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Distribution of free lipids and their fractions in wheat flour milled streams

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Abstract

Polar and non-polar lipids both play an important role in determining the quality of wheat flour and its suitability for different bakery products. In order to develop specific flours for different end-uses, polar and non-polar lipid content were determined in streams and both showed wide variation. The total free non-polar lipid (TFNPL) content varied from 0.54 to 1.8% (db) while total free polar lipid (TFPL) content varied from 0.11 to 0.34% (db) in different flour streams indicating the preponderance of TFNPL. Triglycerides were the predominant fraction present in TFNPL while glycolipids predominated in the TFPL fraction. The amounts of these fractions were greater in the IV break stream. In the case of saturated fatty acids, palmitic acid was predominant in TFNPL fractions, whereas, stearic acid was predominant in TFPL. The levels of oleic acid were higher in TFNPL (16.9 to 33.6%). Linoleic acid was the predominant unsaturated fatty acid in both TFNPL and TFPL fractions.

Keywords: Lipids; Fatty acids; Wheat; Milled streams

1. Introduction

Roller flour milling aims at gradual reduction in size of wheat by passing it through a series of break and reduction rolls to allow maximum removal of bran and germ and to obtain fine white flour for use in bakery products. In this process, wheat is opened up, the endosperm released is separated from the bran coats in break rolls and the resulting endosperm grits are reduced to fine flour in subsequent reduction rolls. Normally, commercial mills have 4–5 break rolls and 5–6 reduction rolls and hence the quality characteristics of the streams are different. The quality of flours obtained in each of the break or reduction rolls is different, since the quality of endosperm depends on its location and it varies from central portion to outer portion (Morrison, 1978). The straight run flour obtained in a roller flour-mill is a blend of all the streams.

The baking quality and storage stability of white flour are affected by its non-starch lipid contents and by the proportions of non-polar and polar lipids (Morrison, 1978, 1979). Lipids have been reported to markedly influence the baking quality of flours, particularly bread (Addo & Pomeranz, 1992). Among the lipids, polar lipids have more beneficial effects on loaf volume (Bekes, Zawistowska, Zillman & Bushuk, 1986; McCirnack, Panozzo & MacRitchie, 1991). Chung, Pomeranz and Finney (1982) reported a good correlation between polar lipid content in flour and loaf volume ($r=0.877$; $P<0.001$). Most of the polar lipids are found in bound form, complexing with protein and starch (Pomeranz, 1988). Fatty acids, particularly unsaturated fatty acids, are reported to strengthen the gluten by way of oxidation of ‘SH’ group through enzyme-coupled reactions (Addo & Pomeranz, 1992; Morrison & Panpaprai, 1975).

There are many reports on content of different types of lipids in straight-run flours. However, no information is available on these in different milled streams, except for one recent report on free and bound lipid content (Prabhasankar & Haridas Rao, 1999). Also, there are no scientific data available on polar and non-polar contents of free lipids or their fatty acid composition in

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Abbreviations: GC, gas chromatography; AACC, American Association of Cereal Chemists; DEGS, diethylene glycol succinate; TFL, total free lipids; TFNPL, total free non-polar lipids; TFPL, total free polar lipids; STR, straight run flour.

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commercial milled flour streams. This information is necessary to develop flour of specific quality by blending selected streams for use in different bakery and traditional products. Therefore, studies were carried out to determine the free non-polar and free polar contents and their fatty acid composition in flour mill streams.

2. Materials and methods

2.1. Raw materials

Break and reduction flour streams were obtained from a commercial roller flour mill which separates 50–52% wheat flour, 10–12% semolina and 8–10% resultant *atta* and 20–22% bran. Commercially available medium hard, aestivum wheat, having grain hardness of 11.5 kg/grain and hectolitre weight of 83 kg/hectolitre was used for milling. The mill, with the capacity of 80 tonnes/day, had four break rolls and six reduction rolls. One stream was collected from each of the break and reduction rolls and their flow rates were also noted. Straight-run flour (STR) was collected for comparison.

Analytical grade reagents, distilled and dry solvents were used throughout the study. Fatty acid standards were procured from Sigma Chemicals, USA.

2.2. Extraction of total free lipids (TFL)

Total free lipids from the milled streams were extracted according to the standard method (AACC, 1995). The physical and chemical characteristics of wheat were also determined using standard methods. Each sample was replicated.

2.3. Fractionation of total free lipids into total free non-polar lipids (TFNPL) and total free polar lipids (TFPL)

TFNPL and TFPL fractions of TFL were separated by thin-layer chromatography (TLC) with the solvent system $CHCl_3$:CH_3OH (8:1 v/v). After the development of each chromatogram, individual lipid fractions (TFNPL and TFPL) were identified by exposing to iodine vapours; fractions were scraped off and eluted from the silica gel by using $CHCl_3$: CH_3OH (2:1 v/v). The eluted fractions were dried and quantified. Phospholipid and glycolipid contents in the TFPL were estimated according to the method of Stewart (1980) and Morrison (1986) and Dubois, Gilles, Hamilton, Rebers and Smith (1956), respectively. Triglyceride content in TFNPL was estimated by the method of Fletcher (1968). Each analysis was replicated four times, expressed on a dry basis and statically analysed by Duncan's new multiple range test (Steel & Torrie, 1980).

The fractionated TFNPL and TFPL were saponified and methylated with 14% BF_3 in methanol in order to prepare fatty acid methyl esters (FAME) (Morrison & Smith, 1964).

2.3.1. FAME analysis by gas chromatography (GC)

The FAMEs were analysed by capillary GC (14 B Shimadzu, German) with an omega wax capillary column (Supelco, Bellefonte, PA, USA) (30 m × 2 mm i.d.) fitted with ionization detector and connected to an online CR-4A chromatorpac integrator. The operating conditions were column temperature 160°C, injection temperature 210°C and detector temperature 250°C. Column temperature was programmed to rise 10°C/min and final temperature was 240°C. Nitrogen gas (30 ml/min) was used as carrier. Individual fatty acids were identified and quantified by comparing their authentic standards. Each sample was done in duplicate.

3. Results and discussion

3.1. Quality characteristics of wheat

The wheat used in the mill had the following quality characteristics on 14% mb; ash 1.6%; falling number 392; SDS-sedimentation value 49 ml and protein 10.7%. This indicated the medium hard nature of the wheat used in the study. The total free lipid (TFL) content in wheat was 1.3% and the TFNPL and TFPL lipid contents were 1.0 and 0.3%, respectively.

3.2. Lipid content in flour streams

The TFL content in flour streams ranged from 0.65 to 2.14%. The last break stream had the maximum value of TFL while the minimum value was in I BK. This is possibly due to increase in the concentration of germ as well as bran and aleurone layer in later stages of break which are rich in lipid. In general, the break flour stream had a higher content of the TFL than the reduction stream.

3.2.1. Total free non-polar lipid (TFNPL)

Table 1 indicates an increase in TFNPL content from 0.54 to 1.8% as the grinding progresses from first to fourth break, possibly due to increase in the concentration of lipid-rich germ fraction in the later stages of breaks. The highest content of TFNFL was found in the IV break system. Similarly, an increasing TFNPL content from 0.64 to 1.16% was observed for flour in the progressive reduction passage system. This could be due to the release of more lipids from germ into flour as the germ gets pressed in a series of reduction rolls (Morrison, Coventry & Barnes, 1982). The maximum value was found in the sixth reduction flour stream.

Among the TFNPL fractions, triglyceride (TGL) content was greater than MG, DG and FFA. This was

Table 1
Composition of free lipids in milled streams

Sample code	Total free lipids (%)[a,b]	Free non-polar lipids (%)[a,b]			Free polar lipids (%)[a,b]		
		Total (%)	TGL (%)	DG, MG, FFA (%)	Total (%)	Glycolipids (%)	Phospholipids (%)
Break flours							
I Break	0.650k	0.540h	0.390m	0.150 l	0.110 l	0.090i	0.020d
II Break	1.170d	0.970e	0.710e	0.260e	0.200f	0.180d	0.020d
III Break	1.810b	1.520b	1.110b	0.410b	0.290b	0.280b	0.010e
IV Break	2.140a	1.800a	1.300a	0.500a	0.340a	0.300a	0.040b
Grader	1.160d	0.950e	0.700f	0.250f	0.210e	0.140f	0.070a
Reduction flours							
Semolina passage	0.770I	0.640g	0.470k	0.170j	0.130k	0.090i	0.040b
1st middling	0.960 f	0.800f	0.580n	0.220g	0.160h	0.130g	0.030c
2nd middling	0.830g	0.680g	0.490j	0.190i	0.150i	0.110h	0.040b
3rd middling	0.700j	0.570h	0.420l	0.150k	0.130k	0.090i	0.040b
4th middling	1.370c	1.130d	0.830d	0.300c	0.240c	0.220c	0.020d
5th middling	0.800h	0.660g	0.530i	0.130m	0.140j	0.110h	0.040b
6th middling	1.370c	1.160c	0.890c	0.270d	0.230d	0.220c	0.010e
Straight run	1.000e	0.820f	0.610g	0.210n	0.180g	0.160e	0.020d
S.E.M.[c] (±)	0.007						

[a] Percentage based on flour weight basis.
[b] Near values are for a particular column with different letter differ significantly ($P < 0.05$).
[c] Standard error of means at 39 df.

found to be true in all break and reduction streams. The TGL content ranged from 72.1 to 80.3% of the TFNFL except in the case of the fifth middling, which had a higher value of 80.3%. Among the mill streams, the highest content of TGL was found in the IV BK (1.3%) and lowest content was found in the I BK (0.39%).

3.2.2. Total free polar lipid (TFPL)

The TFPL also increased from 0.11 to 0.34% as grinding progressed from the I to the IV break while it increased from 0.13 to 0.24% in the reduction passage. The last passage of break (IV break) contained the maximum amount of TFPL possibly due to extraction of the aleurone layer adhering to the bran which contained a higher amount of TFPL (Morrison, 1979; Morrison & Barnes, 1983; Morrison et al, 1982; Morrison & Hargin, 1981). The TFPL content in different streams was low and it ranged from only 16.0 to 19.1% of the total free lipid content.

Among the TFPL fractions, glycolipids are predominant and ranged from 66.7 to 95% of the TFPL in different streams. Highest content was found in the IV Break (0.3%) and lowest content in the I Break (0.09%) and semolina passage (0.09%). But, in the case of phospholipid, the highest value was found in the IV break and many of the reduction passages, and lowest value was in the III break and last reduction passage (0.01%).

The straight run flour had TFNPL and TFPL contents of 0.80 and 0.180%, respectively. These values were comparable to calculated values from the sum of lipid contents in different streams expressed as percentage of total flour yield (Table 2).

Cumulative TFNPL and TFPL contents of flour streams drawn against cumulative flour yield are depicted graphically in Figs. 1 and 2, respectively. These curves are similar to the well known "ash curve". These typical lipid curves enable the miller to select suitable streams for blending to obtain flour with desired levels of FPL and FNPL lipid content.

Table 2
Mass balance of total free non-polar and total free polar lipid content in milled streams

Sample code	Flour yield (%)	Total free non-polar units	Total free polar lipid units
Break flour			
I Break	1.50	0.0081	0.0017
II Break	4.20	0.0410	0.0084
III Break	0.60	0.0090	0.0017
IV Break	2.30	0.0410	0.0078
Grader	5.60	0.0530	0.0120
Reduction flour			
Semolina passage	10.70	0.0680	0.0140
1st middling	20.10	0.1610	0.0322
2nd middling	16.10	0.1090	0.0242
3rd middling	9.10	0.0520	0.0275
4th middling	10.70	0.1210	0.0260
5th middling	15.40	0.1020	0.0220
6th middling	3.70	0.0430	0.0078
Straight run flour			
Calculated		0.8081	0.1690
Estimated		0.8200	0.1800

3.3. Fatty acid composition of flour streams

The percentage of different fatty acids present in the milled streams was calculated, based on the individual peak areas of corresponding chromatograms, and the results were expressed on the basis of FAME recovered. To allow positive identification of the fatty acid, standards were run along with the samples.

3.3.1. Fatty acid composition of free non-polar lipids (TFNPL)

The fatty acid composition of TFNPL given in Table 3 indicates that, among the saturated fatty acids, palmitic acid was predominant and it ranged from 17.4 to 23.4%. The highest content of palmitic acid (29.3%) was found in the semolina passage. This is possibly due to accumulation of more central endosperm from the

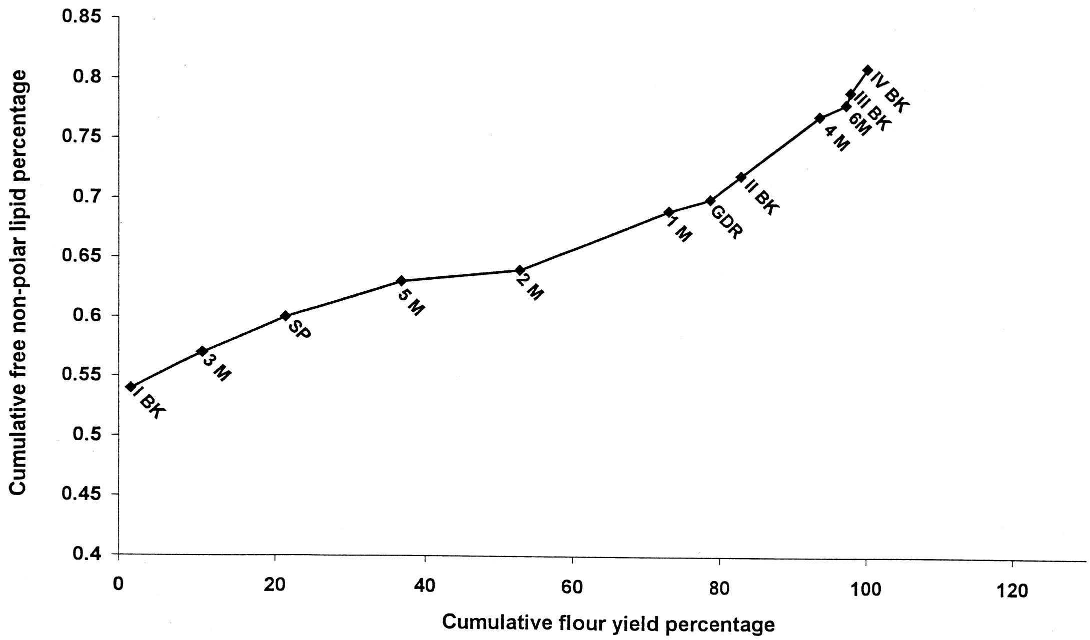

Fig. 1. Typical free non-polar lipid curve of milled streams.

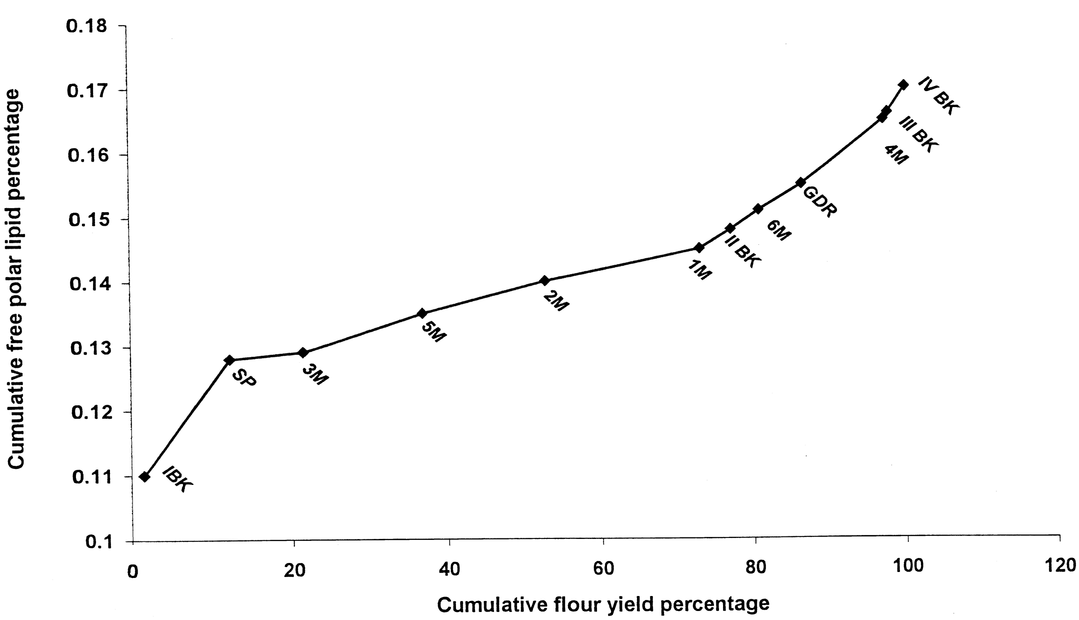

Fig. 2. Typical free polar lipid curve of milled streams.

Table 3
Fatty acid composition of lipid fractions of milled streams

Sample code	$C_{14:0}$ (%)[a]		$C_{16:0}$ (%)[a]		$C_{18:0}$ (%)[a]		$C_{18:1}$ (%)[a]		$C_{18:2}$ (%)[a]		$C_{18:3}$ (%)[a]	
	NP[b]	P[b]	NP	P	NP	P	NP	P	NP	P	NP	P
I Break	2.1	0.8	20.8	20.0	2.9	25.2	33.6	14.6	38.2	30.7	2.4	8.7
II Break	0.7	0.7	21.3	18.4	3.1	24.0	18.4	10.8	52.6	38.9	3.8	7.4
III Break	1.2	1.0	20.0	19.8	2.0	24.2	20.1	9.9	52.6	37.3	4.1	7.8
IV Break	1.8	0.9	20.1	18.9	1.6	21.6	22.6	13.8	50.0	31.3	3.9	9.0
Grader	0.8	1.8	23.4	18.1	2.3	17.9	20.1	9.9	51.0	40.6	4.1	11.7
Reduction flours												
S P	1.2	0.6	29.3	18.9	2.0	19.2	16.9	11.1	43.4	39.8	2.9	10.4
1st middling	1.8	1.0	21.9	18.9	1.8	22.0	17.5	9.6	58.8	41.5	4.0	7.0
2nd middling	0.7	0.7	23.2	21.5	1.6	20.2	18.2	10.9	53.3	41.4	3.4	3.6
3rd middling	0.4	1.7	17.4	17.2	2.1	20.8	19.9	11.1	58.3	40.8	3.2	5.8
4th middling	1.4	0.8	21.2	20.5	2.6	21.9	19.4	11.2	56.0	40.9	3.2	5.6
5th middling	1.2	0.8	21.7	16.1	1.4	20.7	19.5	9.1	52.8	44.2	3.7	8.5
6th middling	0.7	0.7	20.9	18.1	1.6	19.6	19.6	9.7	54.6	42.1	3.8	8.3
Straight run flour	0.6	4.1	21.4	16.8	1.6	20.9	18.1	9.8	52.7	40.5	3.0	7.6

[a] Percentage based on FAME recovery.
[b] NP, total free non-polar lipids; P, total free polar lipids.

wheat grains, which is rich in palmitic acid (Morrison & Barnes, 1983). Myristic and stearic acid contents, present in the mill streams in general are much lower than palmitic acid. The stearic acid ranges from 1.4 to 3.1% whereas myristic acid ranges from 0.4 to 2.1% in TFNPL extracted from different mill streams.

Among the unsaturated fatty acids, linoleic acid was the predominant acid among the lipids of different

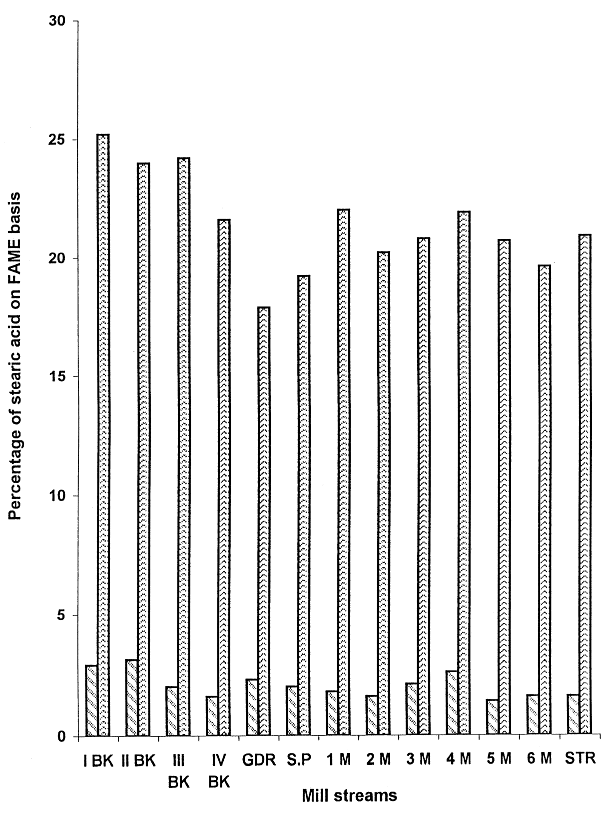

Fig. 3. Percentage of stearic acid content in TFNPL and TFPL of milled streams.

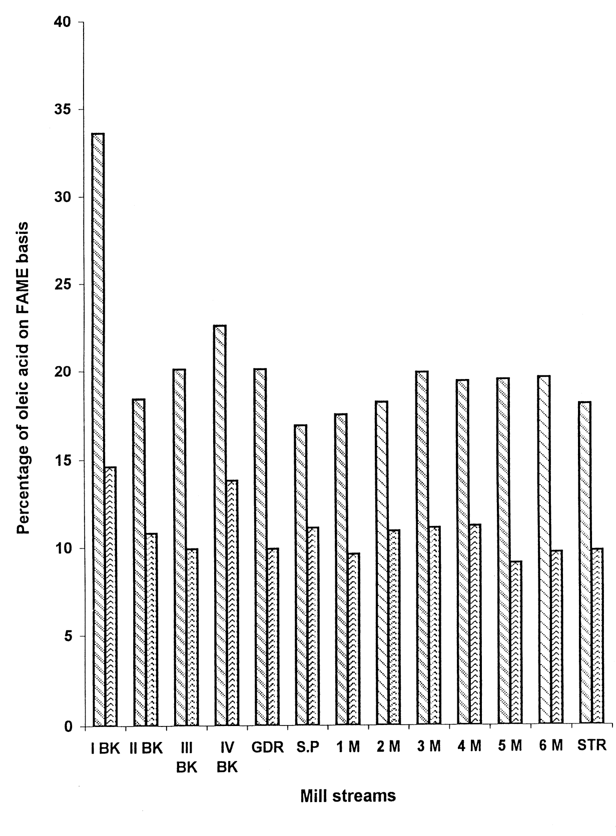

Fig. 4. Percentage of oleic acid content in TFNPL and TFPL of milled streams.

streams. The highest content of 58.5% linoleic acid was found in the 1st middling and the lowest content of 38.2% in the I break passage. Since, in the initial break passage, grains are opened, most of the flour originates from the central portions of endosperm which are low in linoleic acid content whereas, at the reduction stages, maximum amount of lipid is due to extraction of the aleurone layer adhering to the bran which contains higher amounts of linoleic acid (Morrison & Hargin, 1981). After linoleic acid, oleic acid content ranged from 16.9 to 33.6% whereas linolenic acid content was low and it ranged from 2.4 to 4.1%.

3.3.2. *Fatty acid composition of free polar lipids (TFPL)*

The fatty acid composition of TFPL given in Table 3 indicates that stearic acid was the predominant acid among the saturated fatty acids and it ranged from 17.9 to 25.2%. These results are different from those present in TFNPL where palmitic acid was predominant. The highest stearic acid content of 25.2% was present in the I break whereas the lowest content was present in the semolina passage. Palmitic acid ranged from 16.1 to 21.5% followed by myristic acid (0.6 to 1.7%) in the streams. Levels of stearic acid are greater in TFPL than in TFNPL obtained from streams (Fig. 3). In general,

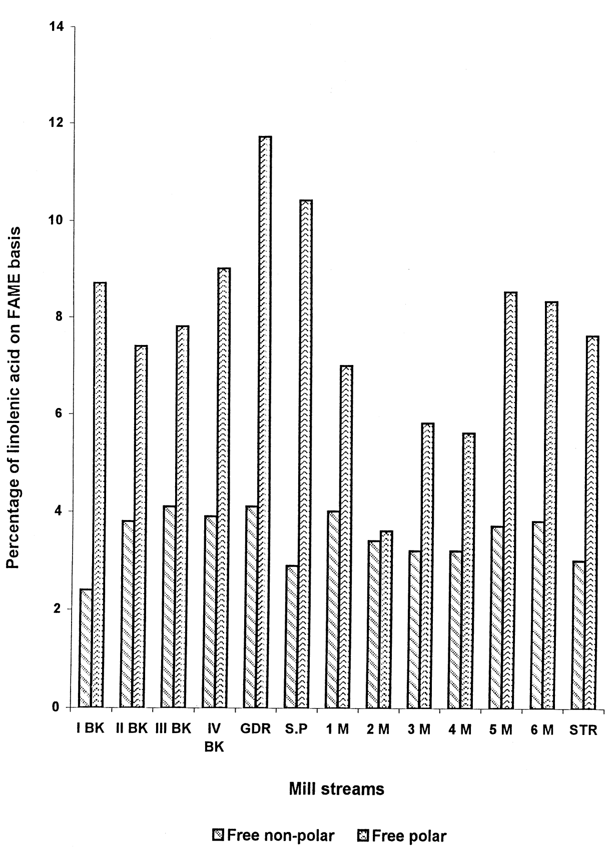

Fig. 5. Percentage of linolenic acid content in TFNPL and TFPL of milled streams.

break stream flours contained more stearic acid than reduction stream flows.

In the case of unsaturated fatty acids, linoleic acid was the predominant acid present in the streams. The highest content of linoleic acid of 44.2% was present in the fifth middling, while the lowest content of linoleic acid of 30.7% was present in the first break. Linoleic and oleic contents were lower in TFPL than in TFNPL. The oleic acid ranged from 9.1 to 13.8% in TFPL whereas it ranged from 16.9 to 33.6% in TFNPL (Fig. 4). But linolenic acid content is higher in TFPL than in TFNPL. It ranged from 3.6 to 10.4% in TFPL whereas, in TFNPL, it ranged from 2.4 to 4.1 (Fig. 5). In general, break stream flours contained lower amounts of linoleic acid than reduction streams.

4. Conclusions

TFNPL, TFPL and their fatty acid composition in commercially milled streams indicated that TFNPL preponderated over TFPL among the milled streams. Among TFNPL fractions, TGL was predominant whereas, in the case of TFPL, glycolipid was predominant. Maximum levels were found in the IV break passage. Palmitic acid was the predominant saturated fatty acid in TFNPL, whereas stearic acid was predominant in TFPL. Maximum level of palmitic acid was present in the semolina passage of TFNPL. Maximum level of stearic acid was present in the I break of TFPL. In the case of unsaturated fatty acids, linoleic acid is predominant in both TFNPL and TFPL. But the level of oleic acid was lower in TFPL than in TFNPL, whereas, level of linolenic acid was greater in TFPL than in TFNPL. In general, break flour contained more amounts of TFL and its fractions than reduction streams. With respect to fatty acids, linoleic acid was predominant acid in both TFNPL and TFPL.

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