



(51) International Patent Classification:

A21D 2/18 (2006.01) A21D 13/066 (2017.01)

A21D 2/36 (2006.01)

(21) International Application Number:

PCT/US2018/016789

(22) International Filing Date:

05 February 2018 (05.02.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/458,049 13 February 2017 (13.02.2017) US

(71) Applicant: DOW GLOBAL TECHNOLOGIES LLC

[US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors: GUO, Jing; 1801 Larkin Center Drive, Mid-

land, MI 48641 (US). TAN, Yujing; Bldg. 1897, Washing-

ton Street, Midland, MI 48667 (US).

(74) Agent: CRIMALDI, Kenneth; Dow Global Technologies

LLC, 2040 Dow Center, Midland, Michigan 48674 (US).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: USE OF XYLOGLUCAN IN GLUTEN-FREE BREAD

(57) Abstract: A method for making gluten-free bread. The method comprises incorporating into a gluten-free dough formulation comprising gluten-free flour from 0.1 to 2 wt% xyloglucan.



USE OF XYLOGLUCAN IN GLUTEN-FREE BREAD

This invention relates to a method for preparing bread using gluten-free flour and xyloglucan.

5 Gluten is a protein complex found in some grains, including wheat, barley and rye. The gluten content in wheat flour provides desirable organoleptic properties, such as texture and taste, and also improves processing qualities. It is very difficult to make bread using gluten-free flours. When dough containing gluten is fermented with yeast, the carbon dioxide generated by fermentation is retained by the gluten so that the dough rises. In the
10 case of dough using gluten-free flour, the carbon dioxide is not retained within the dough so that the dough does not rise efficiently.

 However, gluten has its drawbacks. The gluten protein complex, upon entering the digestive tract, breaks down into peptide chains which, in some people, trigger an immune response commonly referred to as celiac disease. Accordingly, much research has been
15 spent on finding gluten-free food products.

 The use of xyloglucan in dough containing gluten is known. For example, T. Maeda et al., *Carbohydrate Polymers*, 68 (2007) pp. 658 – 664 reports use of xyloglucan in normal breadmaking. However, this reference does not address the problems in processing of gluten-free bread.

20 Statement of the Invention

 The present invention is directed to a method for making gluten-free bread; said method comprising incorporating into a gluten-free dough formulation comprising gluten-free flour from 0.1 to 2 wt% xyloglucan.

 The present invention is further directed to a composition which is a gluten-free
25 dough formulation comprising gluten-free flour and from 0.1 to 2 wt% xyloglucan.

Detailed Description of the Invention

 Unless specified otherwise, all percentages are weight percentages (wt%), all temperatures are in °C and all operations are performed at room temperature (20-25°C). Weight percentages are based on the entire weight of the dough formulation unless
30 otherwise specified. The “dough formulation” is the mixture of ingredients which forms the dough. The composition of the dough formulation is substantially identical to that of the dough, although the dough will contain some carbon dioxide from the activity of the yeast and possibly slightly less sugar due to its consumption by yeast. The term “gluten-free flour” as used herein is a powder made by grinding cereal grains or other seeds, roots (like

cassava) or other parts of gluten-free plants. "Gluten-free" flour or bread may contain traces of gluten, although typically not above the current regulatory threshold of 20 ppm. The term "a gluten-free flour" or "the gluten-free flour" is not limited to flour from a single source but also encompasses a mixture of flours of different sources. The term "gluten-free flour" as used herein also encompasses starches in powder form extracted from gluten-free plants, such as tapioca starch or potato starch. This means that the composition itself and food products comprising or produced from the composition typically are also gluten-free. A typical method of making gluten-free food products consists of using only ingredients derived from gluten-free starting materials, rather than using flour derived from a gluten-containing grain, such as wheat. Accordingly, the composition of the present invention comprises a) a gluten-free flour, such as: amaranth flour, arrowroot flour, rice flour, buckwheat flour, corn flour, polenta flour, sweet potato flour, lentil flour, grape seed flour, garbanzo bean flour, garfava flour (a flour produced by Authentic Foods which is made from a combination of garbanzo beans and fava beans), millet flour, oat flour, potato flour, quinoa flour, Romano bean flour, sorghum flour, soy flour, sweet rice flour, tapioca flour, psyllium husk powder, powder produced from bamboo fibers or teff flour or a combination of two or more such flours. Preferred are tapioca starch, rice flour, maize flour, potato starch, powder produced from bamboo fibers and psyllium husk powder. Preferably the composition of the present invention comprises at least three, preferably at least four, preferably at least five gluten-free flours selected from the group consisting of tapioca starch, corn starch, rice flour, maize flour, potato starch, powder produced from bamboo fibers and psyllium husk powder.

The dough formulation preferably comprises gluten-free flour in an amount of from 30 to 70 wt%; preferably at least 33 wt%, preferably at least 36 wt%; preferably no more than 65 wt%, preferably no more than 60 wt%, preferably no more than 55 wt%.

Preferably, xyloglucan has Mw from 500,000 to 1,500,000, preferably from 700,000 to 1,300,000. Preferably, the xyloglucan is present in the dough formulation in an amount of at least 0.15 wt%, preferably at least 0.2 wt%, preferably at least 0.3 wt%, preferably at least 0.4 wt%; preferably no more than 1.8 wt%, preferably no more than 1.6 wt%, preferably no more than 1.4 wt%. In an embodiment of the invention, xyloglucan is enzymatically modified. Enzymatic modification is believed to remove side-chain galactose units from the basic hemicellulose backbone of xyloglucan. A preferred enzyme is β -galactosidase. Preferably, the enzymatic modification produces non-gelling xyloglucan, i.e., xyloglucan which is not a gel in the range from 30-75°C. Times for enzymatic

modification depend on other parameters but can easily be determined. Preferably, from 0 to 30% of the galactose units are removed, preferably 0 to 15%.

Preferably, the composition of the present invention comprises a carboxymethyl cellulose. The term “carboxymethyl cellulose” or “CMC” as used herein encompasses
5 cellulose substituted with groups of the formula $-\text{CH}_2\text{CO}_2\text{A}$, wherein A is hydrogen or a monovalent cation, such as K^+ or preferably Na^+ . Preferably the carboxymethyl cellulose is in the form of its sodium salt, i.e., A is Na^+ . Typically, the carboxymethyl cellulose has a degree of substitution of from 0.20 to 0.95, preferably from 0.40 to 0.95, preferably from 0.65 to 0.95. The degree of substitution is the average number of OH groups that have been
10 substituted in one anhydroglucose unit. It is determined according to ASTM D 1439-03 “Standard Test Methods for Sodium Carboxymethylcellulose; Degree of Etherification, Test Method B: Nonaqueous Titration”. The treatment of a solid sample of the CMC with glacial acetic acid at boiling temperature releases an acetate ion quantity equivalent to the sodium carboxymethyl groups. These acetate ions can be titrated as a strong base in
15 anhydrous acetic acid using a perchloric acid standard solution. The titration end point is determined potentiometrically. Other alkaline salts of carboxylic acids (e. g. sodium glycolate and di-sodium diglycolate) behave similarly and are co-titrated. The viscosity of the carboxymethyl cellulose generally is from 20 to 30,000 mPa·s, preferably from 25 to 12,000 mPa·s, more preferably from 100 to 5,000 mPa·s, and most preferably from 500 to
20 4000 mPa·s, determined in a 1% by weight solution in water at 20°C, using a Brookfield LVT viscosimeter, spindle No. 3, at 30 rpm. Preferably, carboxymethyl cellulose is present in the dough composition in an amount from 0.01 to 5 wt%; preferably at least 0.1 wt%, preferably at least 0.2 wt%, preferably at least 0.3 wt%; preferably no more than 3 wt%, preferably no more than 2 wt%, preferably no more than 1 wt%, preferably no more than
25 0.8 wt%. In a preferred embodiment of the invention, carboxymethyl cellulose is substantially absent from the composition, i.e., the composition comprises no more than 0.1 wt% carboxymethyl cellulose, preferably no more than 0.05 wt%, preferably no more than 0.01 wt%.

Preferably, the dough composition comprises from 30 to 70 wt% water; preferably at
30 least 32 wt%, preferably at least 34 wt%, preferably at least 35 wt%; preferably no more than 65 wt%, preferably no more than 60 wt%, preferably no more than 55 wt%.

Examples of other optional ingredients in gluten-free compositions and food products are as follows: gums, including xanthan gum and guar gum; gelatin; eggs, such as egg white; egg replacers; sweeteners, including sugars, molasses, and honey; salt; yeast;

chemical leavening agents, including baking powder and baking soda; fats, including margarine and butter; oils, including vegetable oil; vinegar; dough enhancer; dairy products, including milk, powdered milk, and yogurt; soy milk; nut ingredients, including almond meal, nut milk, and nut meats; seeds, including flaxseed, poppy seeds, and sesame seeds; 5 fruit and vegetable ingredients, including fruit puree and fruit juice; and flavorings, including vanilla, cocoa powder, and cinnamon. However, this is not a comprehensive list of all ingredients that can be used to make gluten-free food products, such as gluten-free bakery products. Preferably, the total amount of optional ingredients is no more than 20 wt%, preferably no more than 15 wt%, preferably no more than 12 wt%; preferably at least 10 2 wt%, preferably at least 3 wt %, preferably at least 4 wt%, preferably at least 5 wt%, preferably at least 6 wt%. Preferably, the composition comprises from 1 to 5 wt% vegetable oil; preferably at least 1.5 wt%, preferably at least 2 wt%; preferably no more than 4.5 wt%, preferably no more than 4 wt%.

The composition of the present invention is useful for preparing gluten-free food 15 products, such as gluten-free bakery products, like breads, muffins, cakes, cookies or pizza crusts; gluten-free pasta, cereal products, crackers, and bar products. The composition of the present invention can be processed to the gluten-free food product in a conventional manner, for example by producing a dough or a batter from the composition of the present invention, subjecting it to molding or casting, optionally leavening the composition, and 20 optionally baking it, depending on the kind of food product to be produced.

Preferably, the xyloglucan comprises less than 0.5 wt% organic solvents, preferably less than 0.2 wt%, preferably less than 0.1 wt%. Preferably, the xyloglucan comprises less than 1 wt% chitosan, preferably less than 0.5 wt%, preferably less than 0.2 wt%, preferably less than 0.1 wt%. Preferably, the xyloglucan comprises less than 1 wt% pectin, preferably 25 less than 0.5 wt%, preferably less than 0.2 wt%, preferably less than 0.1 wt%.

Examples

Enzymatic modification process: 1mg/ml of β -galactosidase is added into 3% of xyloglucan (in PBS buffer, pH 5.5), the reaction is conducted in oven (55-60 °C). Then the enzymatically modified xyloglucan is freeze-dried.

5 In gluten free bread application, both enzymatically modified xyloglucan and non-modified xyloglucan were tested, and it turned out the non-enzymatically modified xyloglucan and the non-gelling enzymatically modified xyloglucan showing texture enhancement (volume increase). The intention of doing enzymatic modification is to obtain a thermal gelling xyloglucan.

10 Unless otherwise mentioned, all parts and percentages are by weight. In the Examples the following test procedures are used.

Firmness of Bread Crumb

The firmness measured 1 day after baking is designated as “initial firmness”. The
15 firmness measured later than 1 day after baking is called firmness over storage time and is a measure for determining shelf life. In the time period between i) baking and cooling and ii) the firmness measurement the bread loaves are stored in polyethylene bags. A low initial firmness and/or a low firmness over storage time are desirable.

For texture analysis, a modified version of AACC method 74-09 (American Association
20 of Cereal Chemists) was applied. Firmness of wheat bread and gluten-free bread was measured with a texture analyzer TA.XT plus (Stable Microsystems Ltd., Godalming, Surrey, UK) using the following settings:

- Sample preparation: bread slices of 25 mm thickness freshly cut from the center of loaves;
- 25 - 5 kg load cell;
- Round probe diameter 40 mm;
- Speed 1 mm/s.

The firmness is defined as force needed to press the probe 6.25 mm (25 % of the slice's thickness) into the bread crumb.

30

Example 1. GF strip down bread

Table 1. GF strip down bread formulation (basic formulation).

	A	C	D	E	F	G
	Control w K4M; CMC	1.67% Xyloglucan	1.14% Xyloglucan	0.7% Xyloglucan	0.2% Xyloglucan	Negative Control
	wt percent	wt percent	wt percent	wt percent	wt percent	wt percent
Rice Flour	30.00%	30.00%	30.00%	30.00%	30.00%	30.00%
Tapioca Flour	10.00%	10.00%	10.00%	10.00%	10.00%	10.00%
Potato Flour	10.00%	10.00%	10.00%	10.00%	10.00%	10.00%
METHOCEL K4M	1.14%	0.00%	0.00%	0.00%	0.00%	0.00%
Xyloglucan	0.00%	1.67%	1.14%	0.70%	0.20%	0.00%
WALOCEL CRT 20000 PA	0.53%	0.00%	0.00%	0.00%	0.00%	0.00%
Salt	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%
Sugar	4.00%	4.00%	4.00%	4.00%	4.00%	4.00%
Vegetable oil	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%
Yeast	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%
Water	39.33%	39.33%	39.86%	40.30%	40.80%	41.00%
Total	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%

- 5 Bread heights were as follows: A-E were all from 9-10 cm, F was 8 cm and G was 3 cm. Without xyloglucan, the control bread doesn't rise during proving, which results in a flat and dense brick-like biscuit texture. With the addition of 1.14% of METHOCEL K4M and 0.53% of WALOCEL CRT 20000PA, the GF bread rises to an appropriate volume by trapping the yeast released carbon dioxide with the thermal gelling property. Similar to
- 10 K4M/CMC, when either xyloglucan (Glyloid 3S) or enzymatically modified xyloglucan (EM-Glyloid 3S) which has no gelling property was used, only at lower dosage level (1.14% vs. 1.67%), similar volume was obtained in GF bread, suggesting that xyloglucan helps in improving the GF bread texture, which can be used in replacement of K4M/CMC.

Example 2. GF white dough bread

Table 2. GF white dough bread formula.

	A	B	C	D
	Control	Xyloglucan	Gelling Xyloglucan	Negative Control
INGREDIENTS	Weight %	Weight %	Weight %	Weight %
Water	50.97	51.5	51.67	52.64
Tapioca Starch	10.61	10.61	10.61	10.61
Rice Starch	9.09	9.09	9.09	9.09
Bamboo Fiber	5.68	5.68	5.68	5.68
Egg White Powder	4.17	4.17	4.17	4.17
Canola Oil	3.79	3.79	3.79	3.79
Potato Starch	3.41	3.41	3.41	3.41
Psyllium Husk Powder	3.03	3.03	3.03	3.03
Maize Flour	2.27	2.27	2.27	2.27
Sugar	2.27	2.27	2.27	2.27
Yeast-Cake	1.9	1.9	1.9	1.9
METHOCEL K4M	1.14	0	0	0
Xyloglucan	0	1.14	0	0
Gelling Xyloglucan	0	0	0.975	0
Salt	1.14	1.14	1.14	1.14
WALOCE 20000 PA	0.53	0	0	0
	Total %	Total %	Total %	Total %
	100	100	100	100
Specific Volume (cm ³ /g)	1.67	1.70	1.61	1.68

TPA data indicate that in the characteristics of hardness, adhesiveness, springiness, cohesiveness, chewiness and resilience of GF white dough bread slices made with xyloglucan is very similar to the bread made with K4M. This suggests that xyloglucan could be used as a clean label additive in GF bread to replace METHOCEL K4M.

5

	H, g	C, ratio	A, g s	C', g	S, ratio	R, ratio
METHOCEL	174 ± 7.7	0.79 ± 0.00	-0.82 ± 0.19	198 ± 87	1.43 ± 0.60	0.41 ± 0.01
Xyloglucan (Glyloid 3S)	135 ± 11.4	0.79 ± 0.00	-0.79 ± 0.19	182 ± 90	1.67 ± 0.76	0.42 ± 0.01
Negative Control	195 ± 35	0.80 ± 0.00	-2.19 ± 0.19	238 ± 83	1.56 ± 0.58	0.43 ± 0.01
Gelling- xyloglucan (EM-Glyloid 3S)	375 ± 33.6	0.78 ± 0.00	-2.10 ± 0.19	411 ± 165	0.51 ± 0.23	0.44 ± 0.01

H=hardness, C=Cohesiveness, A=Adhesiveness, C'=chewiness, S=springiness,
R=resilience

Claims

1. A method for making gluten-free bread; said method comprising incorporating into a gluten-free dough formulation comprising gluten-free flour from 0.1 to 2 wt% xyloglucan.
2. The method of claim 1 in which the dough formulation comprises from 30 to 70 wt% gluten-free flour and from 30 to 70 wt% water.
3. The method of claim 2 in which the dough formulation comprises from 0.3 to 1.8 wt% xyloglucan.
4. The method of claim 1 in which the dough formulation further comprises carboxymethyl cellulose in an amount from 0.01 to 5 wt%.
5. The method of claim 4 in which the dough formulation comprises from 30 to 65 wt% gluten-free flour and from 30 to 65 wt% water.
6. The method of claim 1 wherein the dough formulation is substantially free of carboxymethyl cellulose.
7. The method of claim 6 in which the dough formulation comprises from 30 to 65 wt% gluten-free flour and from 30 to 65 wt% water.
8. A composition suitable for making gluten-free bread; said composition comprising 30 to 65 wt% gluten-free flour, from 30 to 65 wt% water, from 1 to 5 wt% vegetable oil and from 0.1 to 2 wt% xyloglucan.
9. The composition claim 8 comprising from 0.3 to 1.8 wt% xyloglucan.
10. The composition of claim 9 further comprising carboxymethyl cellulose in an amount from 0.01 to 5 wt%.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/016789

A. CLASSIFICATION OF SUBJECT MATTER
INV. A21D2/18 A21D2/36 A21D13/066
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A21D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, BIOSIS, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	G. Eisenbrand, P. Schreier: "Römp Lexikon Lebensmittelchemie", 2006, Thieme Verlag, Stuttgart, XP002779676, pages 1306-1306, the whole document	1-10
X	----- WO 2015/158959 A1 (TEKNOLOGIAN TUTKIMUSKESKUS VTT OY [FI]) 22 October 2015 (2015-10-22) examples claims 1-19 page 9, line 22 - page 11, line 9 ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 April 2018

Date of mailing of the international search report

13/04/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Barac, Dominika

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/016789

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/127215 A2 (MANNALUTION LTD [GB]; KARCHER KARSTEN [GB]; OBERLECHNER KLAUS [AT]) 27 September 2012 (2012-09-27) claims 1-59 pages 26-31; examples page 4, line 27 - page 9, line 30 -----	1-10
X	US 2011/281010 A1 (PARRY CLARISSA [US]) 17 November 2011 (2011-11-17) the whole document -----	1-10
A	RILTON ALVES DE FREITAS ET AL: "Rheological description of the interaction of xyloglucan and starches: effect of the amylose content in starches", CYTA - JOURNAL OF FOOD, vol. 13, no. 2, 3 April 2015 (2015-04-03), pages 235-242, XP055462878, UK ISSN: 1947-6337, DOI: 10.1080/19476337.2014.946093 the whole document -----	1-10
A	ANURADHA MISHRA ET AL: "Tamarind xyloglucan: a polysaccharide with versatile application potential", JOURNAL OF MATERIALS CHEMISTRY, vol. 19, no. 45, 1 January 2009 (2009-01-01), page 8528, XP0055462910, GB ISSN: 0959-9428, DOI: 10.1039/b9111150f the whole document -----	1-10
A	K. Nishinari ET AL: "Storage Plant Polysaccharides: Xyloglucans, Galactomannans, Glucomannans" In: "Comprehensive Glycoscience", 1 January 2007 (2007-01-01), Elsevier, XP055462893, ISBN: 978-0-444-51967-2 pages 613-652, DOI: 10.1016/B978-044451967-2/00146-X, the whole document -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/016789

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015158959	A1	22-10-2015	NONE
WO 2012127215	A2	27-09-2012	AU 2012232846 A1 31-10-2013
		CA 2830332 A1	27-09-2012
		EP 2685833 A2	22-01-2014
		ES 2585890 T3	10-10-2016
		GB 2503842 A	08-01-2014
		US 2014093611 A1	03-04-2014
		WO 2012127215 A2	27-09-2012
US 2011281010	A1	17-11-2011	NONE