Type of process	Description of the invention	Findings of the patent	Patent number	Publication date	Ref.
Extrusion	Twin screw extrusion of lignocellulosic biomass (preferred wood chips or sawdust) by prior to enzymatic hydrolysis to produce ethanol.	Significant increase in sugar recovery from such biomass.	US2006141584	2006-06-29	[25]
	Natural fiber hydrolytic reactor to treat plant cellulose and hemicellulose mixed with starch or raw materials to prepare a sugar solution.	No further additive needed. Environmental-friendly process, simple control and reduced manufacturing cost.	CN101418353	2009-04-29	[26]
Reactive extrusion	Extrusion of lignocellulosic material at 60-180ºC with 200-450% water plus 0.5-4% strong acid or base for ethanol production.	Fibrillation of the material. 8 fold increase of the enzymatic hydrolysis yield.	WO2010063980	2010-06-10	[30]
Alkaline extrusion	Twin-screw extrusion of lignocellulosic biomass in a with an alkaline solution (NaOH and/or Na_2S) 3 to 30% weight at 60- 230ºC, prior to enzymatic hydrolysis.	Good contact biomass/alkaline solution, continuous pretreatment, short time, low heat required.	US4642287	1987-02-10	[22]
Acid hydrolysis and extrusion	Extruder device composed of two chambers separated by a pressure sensitive die. In the extrusion zone, materials are pretreated at high pressure and temperature, and then pass into a reaction zone where they are mixed with an acidic solution at lower pressure and temperature.	Improved low cost energy efficient extrusion device, unique die construction that avoids surging and blowing of the fibrous materials, minimum acid degradation of the extruder components.	US4728367	1988-03-01	[24]

Steam explosion and extrusion	Pretreatment process of lignocellulosic biomass with multiple applications (ruminant feed, conversion to sugars and alcohols, lignin extraction) consisting in a treatment with steam at high pressure to raise temperature (185-240ºC) in a short time, followed by the release of the pressure by extrusion through a die.	Severe mechanical destructuration of lignocellulosic materials, minimization of hemicellulose degradation, enhanced enzymatic digestibility.	CA1217765	1987-02-10	[23]
	Pretreatment of lignocellulosic biomass in two steps with intermediate filtration. In which step two is carried out in a similar steam explosion-extrusion reactor as in the example above.	Improvement of the process referred above. Sequential hydrolysis of the material that allows removing hemicelluloses and possible inhibitors after the first pretreatment stage.	CA2842781	2013-01-31	[32]
Ammonia fiber explosion and extrusion	Extrusion process of cellulosic material with ammonia to expand the fiber to use it for animal feed or nutrient source for fermentation.	Increased enzymatic and ruminant digestibility, reduction in apparent lignin, high rate of digestion.	WO9956555	1999-11-11	[31]
Extrusion and microwave treatment	Extrusion process on wet lignocellulosic biomass for producing biogas or bioethanol, consisting in a single or twin-screw machine coupled to a microwave process at high temperature (150-250ºC) and pressure where thermal and possibly chemical hydrolysis (if catalyst is added) takes place, followed by anaerobic fermentation.	For biogas production, the dry fermentation process time is reduced to 10-20 days and biomass utilization increases up to 65-80% dry weight basis. For bioethanol, sugar yields increase to 75-85% of polysaccharides in the dry biomass, inhibitory products furfural and HMF remain in low concentrations and final ethanol yields increase.	EP1978086	2008-10-08	[29]
Vacuum extrusion	Pretreatment to produce bioethanol or other	Increase in at least 19% ethanol	EP2226387	2010-09-08	[27]

	valuable products from biomass, consisting in a vacuum extrusion (-3 kPa or more).	production compared to material not subjected to vacuum extrusion.			
Bioextrusion	Mechano-chemical treatment for the production of sugars from lignocellulosic biomass (to ethanol production) comprising consecutive steps of introduction of an alkaline extrusion, neutralization, filtration, and addition of enzyme solution into the extruder.	Reduced treatment time, low or no production of inhibitors for the enzymatic hydrolysis and fermentation, method easy to implement in pre-existing industrial installations.	US2015299751	2015-10-22	[28]

Variable	Feedstock	Extrusion conditions	Analyzed parameters	Results	Ref.
Screw profile	Hardwood	0.83 Hz; 70-120ºC; L/S = 1.1-2.7 Catalyst: White/black liquor **Screw profile composed of three mixing zones with different severity**	• Collecting of samples from the different mixing zones along the screw and analysis by SEM	• Visible destructuration and separation of the cellulosic fiber bundles after the most severe mixing zone (including reverse elements)	[13]
	Sweet corn cobs	1.67 Hz; 75ºC; Moisture 40% **3 screw profiles changing one element (conveying, by kneading or reverse)** Subsequent NaOH treatment	• Carbohydrate analysis • Particle size measurements • Crystallinity • SEM • Sugars released by EH	• Increased lignin removal (after NaOH treatment) with functional elements profiles • Pores blockage with reverse element (due to lignin re-distribution) • Enhanced enzymatic digestibility, increases after NaOH treatment in profiles with kneading and reverse elements	[46]
	Rape straw	0.5-1 Hz, 160-175ºC L/S =13.4 Catalyst: H_2SO_4 0.013-0.067 g/g biomass **3 screw profiles**	• Carbohydrate analysis • Sugars released by EH	• No differences in biomass composition among profiles • Increased sugars release with increasing severity of the profiles	[55]
	Sugarcane bagasse (B) and straw (S)	2.5 Hz (B)-1.4 Hz (B); 150ºC (B)-85ºC (S) Catalyst: 0.75 (B)-0.53 (S) weight glycerol/biomass 3 extrusion passes **2 screw profiles (with/without reverse)**	• Residence time • Crystallinity • Glucose released by EH	• Increased residence time from 1-4 min to 5-10 min with reverse element • No changes in crystallinity for (B)/Reduction of CrI for (S) with reverse • Increased glucose EH yield 1.4-fold with reverse compared without	[56]
	Steam-exploded	1.67 Hz; 100ºC; L/S =0.73 (H_2O/biomass)	• Pressure profile • Liquid/solid	• Increasing pressure, flow of filtrate and xylose recovery as the	[57]

	corn cobs	6 min residence time **8 screw profiles**	separation • Xylose recovery in filtrate	number of reverse elements increases	
Screw speed and residence time	Switchgrass Prairie cord grass	**0.83-2.5 Hz;** 50-150ºC; Moisture 15-45%	• Sugars released by EH	• <u>Switchgrass</u>: increasing glucose released with increasing screw speed up to 1.66 Hz, then decrease; other sugars release increase as screw speed increase • <u>Prairie cord grass</u>: increasing sugars released as screw speed decreases	[7]
	Corn stover	**0.67-2.33 Hz**; 50-140ºC; Moisture 22.5-27.5%	• Glucose released by EH	• Increasing glucose released with increasing screw speed up to 1.33 Hz, then decrease	[9]
	Soybean hulls	**4.7-7 Hz**; 80ºC; Moisture 40%	• Glucose released by EH	• Increasing SME with increasing screw speed • Increasing glucose yields as screw speed increases up to 350 rpm, then decrease	[51]
	Wheat bran	**3.7-7 Hz**; 110-150ºC	• Reducing sugars after EH	• Effect of screw speed depending on temperature. Same yield by low screw speed (high residence time) and mild temperature, or high screw speed (low residence time) and high temperature.	[52]
	Corn stover	**0.66-1.67 Hz**; 50-140ºC Previous soaking in NaOH (0.004-0.04 g/g biomass)	• Glucose released by EH	• Compared to the prominent effects of alkali concentration, screw speed was non-significant • Behavior different from extrusion only with water in ref. 9 above	[58]

Variable	Feedstock	Extrusion conditions	Analyzed parameters	Results	Ref.
Temperature	Switchgrass Prairie cord grass	0.83-2.5 Hz; **50-150ºC**; Moisture 15-45%	• Sugars released by EH	• Switchgrass: sugars released increased up to 100ºC, then decrease • Prairie cord grass: sugars release decrease from 100ºC	[7]
	Pine wood chips	1.67-3.3 Hz, **100-180ºC** Moisture 25-45%	• Sugars released by EH	• Increasing sugars released as temperature increases	[16]
	Switchgrass	0.33-2 Hz, **45-225ºC** Particle size 2-10 mm Moisture 10-50%	• Sugars released by EH	• Increasing sugars released as temperature increases • Temperature was the most prominent effect on xylose release, over screw speed	[17]
	Barley straw	2.5 Hz, **50-100ºC** Catalyst: NaOH 0.025-0.75 g/g dry biomass	• Sugars released by EH	• Increasing glucose released with increasing temperatures up to 75ºC, then slight decrease • Increasing xylose released as temperature increases	[47]
	Sugarcane bagasse	0.2 Hz, **140-180ºC** L/S = 2-8 1 to 3 passes Catalyst: 1-ethyl-3-methylimidazolium acetate	• Sugars released by EH • SEM	• Glucose released did not increase from 140 to 160ºC and decreased above that point • Xylose released increased with temperature up to 160ºC, then decreased • Greater structure disruption and fibrillation (<100 nm fiber diameter) up to 160ºC • At 180ºC, collapsed structure and partial charring	[59]

Variable	Feedstock	Extrusion conditions	Analyzed parameters	Results	Ref.
L/S	Switchgrass Prairie cord grass	0.83-2.5 Hz; 50-150ºC; **Moisture 15-45%**	• Sugars released by EH	• Sugars release decrease as moisture increases for both LB	[7]
	Hardwood	0.83 Hz, 70-120ºC **Moisture 44-60%** Catalyst: NaOH, CMC	• SEM	• Increasing torque and pressure as moisture decreases • Reduction of the fibers diameter as moisture decreases	[13]
	Barley straw	2.5 Hz, 50-100ºC **L/S= 0.25-0.75** Catalyst: NaOH 0.025-0.75 g/g dry biomass	• Sugars released by EH	• Higher L/S means higher catalyst addition (concentration of the catalyst solution constant) • Sugars released increase with increasing L/S	[47]
	Soybean hulls	7 Hz, 80ºC **Moisture 45-50%** 0-5% starch addition	• Glucose released by EH	• Torque increases with low moisture • Glucose yield increases at low moisture	[51]
	Rape straw	0.33 Hz, 150-170ºC **L/S= 9-13** Catalyst: H_2SO_4 (31-48% w/w biomass)	• Carbohydrates composition	• More liquid and more acidity result in higher cellulose content and lower hemicellulose content in the solid fraction of extrudates	[62]
	Sugarcane bagasse	0.2 Hz, 140-180ºC **L/S = 2-8** 1 to 3 passes Catalyst: 1-ethyl-3-methylimidazolium acetate	• Sugars released by EH	• Sugars released decrease as biomass loading increases	[59]

Table 5. Examples of different case pretreatment configurations using extrusion process found in recent literature and its effects on the LB.

Configuration	**Pretreatment**	**Biomass**	**Operation conditions**	**Proven positive effect on***	**Ref.**
Only extrusion	Single-screw extruder	Pine wood chips	2.5 Hz, 180ºC, 25% moisture	CH, NTCR	[16]
	Twin-screw extruder	Corn fiber	5 Hz, 140ºC, 30% moisture Die 3 mm	CH, PSR	[11]
Sequence of treatments	Autohydrolysis + extrusion	Douglas fir Eucalyptus	0.83-2 Hz, room temperature Previous autohydrolysis at 140-180ºC, 30’	CH, FB	[15]
	Impregnation with glycerol + extrusion	Sugarcane bagasse and straw	0.5 Hz, 50ºC 0.53-0.75 weight glycerol/biomass	CH	[56]
	Impregnation with ionic liquids + extrusion	Sugarcane bagasse	0.25 Hz, 140ºC 25%wt ionic liquid (1-ethyl-3-methylimidazolium acetate)	CH, SSA	[59]
	Extrusion + ozonation	Switchgrass Big bluestern	<u>Extrusion</u>: 2.6 Hz, 176ºC/180ºC, 20% moisture 8 mm particle size <u>Ozonation</u> : 25%moisture, 2.5 min 37/365 mg ozone/h	CH, NTCR	[78]
	Extrusion + microwaves	Switchgrass Big bluestern	<u>Extrusion</u>: 2.6 Hz, 176ºC/180ºC, 20% moisture 8 mm particle size <u>Microwave</u>: 25% moisture, 2.5 min 450W	CH, NTCR	[79]
	Extrusion + organic solvent	Prairie cord grass	<u>Extrusion</u>: 1.1 Hz, 90ºC, 20% moisture 8 mm particle size <u>Organic solvent</u>: 39 min, 129ºC	CH, XS, LR	[43]

			0.7% catalyst (H_2SO_4) 28% methyl isobutyl ketone		
Reactive extrusion	NaOH	Barley straw	2.5 Hz, 68ºC 0.06 g NaOH/g dry biomass Neutralization with H_3PO_4 and filtration inside the extruder	CH, NTCR	[47]
	H_2SO_4	Rapeseed straw	1 Hz, 165ºC 0.27 g H_2SO_4/d dry biomass	CH	[55]
	Hydrolytic enzymes	Barley straw	2.5 Hz, 68- 50ºC 0.06 gNaOH/g dry biomass Neutralization with H_3PO_4, filtration and addition of enzymes inside the extruder 10 mg protein/g dry extrudate	CH, PSR, NTCR	[84]
Combination of technologies in one reactor	Steam explosion & extrusion	Corn stover	150ºC, 2 min	CH, XS, LR	[83]
	Alkaline extended pretreatment	Miscanthus	140ºC, 22% moisture 3 mm particle size 0.16 g NaOH/g dry biomass	CH, LR	[21]
	Hemicelluloses extraction	Steam exploded corn cobs	1.25-1.67 Hz, 65-100ºC 0-0.7 g water/g biomass	XS	[57]

*CH – carbohydrate hydrolysis; PSR – particle size reduction; FB – fibrillation; SSA – specific surface area; NTCR – no toxic compounds release; XS – xylose solubilization; LR – lignin removal