hydrolysis of glucosinolates and not to the partial pyrolysis of glucosinolates (3,5) since heating of the boiled rapeseed did not increase the sulfur level of the oil.

The Effect of pH

The pH during boiling of the ground seed (1) had a significant effect on the sulfur level in the oil (Fig. 1). The sulfur content of the oil increased with increasing pH from ca. 2 ppm at pH 3.1 to ca. 10 ppm at pH 7.6. This could be due to the fact that when the ground rapeseed in the form of clumps was added to the boiling water, inactivation of myrosinase was not instantaneous, especially in the core of the clumps. Before the enzyme inactivation, hydrolysis of the glucosinolates could occur; the extent of this hydrolysis appears to be pH dependent as shown previously by Sosulski et al. (6).

The effect of pH during the subsequent stirring of the boiled ground rapeseed (1) was also examined. However, pH adjustments between 3.9 and 9.7 caused no variation in the sulfur content of the oil.

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The Effect of Processing Operations on the Total Sulphur Content in Rapeseed Oil

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ABSTRACT

The technological difficulties due to the presence of sulphur-containing compounds in rapeseed oil lead to the problem of proper hydrogenation under commercial conditions. The effect of refining operations on the total sulphur content of rapeseed oil was studied. Degumming (phosphoric acid treatment) had an insignificant effect on the sulphur content while deacidification (alkali refining) removed about 30% and bleaching with Fuller's earth removed about 50% of the total sulphur in commercial crude oil. Deodorization affected nearly the complete removal of residual sulphur left after the application of treatments mentioned above.

INTRODUCTION

Today rapeseed ranks fifth among the major oilseeds of the world and is on top in Pakistan. Rapeseed oil, the bulk of which is produced by expression, particularly in developing countries, is mainly processed in the same way as other vegetable oils. The main aim of processing or refining is to remove impurities that contribute unpleasant flavor, which in case of rapeseed oil is chiefly due to sulphur compounds. The level of sulphur compounds (isothiocyanates) in crude rapeseed oil depends on the species, pre-extraction treatment of the seed, and the method of extraction (1-4).

Besides being responsible for undesirable flavors, the presence of sulphur compounds is not only nutritionally objectionable but also causes severe catalyst poisoning during the process of hydrogenation (5-7). The other natural impurities that need elimination to the maximum are free fatty acids, mono- and diglycerides, phosphatides, pigments, proteins and various oxidation products. The processing of rapeseed oil normally consists of degumming, deacidification, bleaching and deodorization. The influence of these unit operations on the total sulphur content of rapeseed oil was studied under industrial conditions.

MATERIAL AND METHODS

Commercially available crude rapeseed oil was analyzed for various physical and chemical characteristics (8) and subjected to processing under industrial conditions at the local processing plant of Morafco Industries Ltd., as given below.

Degumming. The crude oil heated to 70 C in the preneutralizer was treated with 4000 ppm of food grade, 85% phosphoric acid, mixed for 30 min by slow speed mechanical mixer, allowed to settle, centrifuged and finally washed with water at 40 C.

Deacidification. The degummed oil was sprayed over with 15Bé alkali (NaOH – caustic soda) solution at 45 C. The amount of alkali varied according to the free fatty acid content of the oil lot. After contact time of 15 min the mixture was heated to 70 C to facilitate the "break" of emulsion. The soap-stock was separated after settling for 45 min. The neutralized oil so obtained was washed with water to eliminate traces of soap.

Bleaching. The deacidified oil was charged into a bleaching vessel and heated to 90 C under vacuum to ensure complete drying. A mixture of acid-treated Fullers' earth and activated charcoal (20:1) at ca. 3% of the oil volume was added at 85 C and mixed by mechanical agitation for 15 min. Then the oil was cooled to 70 C and filtered through filter press.

Deodorization. The bleached oil was then deodorized under vacuum in steam-stripping conditions (200 C, 6 mm pressure) for 8 hr to remove odor volatiles present in the oil. The deodorized oil was cooled to 50 C before discharging it to storage tanks.

In the first run, ten different batches (each 2 to 2.5 tons) of oil were processed per detail given above, and the sulphur content of the oil in the form of allylisothiocyanate was estimated according to the method

TABLE I

Physical and Chemical Characteristics of Commercial Batches of Rape/Mustard Seed Oil

Specific gravity (20 C/20 C)	0.916-0.920
Refractive index (n_D 40 C)	1.474-1.462
Saponification value (mg KOH/g oil)	171-179
Iodine value (wi js)	105-112
Unsaponifiable residue (%)	1.60-1.81
Acid value (mg KOH/g oil)	0.92-1.16

TABLE II

Residual Sulphur Contents (PPM) in Ten Batches of Rape/Mustard Seed Oil after Each Processing Treatment

Batch	Raw oil	Degummed	Deacidified	Bleached	Deodorized
1	94	117	23	12	5
2	200	200	106	83	5
3	117	117	59	23	0
4	70	59	35	23	5
5	83	83	41	23	0
6	83	70	83	46	0
7	128	190	93	70	0
8	140	152	129	64	0
9	106	117	85	70	5
10	233	129	152	140	5
Mean	125.5	123.4	80.6	55.4	2.5
SD	53.19	47.03	41.76	38.79	2.64
LSD (0.05) between means = 22.9					

TABLE III

Effects of Processing Treatments (Except Degumming) on the Residual Sulphur Contents (PPM) of Rape/Mustard Seed Oil

Batch	Raw oil	Deacidified	Bleached	Deodorized
1	167	140	117	5
2	140	70	46	5
3	94	46	29	0
4	167	117	70	5
5	140	117	70	0
Mean	141.6	98.0	66.4	3.0
SD	29.84	38.65	33.17	2.74
LSD (0.05) between means = 18.5				

described by Wetter (9). The data was statistically analyzed by analysis of variance (10).

RESULTS AND DISCUSSION

The oil traded in Pakistan as "rapeseed oil" is derived mostly from *Brassica juncea* L. by pressing and is mainly used for edible purposes. The chemical and physical characteristics of different oil batches are given in Table I. These are the characteristics involved in fulfilling requirements of the recommended international standard (11).

The method described by Wetter (9) was adopted to determine sulphur using a solution of myrosinase for hydrolysis (pH 4.0). The data in Tables II and III show mean values of three parallel determinations of each batch except ≠4 and 10 (Table II) where five determinations were made for crude samples only. The coefficient of variation (CV) between determinations in the batches were 4.1% and 0.9% respectively.

Table II shows the residual sulphur content of different batches of crude (raw) rapeseed oil, and after each process treatment. The crude rapeseed oil from different batches showed much variation in sulphur contents. The sulphur content in rapeseed oil originates mainly from sulphur-containing glucosinolates in the seed (12) and is much dependent on the pre-extraction treatment of the seed (13). Zeman and Zemonova (2) reported 100-200 ppm isothiocyanates in the expelled oil and 1800-4600 ppm in extracted oil. Franzke et al. (14) reported 10 ppm isothiocyanates in the expelled oil and 100 ppm in extracted oil.

The oil from all batches showed reduction in sulphur content after each treatment except degumming. The fully processed rapeseed oil contained only traces of sulphur (mean value: 2.5 ppm). Daun and Hougen (15) reported that crude rapeseed oil contained 10-50 ppm sulphur and that this sulphur was mostly removed by conventional processing. The analysis of data in Table II eliminating batch variation, indicated highly significant variation between treatments. The least significant difference at the 0.05 level (LSD 0.05) was 22.9. Removal of sulphur from the oil batches under study was significant at all stages except degumming.

In the follow-up five batches of rapeseed oil were processed in the prescribed manner except the phosphoric acid treatment (degumming). The results are given in Table III. In this set of experiments, the statistical analysis of data revealed a significant decrease in sulphur content after each treatment (LSD 0.05 = 18.5). The omission of degumming did not present any serious problem of emulsification at later stages and as such offers great economic impact in the whole refining operation of rapeseed oil leading to a savings of both time and money. In both sets of experiments the maximum reduction in sulphur content occurred during the deodorization process.

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