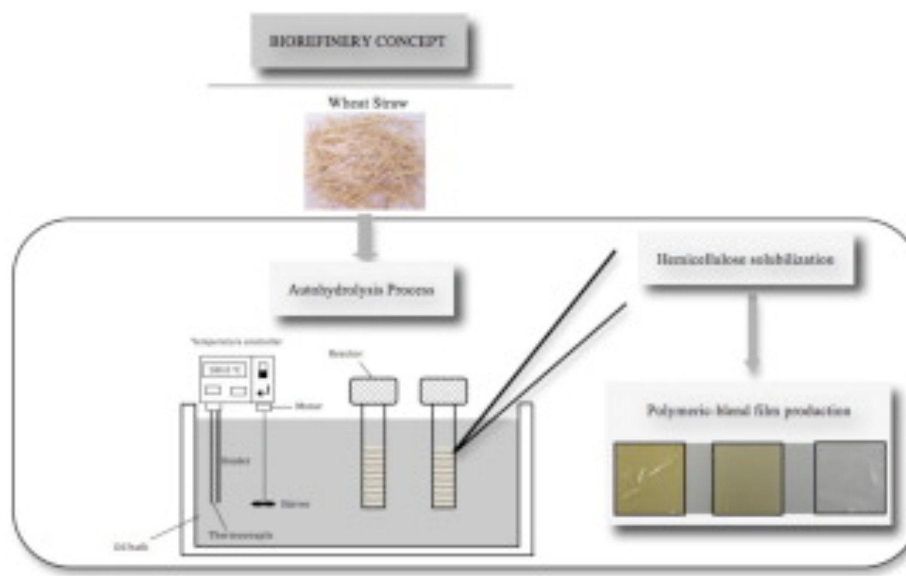
ELSEVIER

Biorefinery valorization of autohydrolysis wheat straw hemicellulose to be applied in a polymer-blend film

Héctor A. Ruiz*, Miguel A. Cerqueira*, Hélder D. Silva, Rosa M. Rodríguez-Jasso, António A. Vicente*, José A. Teixeira

The incorporation of hydrothermal extracted hemicellulose improved the physical properties of: κ-carrageenan/locust bean gum polymeric films

Graphical abstract



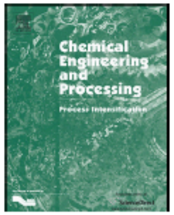
Application of Biorefinery Concept using Hydrothermal Processing

Chemical Engineering and Processing 96 (2015) 72–82

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep



Non-alkaline solubilization of arabinoxylans from destarched wheat bran using hydrothermal microwave processing and comparison with the hydrolysis by an endoxylanase

Mario Aguedo[a,*], Héctor A. Ruiz[b], Aurore Richel[a]

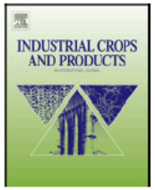
[a] Laboratory of Biological and Industrial Chemistry, Gembloux Agro-Bio Tech – University of Liège, Passage des Déportés 2, 5030 Gembloux, Belgium
[b] Biorefinery Group, Food Research Department, School of Chemistry, Autonomous University of Coahuila, Blvd. V. Carranza e Ing. José Cárdenas Valdés, 25280 Saltillo, Coahuila, Mexico

Industrial Crops and Products 66 (2015) 305–311

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop



Use of wheat bran arabinoxylans in chitosan-based films: Effect on physicochemical properties

Maria J. Costa[a,*], Miguel A. Cerqueira[a,*], Héctor A. Ruiz[b], Christian Fougnies[c], Aurore Richel[d], António A. Vicente[a], José A. Teixeira[a], Mario Aguedo[d]

[a] Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[b] Biorefinery Group, Food Research Department, School of Chemistry, Autonomous University of Coahuila, Blvd. V. Carranza e Ing. José Cárdenas Valdés, 25280 Saltillo, Coah., Mexico
[c] Cosucra Groupe Warcoing S.A., Rue de la Sucrerie 1, 7740 Warcoing, Belgium
[d] Laboratory of Biological and Industrial Chemistry, University of Liège – Gembloux Agro-Bio Tech, Passage des Déportés 2, 5030 Gembloux, Belgium

Perspectives

In general, autohydrolysis (Hydrothermal processing) can be considered a promising technology for the biorefinery concept, obtaining in an only step the fractionation of lignocellulosic materials and products with high added-value according to the biorefinery concept.

Acknowledgement

The University of British Columbia, Canada
Dr. Heather Trajano

University of Liège, Belgium
Dr. Mario Aguedo

University of Minho, Portugal

Dr. Aloia Romaní
Prof. José A. Teixeira
Dr. Miguel Cerqueira
Prof. Antonio Vicente
Dr. Michele Michelin
Dr. Francisco Pereira
Dr. Miguel Cerqueira

University of Vigo, Spain

Dr. Gil Garrote

Autonomous University of Coahuila, Mexico

Prof. Cristóbal N. Aguilar
Dr. Rosa M. Rodríguez Jasso
M.Sc. student Alejandra Aguilar
M.Sc. student Andrea Lara
M.Sc. student Jesús Velazquez
Elisa Zanuso

BIOREFINERYGROUP

DE G DE GRUYTER

BIOREFINERYGROUP

Thank you for listening

BIOREFINERYGROUP

hector_ruiz_leza@uadec.edu.mx

www.biorefinerygroup.com