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CHEMIMECHANICAL PULP FROM REED

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RÉSUMÉ

Le but de la présente recherche est d'explorer le potentiel d'utilisation du roseau, une plante abondante en Chine, comme matière première de fabrication de pâte chimico-mécanique (CM) de bonne qualité. Dans le travail expérimental, les copeaux de roseau furent soumis à une cuisson au sulfite en phase liquide ou phase vapeur, suivie d'un raffinage. Les propriétés physiques de cette pâte ont été évaluées; et le blanchiment à l'hypochlorite et au peroxyde a été étudié.

Une série de cuissons sulfitiques en phase liquide ont été effectuées en utilisant une grande gamme de conditions expérimentales, ce qui nous a permis d'atteindre des rendements de 72% à 78%, et ces pâtes possédaient les caractéristiques suivantes à 150 mL CSF: 1) longueur de rupture: 4.5 - 6.0 km; 2) indice d'éclatement: 2.2 - 3.2 kPa.m^2/g; 3) indice de déchirure: 5.2 - 6.2 mN.m^2/g; 4) volume spécifique (main): 2.2 - 2.8 cm^3/g; 5) blancheur: 32 - 43%; 6) opacité: 93 - 95%. Les effets des variables de cuisson sur les caractéristiques de la pâte ont été examinés. Les propriétés mécaniques des pâtes CM obtenues sont comparables à celles des pâtes de roseau produites avec de la soude. Cependant la pâte CM

sulfitique possède un rendement supérieur à la pâte sodique.

Une autre série de cuissons en phase vapeur ont été réalisées en recyclant la liqueur d'imprégnation. Le processus de cette opération de recyclage offre deux avantages: 1) récupération du SO_2 non utilisé dans la liqueur et 2) réduction de l'énergie thermique durant la cuisson. La liqueur d'imprégnation fut recyclée jusqu'à 17 fois. Aucun effet significatif du recyclage sur les valeurs du rendement de cuisson et des propriétés des pâtes n'a été observé. Dans cette série d'expériences, la dose de SO_2 total a été fixée à 15%, basée sur des copeaux séchés à l'étuve. Une récupération moyenne de SO_2 de 65% (en rapport avec la charge initiale de SO_2 dans le stade d'imprégnation) a été atteinte. La consommation moyenne de vapeur pour le chauffage direct durant la cuisson à température maximale a été de 0.8 kg/kg de copeaux secs. Les pâtes obtenues par cuisson en phase vapeur montrent des caractéristiques similaires à celles obtenues en phase liquide.

Au blanchiment de la pâte CM de roseau, nous avons étudié l'influence de l'application de doses différentes d'hypochlorite et de peroxyde, en accentuant l'effet de l'alcalinité sur les résultats de la blancheur. Ceux-là indiquent que la pâte CM de roseau réagit positivement à l'hypochlorite et au peroxyde dans la séquence à deux stades. Sous des conditions de blanchiment optimales, un gain de plus de 40 points de blancheur (de 32% à 78%) a été noté avec 8% d'hypochlorite et 2% de peroxyde. Les caractéristiques mécaniques de la pâte ont été améliorées de façon significative après blanchiment, mais on note une baisse de rendement se situant entre 8 et 10%. En d'autres termes, le rendement de la pâte (sur des copeaux séchés à l'étuve) fut d'environ 70%.

De ces résultats, on peut conclure que la pâte de roseau convient au procédé chimico-mécanique. Cette pâte recèle de bonnes propriétés mécaniques et optiques et elle est sans doute utile à la production de papiers journal, d'impression, d'écriture et de papiers fins.

SUMMARY

The objective of the present research is to explore the possibility of using reed, an abundant annual plant in China, as a raw material for chemimechanical (CM) pulping to produce pulps with good quality. In the experimental work, reed chips were subjected to liquid-phase or vapour-phase sulfite cooking, followed by refining; pulp properties were then evaluated. The bleaching response of reed CM pulp to hypochlorite and peroxide was studied as well.

One series of liquid-phase sulfite cookings were carried out in a laboratory digester, under very wide range of experimental conditions. Within the range studied, it was possible to attain a yield of 72% to 78%, and the pulps showed the following characteristics, at 150 mL CSF: 1) Breaking length: 4.5 - 6.0 km; 2) Burst index: 2.2 - 3.2 kPa.m^2/g; 3) Tear index: 5.2 - 6.2 mN.m^2/g; 4) Bulk: 2.2 - 2.8 cm^3/g; 5) Brightness: 32 - 43%; 6) Opacity: 93 - 95%. The effects of cooking variables on pulp characteristics were investigated. The strength properties of the CM pulps obtained in this study were comparable to those of the conventional reed soda pulp, while the former possessed a much higher yield than the latter.

Another series of vapour-phase cooking experiments were conducted with recycling of the spent impregnation liquor. The recycling operation rendered the process two main advantages: 1) recovery of the unused SO_2 in the spent liquor, and 2) reduction of the heating energy during cooking. The spent impregnation liquor was recycled up to 17 times. No significant effect of recycling on cooking yield and pulp properties was observed. In this series of experiments, the total SO_2 charge was fixed at 15%, based on o.d. reed chips. An average SO_2 recovery of 65% (with respect to the initial SO_2 charged in the impregnation stage) was attained. The average steam consumption for direct heating during cooking at maximal temperature was about 0.8 kg/kg o.d. chip. The pulps obtained from vapour-phase cooking exhibited similar characteristics to those obtained from liquid-phase cooking.

As to the bleaching of reed CM pulp, the application of hypochlorite and peroxide was studied, emphasizing the effects of alkalinity and charges of hypochlorite and peroxide on bleaching outcome. Results indicated that reed CM pulp responded well to hypochlorite and peroxide in a two-stage sequence. Under optimum bleaching conditions, more than 40 points in brightness gain (from 32% to 78%) could be achieved with 8% hypochlorite and 2% peroxide. The strength characteristics of the pulp were significantly improved after bleaching, but at the expense of a yield loss ranging from 8% to 10%; in other words, the overall pulp yield (on o.d. reed chips) was around 70%.

From the results of the present work, it can be concluded that reed pulp could be properly fabricated through the chemimechanical process. Reed CM pulp displays good strength properties, as well as good bleachability, it would be thus a potential furnish in the production of newsprint, printing, writing and fine papers.

TABLE OF CONTENTS

page

ACKNOWLEDGEMENT i

RÉSUMÉ ii

SUMMARY v

TABLE OF CONTENTS viii

LIST OF FIGURES xii

LIST OF TABLES xv

CHAPTER 1 INTRODUCTION 1

CHAPTER 2 BIBLIOGRAPHY SURVEY 4

- 2.1 INTRODUCTION 4
- 2.2 STRAW PULPING IN CHINA 6
  - 2.2.1 Characteristics of non-wood fibres . . 6
  - 2.2.2 Major pulping processes for reed straw 9
- 2.3 CHEMIMECHANICAL PULPING 11
  - 2.3.1 Mechanism of CM pulping 12
  - 2.3.2 Factors affecting CM pulping 13
  - 2.3.3 CM pulping of non-wood fibres 14
  - 2.3.4 Vapor-phase CM pulping 19
  - 2.3.5 Characteristics and utilization of CM pulp 21
  - 2.3.6 Influence of CM pulping on environment 22
- 2.4 BLEACHING OF MECHANICAL PULP 22
  - 2.4.1 Factors affecting peroxide bleaching . 23

CHAPTER 3 EXPERIMENTAL 29

3.1 PREPARATION OF CHIPS 29

3.2 COOKING 30

3.2.1 Preparation of fresh liquor 30

3.2.2 Liquid-phase cooking 31

3.2.3 Vapor-phase cooking 33

3.2.4 Spent liquor recycling 34

3.3 DEFIBRATION AND REFINING 36

3.4 PULP EVALUATION 37

3.4.1 Pulp testing 37

3.4.2 Sulphonate content of pulp 37

3.5 BLEACHING 39

3.5.1 Preparation of pulp 39

3.5.2 Preparation of bleaching liquor . . . 39

3.5.3 Bleaching methods and conditions . . . 40

CHAPTER 4 RESULTS AND DISCUSSION 43

4.1 LIQUID-PHASE CM PULPING OF REED 43

4.1.1 Pulping yield 43

4.1.2 Effects of cooking variables on pulp properties 48

4.1.3 Relationships between pulp properties 61

4.1.4 Refining energy 64

4.1.5 Effect of SO_2 charge on residual SO_2 . 76

4.2 PULPING WITH VAPOR-PHASE COOKING 80

4.2.1 Cooking without spent liquor recycling 80

4.2.2 Cooking with spent liquor recycling . 82

4.2.2.1 Pulp yield and refining energy 82

4.2.2.2 Handsheet Characteristics . . 85

4.2.2.3 Effects of refining energy on physical properties 90

4.2.2.4 Spent impregnation liquor Characteristics 92

4.2.2.5 Pollution 100

4.2.2.6 Comparisons of pulps produced from different processes . 104

4.3 BLEACHING OF REED CM PULP 106

4.3.1 Effects of peroxide and total alkalinity charges 106

4.3.2 Two-stage HP bleaching 112

4.3.3 Effect of bleaching on pulp yield . 114

4.3.4 Pulp opacity after bleaching 118

4.3.5 Effects of HP bleaching on physical properties 121

4.3.6 Effects of cooking liquor pH and SO_2 charge on brightness 123

CHAPTER 5 CONCLUSIONS 129

5.1 LIQUID-PHASE CM PULPING OF REED 129

5.2 VAPOR-PHASE CM PULPING OF REED 130

5.3 RECYCLING OF SPENT IMPREGNATION LIQUOR FOR PULP PRODUCTION 131

5.4 BLEACHING 131

5.5 GENERAL REMARKS 132

REFERENCES 134

APPENDIX 138

LIST OF FIGURES

Page

Figures

1 Effect of fresh liquor pH on yield 44

2 Effect of SO_2 charge on yield 45

3 Effect of cooking time on yield 47

4 Effects of fresh liquor pH (4.5-12) on physical properties 49

5 Effects of fresh liquor pH (7.5-12) on physical properties 51

6 Brightness versus cooking liquor pH 52

7 Opacity versus cooking liquor pH 53

8 Effects of SO_2 charge on physical properties 55

9 Effects of sulphonation on yield and physical properties 56

10 Brightness versus SO_2 charge 58

11 Opacity versus SO_2 charge 59

12 Physical properties versus cooking time 60

13 Relationship between breaking length and yield 62

14 Physical properties versus breaking length 63

15 Effect of fresh liquor pH on specific refining energy 67

16 Specific refining energy versus SO_2 charge 68

17 CSF versus specific refining energy 70

18 Bulk versus CSF 71

19 Relationships between physical properties and CSF . . 72

20 Brightness versus CSF 73

21 Opacity versus CSF 74

22 Residual SO_2 versus SO_2 charge at two levels of pH . . 77

23 Residual SO_2 versus SO_2 charge at two levels of cooking time 78

24 Relationship between yield and number of recyclings . 83

25 Specific refining energy versus number of recyclings . 84

26 CSF versus specific refining energy 86

27 Physical properties versus number of recyclings . . . 87

28 Brightness versus number of recyclings 88

29 Opacity versus number of recyclings 89

30 Physical properties versus CSF 91

31 Relationship between spent liquor pH and number of recyclings 93

32 Relationship between spent liquor density and number of recyclings 94

33 Relationship between spent liquor volume and number of recyclings 96

34 Percent of the SO_2 charge recovered versus number of recyclings 98

35 Relationship between cooking condensate volume and number of recyclings 99

36 Percent of the SO_2 charge appearing in cooking condensate versus number of recyclings 101

37 Stripped SO_2 in condensate versus number of recyclings 102

38 Relationship between cooking condensate pH and number of recyclings 103

39 Effect of NaOH charge on brightness 109

40 Effect of peroxide charge on brightness 111

41 Effect of NaClO charge on brightness 113

42 Effect of NaClO charge on yield 115

43 Effect of H_2O_2 charge on yield 116

44 Bleaching yield versus NaClO charge at a given H_2O_2 charge 117

45 Effect of NaClO charge on opacity 119

46 Opacity versus NaClO charge for 2% H_2O_2 and 1.5% NaOH 120

47 Physical properties versus NaClO charge 122

48 Comparisons of physical properties between bleached and unbleached pulps 124

49 Brightness versus pH of cooking liquor 125

50 Brightness versus SO_2 charge in cooking liquor . . . 127

A1 Burst index versus CSF for pulp refined with blender and with PFI mill 139

A2 Breaking length versus CSF for pulp refined with blender and with PFI mill 140

A3 Tear index versus CSF for pulp refined with blender and with PFI mill 141

A4 Bulk versus CSF for pulp refined with blender and with PFI mill 142

LIST OF TABLES

Page

TABLES

1 Chemical analysis: basic properties of non-woods . . . 7

2 Fibre dimensions (in microns) of non-woods and woods . 7

3 Characteristics of reed straw used in the study . . . 8

4 Properties of papers made from reed chemical pulps . . 10

5 Size distribution of reed chips 30

6 Conditions used for liquid-phase cooking 32

7 Conditions used for vapor-phase cooking without and with recycling spent impregnation liquor 35

8 Bleaching conditions for Hypochlorite-Hydrogen peroxide sequence 41

9 Specific refining energy for liquid-phase reed CM pulp 65

10 Vapor-phase CM pulping without recycling of spent impregnation liquor 81

11 Comparisons of reed CM pulps with reed pulps produced from other processes 105

12 Bleaching of reed CM pulps with various processes . 107

CHAPTER 1 INTRODUCTION

Since decades, China has suffered a serious shortage of wood fibre source for pulp and paper industry. Actually, pulps made from wood represent only about 25% of the total pulp output, other 75% mainly from the non-wood raw material. The principal non-wood plant materials used in China for paper-making are: rice straw, wheat straw, bagasse, bamboo and reed. Among them, pulps from reed represent about 15% of the non-wood pulp production. Reed pulps have been widely used in the production of printing, writing and fine papers. Furthermore, unlike other non-wood plants which are cultivated or limited in certain regions, reed grows widely and abundantly in marshes throughout the country. Therefore, it is important and worthwhile to fully develop the potential use of reed in paper-making industry.

In China, most mills are pulp and paper integrated, the pulp production capacities are 20-50 t/d (metric ton/day) and 100-500 t/d, respectively, for small and big mills. In general, the big mills produce pulps from wood fibres, while the small ones use non-wood fibres. For reed pulping, the processes of kraft, sulfite and soda are employed. Pulping yield ranges from 40 to 45% for kraft, 45 to 55% for sulfite and 35 to 43% for soda process. None of these mills (small mills) possesses an effluent treatment system, it is thus one of their imperative tasks to find a solution for facing the government's anti-pollution regulations.

During last two decades, the demand for various papers is increasing rapidly in China. As an example, 4 million tons and 11.4 million tons of papers were manufactured in 1977 and 1987, respectively. The average annual increase rate was 10% for papers, and 5% for pulps. Consequently, about one million tons of pulps have to be imported each year from abroad; this is a big burden to China who has a limited foreign currency. Therefore, it is a challenge for China's pulp and paper industry to encounter the continuously increasing demand, bearing in mind that the main barriers are the shortage of wood-fibre resources, the very low yield of non-wood pulps, and the heavy pollution.

In recent years, the studies on chemimechanical (CM) and chemithermomechanical (CTM) pulping have brought forwards fruitful results that CM and CTM pulps have been widely used as furnish components for newsprint, printing and writing papers, as well as for computer and copying papers. Nevertheless, the CM or CTM pulping is still considered as a new technology in China, more studies are thus needed to implant this technology in

China's pulp and paper industry.

When taking into account the existing barriers in China's pulp and paper industry, the purpose of this research is to explore the use of non-wood plants, notably reed, as a raw material to produce CM pulp. The principal objectives are to obtain CM reed pulps having good quality, and to adapt a process (i.e., vapour-phase cooking) which would substantially reduce the cost in chemicals and heating energy, as well as the pollution of pulping effluent.

The study described in this thesis forms a part of the research program which is sponsored by the Canadian International Development Agency and carried out in the Centre de Recherche en Pâtes et Papiers of the Université du Québec à Trois-Rivières.

CHAPTER 2 BIBLIOGRAPHY SURVEY

2.1 INTRODUCTION

The increasing demand for paper production has induced a widespread search for fibrous raw materials other than wood. Non-wood fibre plays an important role in paper-making industry in the countries suffering from the shortage of wood fibre resources. The major non-wood fibre species used for pulping are wheat straw, rice straw, bagasse, and reed. The pulps from these non-wood plant present about 75% of the total pulp output in China, since the past few decades [1].

In the past two decades, high yield pulps have been experiencing a much more drastic pace in development than chemical pulp, several new type of pulps and technologies have been introduced, such as pressure ground wood (PGW) pulping, thermomechanical (TM) pulping, chemithermomechanical (CTM) pulping and Ontario Paper Company's high-yield pulping (OPCO), as well as chemimechanical (CM) pulping. CM pulping represents a technology combining the refiner mechanical pulping and the older high-yield sulfite cooking.

CM pulp exhibits better fibre flexibility than thermomechanical and other mechanical pulps but at the expense of reduced yield [12]. This manifests itself in higher sheet density and in such dependent properties as tensile index and burst index. The strength properties of CM pulp are closer to those of chemical pulp than mechanical pulp, while still possessing certain mechanical pulp characteristics such as good printability. CM pulp is suitable for use as a reinforcing pulp to replace chemical pulp in the production of newsprint as well as for use as a major furnish component for producing printing and writing papers.

The properties of CM pulps can be strongly modified by chemical treatment of chips, usually with sulfites, and more emphasis is being placed on preserving pulp yield and mechanical pulp characteristics. When employed in the production of printing and other paper grades, CM pulp can be bleached to high brightness with peroxide, while maintaining its high yield. Depending on raw material and chemical application level, unbleached pulp yield is practically in the range of 87% to 91% for softwood, and 80% to 88% for hardwood.

2.2 STRAW PULPING IN CHINA

2.2.1 Characteristics of non-wood fibres

Unlike wood, straw is a heterogeneous material, the stalk is separated at intervals by nodes. The open structure of straw material makes it easier to be penetrated with cooking liquor. Therefore, usually less chemical usage and cooking time is used. Chemical analysis of certain non-woods (Table 1) [2, 3] indicates that straw material has a very high ash content, mainly silica, especially for rice straw. Knowing that, for commonly used pulping woods, the amount of lignin is more than 25% in softwood and about 20% or less in hardwood, the lignin content of non-wood material is lower than that of softwood, but is comparable to hardwood. The extractives in 1% NaOH solution and in hot water are high in rice and wheat straws; amounting to 47.7 and 28.5%, respectively, for rice straw, and 44.6 and 23.2% for wheat straw. The fibre lengths of straws are comparable to that of hardwood (e.g., birch) and much shorter than that of softwood (e.g., spruce), as can be seen from Table 2 [3, 4]. On the other hand, the slenderness (i.e., the ratio of width to length) of straw fibres is higher than that of wood fibres.

The reed (*Phragmites Communis Trin*) used in the present

Table 1 Chemical analysis : basic properties of non-woods

	Rice straw	Wheat straw	Depithed bagasse	Reed straw
Ash, %	17.7	6.9	1.4	4.6
Lignin, %	11.4	16.9	22.0	20.0
Holocelluloses, %	65.1	68.7	66.4	78.0
1% NaOH soluble, %	47.7	44.6	29.1	34.9
Hot water soluble, %	28.5	23.2	2.3	6.9

Table 2 Fibre dimensions (in microns) of non-woods and woods

Type	Length	Width	Slenderness Width/length
Rice straw	1500	8.5	176
Wheat straw	1500	13.5	112
Bagasse	1700	20.0	85
Reed straw	1120	9.7	115
Birch	1200	18.0	66
Scan. spruce	3500	36.0	97

research was provided from the province of Heilongjiang in northern China. Since this species was the focus of the study, some of its important characteristics and chemical components are presented in Table 3 [4].

Table 3 Characteristics of reed straw used in the study.

Structural components	
Fibre, %	64.5
Vessel, %	6.9
Parenchyma cell, %	26.4
Epidermal cell, %	2.2
Chemical components	
Ash, %	3.0
Lignin, %	25.4
Pentose, %	22.5
Cellulose, %	43.6

This reed material has a high content (26.4%) of parenchyma cell which could cause poor drainage of pulp and is an undesirable component from the view point of papermaking. Its ash content is higher than that of wood material, for ash content rarely exceeds 0.5% in wood. The contents of lignin, pentose and cellulose are comparable to that of hardwood (e.g., white birch: lignin, 19.0%; pentose, 25,5%; cellulose, 44.5%).

2.2.2 Major pulping processes for reed straw

High yield pulping technique has not yet been employed in China for producing pulp from non-wood plant fibres. The major pulping processes currently used for reed pulp production are: kraft, sulfite and soda. Chemical reed pulp occupies an important position in printing paper manufacturing. As an example, about 731,000 tons of reed pulp (equivalent to 11.9% of the total pulp production) were produced in 1985 [1]. About 70% of these was used for printing grades, the other 30% mostly for writing grades and manila boards. Of the total reed pulp, 30% were produced from bisulphite, 8% from neutral sulfite, and 62% from alkaline (mostly sulfate) processes [5].

Strength properties of pulps made from these processes are similar in general, as presented in Table 4, except that a higher value in folding endurance is observed for neutral sulfite pulp. From a comparison among these pulps [5], magnesium bisulphite pulp has been reported to display superior opacity, plasticity, and ink receptivity, though low in breaking length. However, linting apparently is a major problem for papers made from this pulp. On the other hand, papers made from sulfate pulps are better in surface strength and caused less linting problems in press room operations, but opacity, plasticity and ink receptivity are inferior. Neutral sulfite pulps have the best strength properties, with others in between those of bisulphite and sulfate pulps.

Table 4 Properties of papers made from reed chemical pulps.

	Magnesium bisulphite	Neutral sulfite	Sulfate
Wet strength at 72% moisture, g	195-220	190-220	200
Folding, double fold	22-39	110-130	15
Tear, g	23-31	31	21
Breaking length, km	4.4-5.4	6.8	6.1
Opacity, %	89-91	78-85	80

Paper made from 100% reed; grammage, 52 g/m^2 [5].

In chemical recovery system, there are serious problems for straw cookings, due to the high contents of foreign matter and silica in straws. Spent liquor recovery is practically impossible for rice straw, and that for wheat straw also has certain problems with silica and fines. Recovery system has not yet been well established for reed bisulphite or neutral sulfite pulping, but has been in successful operation for reed sulfate pulping. However, the system exists only in big pulp and paper mills, and its efficiency is low [5]. As a fact, the investment of installing chemical recovery system is too high for small mills (20-50 t/d), coupling with high operation cost. China's pulp and paper industry has 1600 mills, only 35 of them have a capacity of 50-500 t/d, the rest has a capacity ranging from 20 to 50 t/d.

2.3 CHEMIMECHANICAL PULPING

Chemimechanical pulping represents a combination of chemical pretreatment (usually with sulfites) with mechanical refining. Before refining, chips are impregnated with chemicals and digested, then refined under atmospheric or high pressure. The usual objective of such chemical treatment is to improve the strength properties of the pulp, while maintaining as much as possible the advantages of mechanical pulp such as high yield, good printing properties, and low BOD loading. Chemical pretreatment leads to more selective fibre separation and results in a higher long fibre content and very much lower shives content. CM pulp exhibits better fibre flexibility than TMP and other mechanical pulps, but has a lower opacity and brightness [6].

2.3.1 Mechanism of CM pulping

Steam preheating and chemical pretreatment soften lignin by reducing the interchain hydrogen bonding and render it more hydrophilic. The steam-induced softening (as in TMP) is temporary, but the softening through a chemical pretreatment process is irreversible and depends on the extent of sulphonation reaction [7, 8]. Hence presteaming preserves fibre length, but without losing fibre flexibility. Sulphonation reaction involves interaction between bisulfite ion and the phenolic group of lignin, proceeding via a quinonemethide intermediate. As a result of sulphonation, highly ionized sulphonate groups on lignin soften the middle lamella of fibres and impart a permanent softening as well as more intact fibre liberation [9]. Thus CM pulping produces pulps with a higher tear index than that produced with TMP.

2.3.2 Factors affecting CM pulping

Production of CM pulp can be performed in an uncomplicated process. All CM pulping installations are basically normal atmospheric refining systems supplemented with equipment for good impregnation of chips with chemicals and digestion prior to refining. This high yield pulp has been successfully introduced in production of newsprint and high quality papers at lower basis weights, where the high scattering factor is the most valuable asset, and in some fine papers [6].

The pH during pretreatment affects the sulphonation rate and the pulp yield, as well as brightness. The extent of the increase in fibre flexibility and bonding is determined by the extent of the sulphonation reaction above a certain value. Sulfite concentration, cooking temperature and cooking time are the key determinants of pulp properties [10].

Impregnated chips are usually cooked at a temperature ranging from 140°C to 175°C for softwood, 130°C to 160°C for hardwood [6], and 80°C to 145°C for non-wood materials [10, 11]. The use of suitable chemicals can apparently lower the glass transition temperature of lignin, so that optimum pulp properties could be obtained at a considerably lower temperature.

Refining temperature, consistency and clearance between discs are important variables in refining stage, but the most important variable affecting pulp quality in mechanical pulping is specific energy applied in the refining. Increasing the refining energy will increase the strength of the pulp with the exception of tear strength, which is first increased and then decreased as the energy is increased. The amount of energy required is increased as the steaming temperature is increased and further increase can be expected by chemical pretreatment. The specific energy consumption for CM pulp is 5.0 to 6.1 MJ/kg [6]. Although high specific refining energy is required to attain a CSF level of 100 to 150 mL, which is characteristic of mechanical pulps, CM pulp at 300 to 400 mL CSF level needs about 5.0 to 5.5 MJ/kg, certainly less than that required for manufacturing TMP [14]. Since CM pulp displays adequate strength at 300 to 400 mL CSF, there is no advantage to further lower the freeness. To do so would only waste refining energy and destroy the good drainage properties which are important characteristics of a chemical pulp.

2.3.3 CM pulping of non-wood fibres

Chemical straw pulps have some drawbacks of low yield, inferior ink receptivity, and poor opacity. Non-wood fibre chemical pulping is confronted with high production cost and heavy pollution [2, 3]. In addition, paper grades made from straw pulps are restricted by its characteristics. Therefore, application of other pulping methods to non-wood plant fibre to solve the problems mentioned above has a significant meaning for those countries who are lacking of wood fibre resources.

In spite of the fact that the subject of CM pulping has been extensively investigated by numerous groups, the most of these studies were limited to wood species, very little information is available on the extent to which the established high-yield pulping technology can be applied to non-wood plant fibres.

Non-wood fibre materials have low percentage of useful fibre, short fibre length, and high silica content. Straw materials also have a loose structure and low lignin content. In order to maintain the fibre length and strength properties of straw pulp as well as good drainability, an adequate combination of chemical pretreatment and mechanical refining should be searched.

Taraboulsi and Hurter [15] carried out a study on newsprint production from rice straw, using nitric acid CM pulping process. Those researchers recommended to impregnate rice straw first with 5% HNO_3 then with 3% NaOH at 95°C, and cook for 30 minutes, followed by one-stage refining at atmospheric pressure. This combination of conditions produced a pulp with the following characteristics: yield, 78%; breaking length, 3.5 km; tear index, 6.5 $mN.m^2/g$; and opacity, 94%. The pulp after bleaching showed a higher brightness but a little lower opacity and possessed better strength properties, as compared to groundwood pulp. As regard to brightness and strength, bleached nitric acid CM rice straw pulp, when applied as 80% of the furnish of which the rest was bleached softwood kraft pulp, produced a newsprint having superior properties and only slightly lower opacity, in comparison to the reference newsprint from wood.

CM bagasse pulp was also produced by the nitric acid pulping process [15]. The depithed bagasse was impregnated with 4% HNO_3 solution, cooked at 80°C for 30 minutes, followed by another cooking at 95°C with 2% NaOH for 30 minutes, and then a two-stage refining. The resulting pulp had a yield of 91% and a high opacity of 98.5%. Bleached nitric acid CM bagasse pulp produced a paper with satisfactory properties but in low brightness, when used as the major furnish component (80%) for newsprint production.

Lopez et al. [11] also studied the possibility of producing newsprint from CM bagasse pulp. The bagasse was impregnated at a temperature of 80 - 100°C for 10 to 20 minutes when using NaOH solution with a concentration of 6-10 g/L as the impregnation liquor, and for 20 to 40 minutes when using alkaline sulfite solution for impregnation. The characteristics of both CM pulps produced from different chemical pretreatments were similar. Alkaline sulfite CM pulp had slightly higher strength properties than NaOH CM pulp. The strength properties for both CM pulps were much better than those of bagasse mechanical pulp. Using peroxide and hydrosulfite in two stages, these bagasse CM pulps could be bleached to a brightness level satisfactory for newsprint; with 1.5% peroxide and 1.5% hydrosulfite, the brightness obtained was about 67%.

Lai et al. [16] have carried out studies on CM pulping of bagasse using sulfite, alkaline and percarbonate as the chemical treatment agents. They have observed that the beneficial influence of chemical pretreatment on sheet density development decreased in the order of: sulfite, alkali, and percarbonate. Since sheet density, an indication of the degree of wet consolidation, could be primarily determined by fibre flexibility, the major role of chemical pretreatment would be in the enhancement of fibre flexibility. Therefore, sulfite used as the chemical pretreatment agent was more suitable than others.

Liu and Li [10] studied the CM pulping of Amur silver grass (*Miscanthus Sacchariflorus*) (will be called "Amur grass" hereafter). Under the conditions investigated, the effect of cooking variable on yield and extent of sulphonation was found to decrease in the order of: cooking temperature, cooking time, sulfite charge, and liquor to chip ratio. Yield decreased with an increase in cooking temperature. Sulphur content of pulp increased first and then decreased with increasing cooking temperature -- it might be explained as that the rate of dissolution of sulphonated constituents was higher than that of sulphonation when the cooking temperature was over 140°C. In their study, 140°C seemed to be the optimal cooking temperature for CM pulping of Amur grass. The strength properties of the pulp produced increased with sulfite charge. These workers also studied the use of their CM pulp as a major furnish component for newsprint production. The strength properties of the paper sheet made from 100% Amur grass CM pulp were higher than those of a paper sheet made from a furnish composed of 88% masson pine groundwood (GW) pulp and 12% kraft pulp. A newsprint sheet produced with the use of 88% Amur grass CM pulp and 12% kraft pulp possessed strength properties comparable to those of the newsprint made from a furnish of 75% GW pulp and 25% kraft pulp, that is a typical furnish in China for newsprint production.

2.3.4 Vapor-phase CM pulping

Liquid-phase cooking system is the basic configuration used in mill installation. Laboratory and pilot plant trials as well as commercial installation have shown that vapor-phase cooking also works well with achievement in energy saving.

Lo and Valade [17] carried out a study on vapor-phase cooking of aspen. A pulp with a yield over 92% and having good strength properties was obtained. To recover the unused residual SO_2 in the spent impregnation liquor, recycling of the liquor was practised in that study. It was found that recycling of spent impregnation liquor for pulp production could be practised without limit in number of times.

Commercial scale vapor-phase cooking has been shown to be equivalent to liquid-phase cooking [18, 19], provided that the chips were thoroughly impregnated with cooking liquor in a pressurized vessel and the cook proceeded immediately after impregnation in the absence of air. The emergence of the vapor-phase CM pulping is an alternative to its commercially viable liquid-phase counterpart. Much of the early vapor-phase

CM pulping work was conducted by preimpregnation of the chips with sulfite solution followed by vapor-phase cooking using direct steaming. In vapor-phase cooking, since there is no excess liquor to provide a constant driving force for sulphonation, the liquor contained by the chips during the impregnation stage must have a higher chemical concentration than in the liquid-phase cooking so that a satisfactory level of sulphonation can be achieved.

Dines and Tyminski [20] reported that a fresh liquor with a concentration of about 20% sodium sulfite on o.d. wood would be required to produce a pulp equivalent to liquid-phase CM pulp. In vapor-phase cooking, the chips can be compressed by an efficient screw press to a compression of about 5.5:1. The pressure removes most of the air and part of the water presented in the chips. When the pressure is removed, the chips would expend while absorbing the impregnation liquor like a sponge, being the principal step of a practical vapor-phase CM pulping process, which permits the use of fresh liquor with lower sodium sulfite concentration. Vapor-phase cooking also exhibits some possible advantage over the liquid-phase system. The digester for vapor-phase cooking is basically a simpler and thus a less expensive unit than its liquid-phase counterpart. More important is the elimination of any solids deposition anywhere in the system. All this results in a further lowering of both capital and operating costs.

A production line of a 400 t/d vapor-phase CM plant in the mill of NBIP Forest Products Inc. in Dalhousie, New Brunswick, has been operated since 1983 [20]. In 1984, Abitibi-Price Inc. also installed a vapor-phase cooking system in its Chandler division, Québec, to manufacture CM pulp for use in newsprint furnish [21].

2.3.5 Characteristics and utilization of CM pulp

Interference contrast micrographs have shown that CM pulp is well fibrillated and its shive content is very low [14]. Chemical pretreatment renders the characteristics of this kind of pulp close to those of chemical pulps. Although CM pulp was initially developed for the replacement of chemical pulp in newsprint, its potential for other applications has also been established. The good strength and high brightness levels of today's CM pulp have made it suitable for use as the major furnish component of printing and writing papers, especially for computer and copying paper. Mill scale trials [18] have indicated that CM pulp could permit a substantial reduction of kraft pulp used in coated publication paper. It could be also used as a partial replacement of kraft pulp in packaging grades such as linerboard and folding carton stock.

2.3.6 Influence of CM pulping on environment

The CM pulping process generates much less biochemical oxygen demand (BOD) in its effluent, as compared to the conventional chemical pulping. The BOD_5 generated is 35-45 kg/tonne by CM wood pulping, 150 kg/tonne by high-yield sulfite, and 250 kg/tonne by low-yield sulfite. A newsprint mill using 35% spruce-balsam CM pulp (~90% yield) and 65% groundwood would produce half the BOD of a mill using 25% high yield bisulphite pulp at 65% yield, and only one third the BOD of a mill using 25% low yield sulfite [14]. Substitution of CM pulp for sulfite pulp considerably improves the effluent quality, in terms of BOD loading, of a newsprint mill.

2.4 BLEACHING OF MECHANICAL PULP

Peroxide was first used commercially by St. Regis paper Co. in 1941 at its Norfork mill in New York, for bleaching groundwood. Since then, hydrogen peroxide, one of the most versatile bleaching agents available, has become the predominant peroxide bleaching chemical for mechanical pulp. Unlike many of the chemicals presently used to bleach pulp, it is relatively non-toxic, non-volatile, and is completely miscible with water at all concentrations [22]. It does not add environmental undesirable chlorinated organic to mill effluent; in some cases, it helps control BOD [23]. In the past two decades, more and more mills used it as a bleaching agent, taking consideration of its lignin-preserving properties and causing fewer pollution problems. Hydrogen peroxide was not only used for bleaching mechanical pulp but also used for bleaching chemical pulps [24].

2.4.1 Factors affecting peroxide bleaching

Perhydroxyl anion (OOH^-), formed from alkaline dissociation of hydrogen peroxide, has been shown to be the active species in peroxide bleaching [25]. It modifies chromophoric conjugated carbonyl groups in lignin without causing lignin fragmentation and subsequent loss in pulp yield. A competing reaction in peroxide decomposition to water and oxygen is catalyzed by cations of transition metals such as iron, manganese and copper [26], resulting in wasted peroxide and reduced bleaching efficiency. Therefore, the most important factors which affect the peroxide bleaching are the alkaline condition and the presence of peroxide stabilizers.

Total alkaline and peroxide levels had to be balanced to ensure that small residuals of each being present toward the end of the bleach reaction. When total alkali was completely consumed, perhydroxyl anions would not be produced, and no further bleaching would occur. On the other hand, when peroxide was totally exhausted while pH level was still high, pulp brightness would be lost through reversion [27]. At a given peroxide charge, an increase in alkalinity had a beneficial effect on brightness, but the trend was reversed with the continued addition of alkali [22].

For most practical purposes, bleaching has been carried out at temperature between 40°C to 70°C with reaction time of up to 2 hours. The rate of bleaching, as well as the decomposition rate of hydrogen peroxide, would increase as the temperature was increased. When bleaching was performed at temperatures above 70°C, a good control of the total alkali/peroxide ratio became increasing important. When the ratio was too high, rapid decomposition of the peroxide would occur; if too low, the bleaching reaction would slow down markedly [13].

Kouk et al. [28] studied the temperature effect on the responses of bleaching process performed at 60°C and 80°C; both TMP and CTMP achieved equivalent brightness regardless of the temperature if the reaction time was optimized. But the situation was not the same for the highly sulphonated CM pulps, which generated a much improved brightness response at high temperature and short reaction time. For CM pulp, about 3 additional brightness points were obtained by bleaching it at 80°C; the optimum reaction time was decreased from 120 to 45 minutes. A severe darkening was observed when the optimum reaction time was exceeded. For a given brightness target, bleaching CM pulp at the elevated temperature could provide savings of 1.0% peroxide applied. Besides, a portion of the alkali could be saved as the optimum alkali level decreased for the increased temperature (4.0% NaOH at 60°C versus 3.5% at 80°C).

Optimum bleaching reaction time depends on the dosage of peroxide, but is usually between 1 to 3 hours. Chen et al. [24] reported that for middle to high consistency pulp, peroxide was consumed rapidly at a raised temperature. The bleaching reaction was characterized by a rapid initial rate in the first half hour, then it was slowed down significantly. After a duration time of 2 hours, pulp brightness increased slightly, while peroxide concentration diminished continuously. The residual percentage of peroxide decreased from 32 (with respect to the initial concentration) to 6 when the reaction time was increased from 2 to 24 hours. They considered that only in the early period of retention time, peroxide ions reacted for brightening the pulp, then peroxide was consumed by some side-reactions, and thus suggested to limit a bleaching operation within two hours.

The responses of mechanical and CM pulps to peroxide bleaching could be enhanced by increasing the consistency [22]. A spruce/fir TMP bleached at 30% consistency in plant trials achieved the same brightness with half the peroxide and alkali consumption as it did at 12-20% consistency in optimized laboratory tests. Further increasing the consistency to 35-40% induced an additional brightness gain of 4-5%, as compared to 25% consistency [29]. A possible explanation for the improved bleaching efficiency observed at higher consistency was that at higher consistency the peroxide concentration is also higher, the bleaching reactions could thus compete more favourably with the alkali promoted color-forming reactions [30].

Generally, peroxide bleaching can be performed at low (3% to 6%), moderate (10% to 15%), or high (20% or higher) pulp consistency [22]. Of the three systems, low-consistency bleaching is the least chemically efficient method; while high-consistency bleaching results in the greatest chemical economy, but requires a higher initial capital investment. Practically, the moderate consistency system has been most widely employed.

DTPA has been the chelating agent most frequently examined for use to control the peroxide decomposition induced by transition metals. Increasing the DTPA dosage up to 0.4% produced a parallel beneficial effect with respect to brightness improvement in the absence of silicate. However, a higher dosage resulted in no further improvement or even in a slightly reduction in brightness, possibly as a consequence of the peroxide being consumed by the chelating agent [27, 31]. It was observed in a TMP bleaching that without DTPA pretreatment, hydrogen peroxide was exhausted after one hour of reaction and peak brightness was not attained; with pretreatment, 8% to 10 % of the initial peroxide charge was still remained after three hours of bleaching, and higher brightness was realized [27].

Sodium silicate has a buffering action in the pH range where peroxide is most active as a bleaching agent, it serves also to inactivate metal ions [13]. Magnesium sulfite has a similar inactivation effect and is especially useful when the hardness of the water is low [32]. The optimum dosage is about 4-5% for silicate, and 0.04% for magnesium sulfate [33].

Lachenal et al. reported that the selectivity of peroxide bleaching reaction could be highly improved when the pulp had been previously treated with small quantities of some oxidative

tive agents such as chlorine, chlorine dioxide, and sodium chlorite in acidic medium. Sodium chlorite in acidic medium allowed a higher brightness to be reached after bleaching while the amount of peroxide actually consumed was considerably reduced from 6.5% to 4.2% for pulp bleached to 83% brightness [34].

CHAPTER 3 EXPERIMENTAL

The reed raw material used in the experiments was obtained from a paper mill in the province of Heilongjiang in northern China. It grows wild (in abundant quantity) or cultivated in the marshes in that province and also throughout China. Its harvest is usually made in winter and stored for about six months before use in papermaking.

3.1 PREPARATION OF CHIPS

Before shipment to Canada, reed stalks were cut in the mill into chips using a drum chipper. The screening of chips was performed at the Centre de recherche en pâtes et papiers (CRPP) using a Williams classifier to remove the undesirable oversize (> 2.86 cm) and undersize (<0.48 cm) fractions.

During screening, some oversize chips passed through the first screen plate and were retained on the other plates, and they were manually removed. All oversize chips were then re-cut to suitable sizes with a hand cutter. The undersize fraction (< 0.48 cm) amounted to approximately 2% of the unscreened chip weight. The weight-average length of the chips used in the experiments was about 1.08 cm, and the size distribution of the chips is presented in Table 5.

Table 5 Size distribution of reed chips

Size of chips, "S", cm	Weight fraction, %
2.86 > S > 2.22	4.72
2.22 > S > 1.59	4.91
1.59 > S > 0.95	50.9
0.59 > S > 0.48	39.5

3.2 COOKING

3.2.1 Preparation of fresh liquor

Fresh liquor was prepared by dissolving technical grade sodium metabisulphite ($Na_2S_2O_5$) in water, at an initial total SO_2 concentration of about 8% by weight (on o.d. chip). For each cooking experiment, the pH of the fresh liquor was adjusted to the desired value by adding concentrated NaOH solution. The actual concentrations of total SO_2 in the fresh and spent liquors were determined following TAPPI Standard T604 pm-79.

3.2.2 Liquid-phase cooking

To explore the possibility of using reed as raw material for CM pulping, a series of liquid-phase cooking experiments of reed were conducted in the laboratory. The variable and fixed cooking conditions presented in Table 6 were chosen for carrying out the experiments. Since non-wood plants have open structure and bulk volume, a liquid to o.d. chip ratio of 6 was used for each set of cooking conditions. In this way, good impregnation of reed chips was obtained, and cooking liquor recycling system also performed well.

An M/K 409 laboratory cooking system (M/K System Inc.) composed of two identical digesters, each having a capacity of 6.4 liters and equipped with a liquor recirculation system heated electrically, was used in the study. Six hundred grams o.d. chips were used in each cooking experiment. After cooking, the chips were immediately withdrawn from the digester and soaked in cold water; the chips were then washed several times with tap water until the discharged water was clear.

To determine the pulp yield of a cook, 45 grams of o.d.

Table 6 Conditions used for liquid-phase cooking

Weight of chips per cook, o.d. kg	0.6	
Ratio of liquor to o.d. chip	6	
Total SO_2/o.d. reed chip, % (SO_2 charge)	7.5, 10, 15, 20, 25	15*
pH of fresh cooking liquor	4.5, 6, 7.5, 9, 10.5, 12	9*
Maximum cooking temperature, T_m, °C	145	
Time for temperature from 20 °C to T_m, min	35	
Cooking time, t_m, at T_m. min	10, 20, 30, 40, 60, 80	40*

* Cooking conditions for the pulp used in bleaching

chips were put inside a circular basket and cooked along with other chips in the digester. The basket was placed in the middle of the digester. The cooked chips were pulped at approximately 2% consistency for 5 minutes in a 4L Waring blender and then thoroughly washed. After washed, the pulp was dried at 105 °C in a laboratory oven to a constant weight. The percentage pulp yield was determined as a ratio of the o.d. weight of the pulp to the initial weight of the chips in the basket.

3.2.3 Vapor-phase cooking

The same M/K 409 system was used to carry out the vapor-phase cooking experiments. Impregnation and cooking of chips were performed in one digester. The other digester was used as a boiler to provide the cooking steam. Six hundred grams o.d. chips were used in each cook.

After loading and closing the digester, chips were then impregnated with recirculated liquor at an impregnation temperature for a predetermined period of time. After, the spent liquor was drawn and recovered from the bottom of the digester. Impregnated chips were then cooked by steam at a maximum cooking temperature for a predetermined period of time, and the resulting steam condensate was removed intermittently from the digester to prevent condensate accumulation. During the cook, both the temperature and time were controlled.

After cooking, the cooked chips were also immediately withdrawn from the digester, soaked in cold water, and then washed several times with tap water. The procedure for the determination of pulp yield was the same as that described in section 3.2.2.

Based on the results obtained from the liquid-phase CM pulps, the conditions presented in Table 7 were used to carry out the vapor-phase cooking experiments. When taking into consideration the yields and strength properties of the pulps produced, a set of cooking conditions presented in Table 7 were chosen, based on the results of the pulps obtained, for the purpose of performing experiments with spent liquor recycling.

3.2.4 Spent liquor recycling

In order to carry out the recycling of spent impregnation liquor, its characteristics had to be known. Thus, the following measurements were made on the recovered spent liquor : 1) recovered volume; 2) SO_2 concentration; 3) pH. New impregnation

Table 7 Conditions used for vapor-phase cooking without and with recycling of spent impregnation liquor

Weight of chips per cook, o.d. kg	: 0.6
Ratio of liquor to o.d. chip	: 6
Total SO_2/o.d. reed chip, % (SO_2 charge)	: 15* and 25
pH of fresh cooking liquor	: 9* and 12
Chip impregnation temperature, T_i, °C	: 100
Impregnation time, t_i, min	: 20
Time from T_i to T_m, min.	: 15
Maximum cooking temperature, T_m, °C	: 145 and 155*
Cooking time, t_m, at T_m. min	: 20 and 40*

* Cooking conditions used in recycling of spent impregnation spent liquor

liquor was then prepared by adding the required amount of $Na_2S_2O_5$ and H_2O to the recovered liquor, followed by the pH adjustment with concentrated NaOH solution.

The following measurements were also made to obtain additional data for the study : 1) density of the recovered liquor; 2) total volume and pH of the condensate composite recovered during the vapor-phase cooking; and 3) SO_2 concentration in the condensate composite.

3.3 DEFIBRATION AND REFINING

After each cook, the chips were immediately washed several times with tap water until the discharged water was clear, and then defibrated in a 12-inch and 40-hp Sprout-Waldron refiner (Model D-2202) with a gap distance of 0.38 mm between the rotor plates (D2A-507). The resultant coarse pulp was washed afterwards 3 - 4 times, and thickened in a Bock extractor (Model 10 XC) after each washing. Further refining of the coarse pulp was performed mostly in a blender (Model Osterizer 14, Sunbeam) at about 2% consistency, refining energy was measured using a wattmeter EW-604. Several refinings were conducted in a PFI laboratory mill.

A batch of liquid-phase cooked chips (prepared under the same set of conditions) was refined in CRPP's single-stage Sunds Defibrator pilot-plant refiner to evaluate the actual specific refining energy. Latency was removed from the refined pulp in a British disintegrator (95 ^{o}C water, 1.5% consistency, for 5 minutes). The freeness of latency-removed pulp was measured in accordance with TAPPI T227 om-85.

3.4 PULP EVALUATION

3.4.1 Pulp testing

Handsheets from latency-free pulp were made according to TAPPI T205 om-88 and conditioned according to T402 om-83. Mechanical and optical characteristics of the experimental pulps were evaluated according to TAPPI standard methods.

3.4.2 Sulphonate content of pulp

The sulphonic acid group content of several pulp samples* was determined following the conductometric titration method proposed by Katz et al. [35]. For this determination, pulp samples were refined to 300 mL CSF in a blender at 2% consis-

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* Since the sulphonate content was not a primary objective of this research work, only certain pulp samples were evaluated for this characteristic.

tency and then thickened. Three grams of pulp was converted to hydrogen form by soaking twice in 0.1 M hydrochloric acid for 45 minutes and then washing with deionized water to a constant conductance. The pulp was drained and dispersed in 450 mL of 0.001 M NaCl solution prepared with deionized water.

Titration was carried out with 0.1 M NaOH solution dispersed from a micro-burette while the suspension was stirred under a nitrogen atmosphere. The addition rate of NaOH solution was controlled via an Apple II computer connected to the titrator (METROHM 655 Dosimat), allowing equilibrium to be reached between readings.

For more stable conductance measurements, the protective glass sheath was removed from the tip-type electrode. The conductivity meter was a Radiometer type CDM83. The contents of sulphonic and carboxylic acids were determined from the two equivalence points located on the titration curve generated by an Apple II computer through a software developed by PAPRICAN.

3.5 BLEACHING

3.5.1 Preparation of pulp

The cooking and refining procedures were the same as those described previously in Sections 3.2.2 and 3.3. In considering the pulp yield and physical properties, one promising pulp was chosen from the pulps produced from liquid-phase CM pulping for the study. The main cooking conditions were : maximum cooking temperature : 145 ^{o}C; cooking time : 40 min ; fresh liquor pH : 9 and SO_2 charge 15% (on o.d. chip). Other conditions have been listed in Table 6.

3.5.2 Preparation of bleaching liquor

Javex bleach water was used in hypochlorite bleaching; available chlorine was determined through titration with sodium thiosulphate. Peroxide bleaching liquor was prepared with: magnesium sulfate ($MgSO_4$), sodium silicate ($Na_2SiO_3.9H_2O$), sodium hydroxide (NaOH), and hydrogen peroxide (H_2O_2 at 35% concentration). The alkalinity and concentration of peroxide in both the fresh and residual solutions were determined, respectively, by acidometric and iodometric titrations.

3.5.3 Bleaching methods and conditions

Two samples of pulps (30 g and 10 g) were used for each bleaching. One (30 g) served for optical and mechanical properties measurements, whereas the other (10 g) served exclusively for the determination of yield after bleaching. After thoroughly mixing each sample with bleaching liquor, bleaching was carried out for a prefixed reaction time in polyethylene bags submerged in a constant-temperature water bath. In the study, a two-stage sequence of hypochlorite and peroxide was selected to explore the possibility of bleaching reed CM pulp to a brightness suitable for printing, writing and fine papers.

In the case of hypochlorite bleaching, the choice of the pulp consistency, bleaching temperature and reaction time was based on the data provided in the literature [36, 37]; the conditions used are presented in Table 8. To minimize the consumption of heating steam and to improve the bleaching efficiency, pulp consistency was in the range of 10-20%. Temperature had to be controlled carefully to avoid pulp degradation, an acceptable range was between 30°C to 40°C. Reaction time could not be very long so as to avoid influence on the polymerization degree of cellulose, but it had to be sufficient enough to benefit the oxidation strength of the hypochlorite.

Table 8 Bleaching Conditions for Hypochlorite-Hydrogen Peroxide sequence

	Charge on o.d. pulp, %	Consistency %	Temp. °C	Reaction time, min	pH initial
First Stage :	Hypochlorite				
NaClO, (% Cl_2) :	4 - 12	12	38	45	10.5
Second stage :	Peroxide				
Magnesium sulfate :	0.5	12	70	120	10.5-11.5
Sodium silicate :	5.0				
Sodium hydroxide :	0.375 - 3				
Hydrogen peroxide :	1.0 - 3.0				
Neutralization					
Sodium metabisulfite :	1.0		ambient (22-24)	15	

Pretreatment : DTPA : 0.25% (o.d. pulp); duration : 10 min.

A duration between 30 and 210 minutes was considered as the normal time of reaction. The pH control was one of the important factors for hypochlorite bleaching; optimal results could be obtained in the alkaline range. It was better to operate at a pH of 8 or higher at the end of this stage in order to minimize the formation of hypochlorous acid (HClO) which would degrade holocellulose [44].

In the case of peroxide bleaching, the dosages of DTPA, magnesium sulfite ($MgSO_4$) and sodium silicate were based on the data provided in the literature [13, 38]. All experimental conditions are also presented in Table 8. At the end of peroxide bleaching, the residual chemical was neutralized by mixing the bleached pulp with a solution of sodium metabisulfite.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 LIQUID-PHASE CM PULPING OF REED

4.1.1 Pulping yield

Depending on the cooking conditions, the total yields of the pulps produced in this study were in the range of 70-90%, In most cases, the yield was decreased with the increasing severity of the cooking variables, as shown in Figures 1 - 3.

The variation in yield is approximately 20 points when the pH of cooking liquor increases from 4.5 to 7.5, as shown in Figure 1; in this range, pulp yield tends to decrease with the increase of pH. As soon as the alkaline condition is attained (i.e., pH $\geq$ 7.5), further increase of pH would not cause any more loss in yield.

Figure 2 indicates that pulp yield is affected by both the total SO_2 charge and the pH of fresh cooking liquor. In general, pulp yield is reduced when either of these two parameters is augmented. At a fixed pH, an increase of SO_2 charge from 10% to 25% causes about 4 points drop in yield; while at a given SO_2

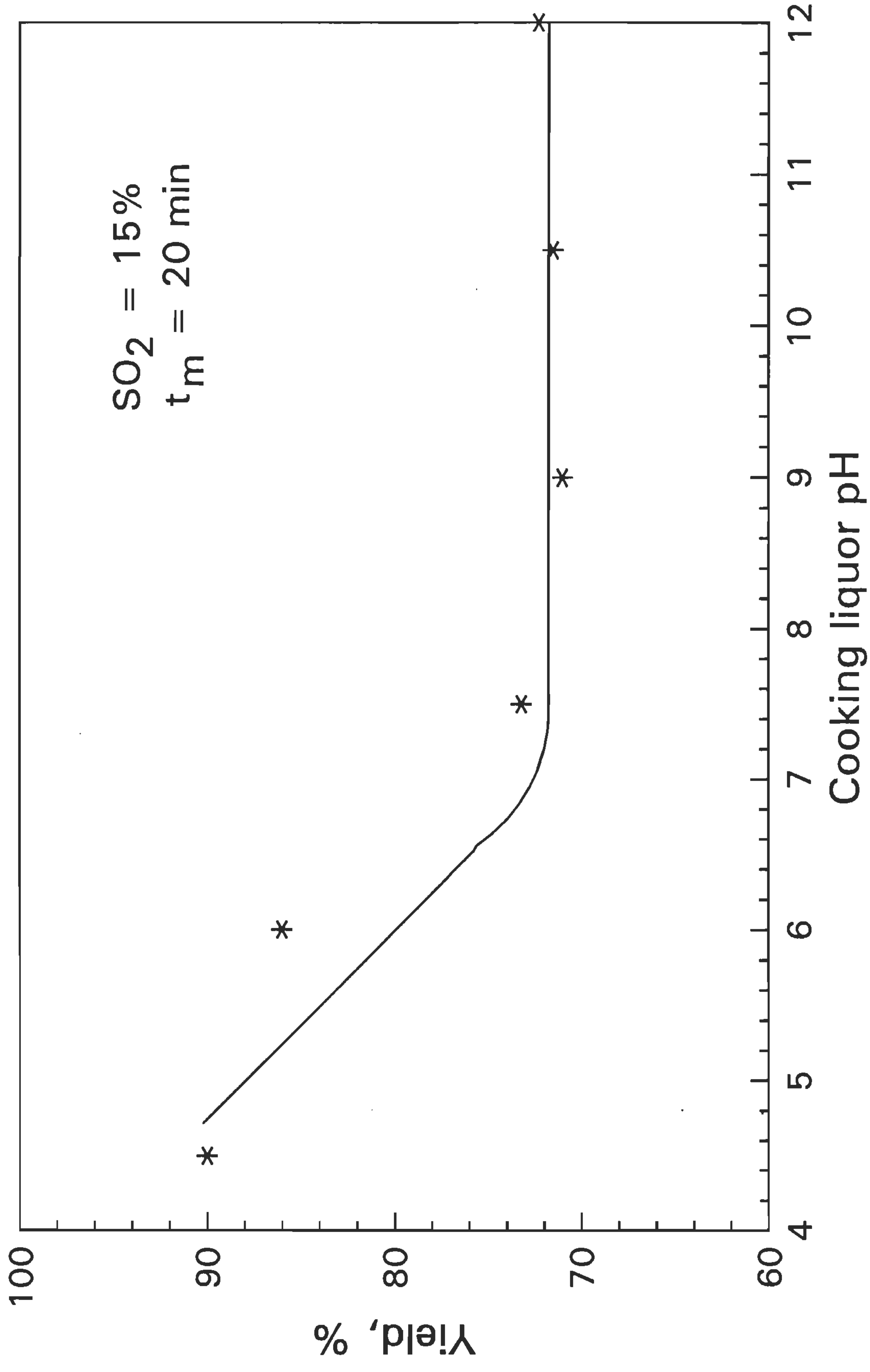


Figure 1 Effect of fresh liquor pH on yield.

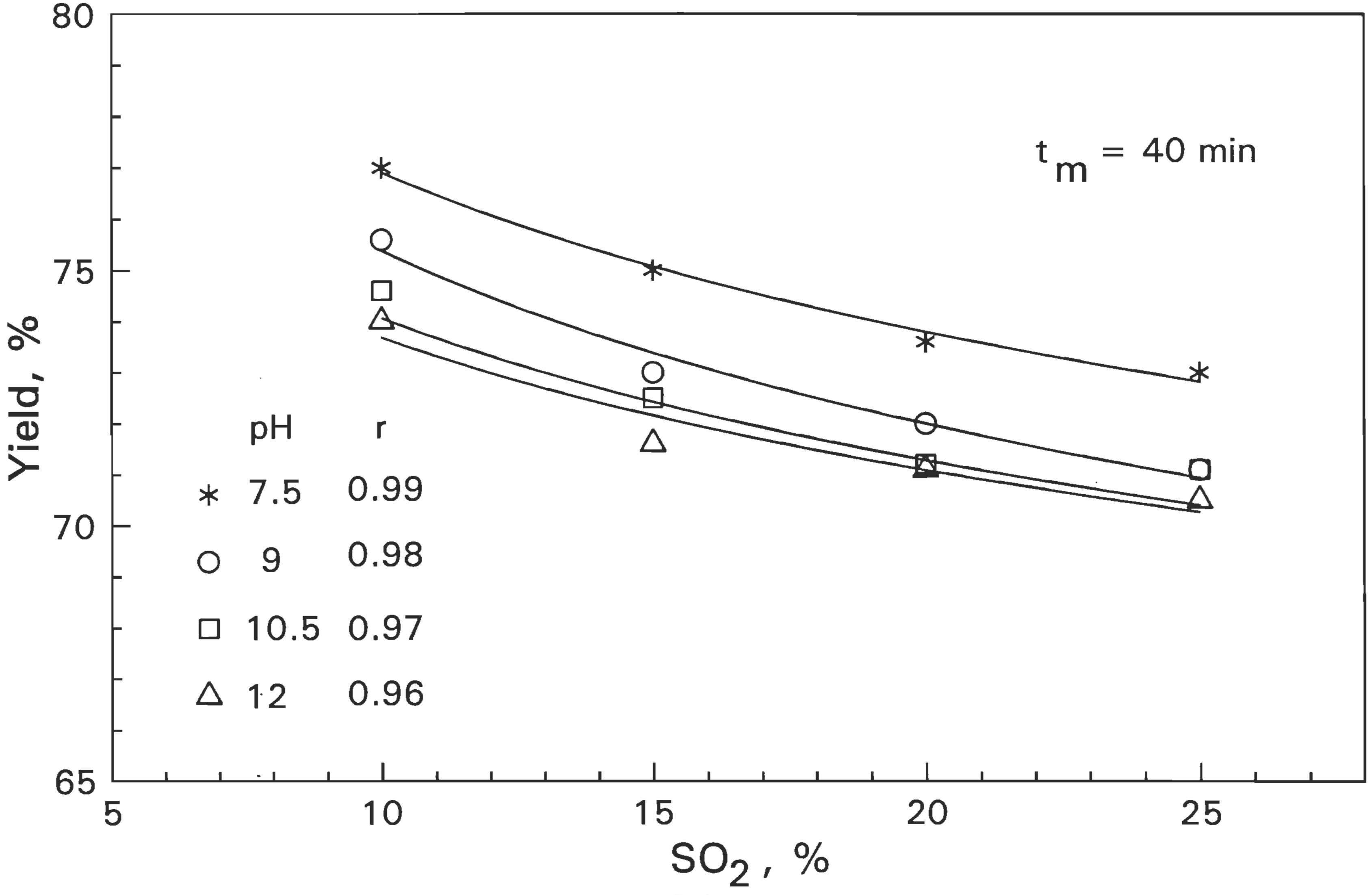


Figure 2 Effect of SO_2 charge on yield.

charge, pulp yield is reduced about 3 points when liquor pH is increased from 7.5 to 10.5, but no significant effect of the liquor pH on yield is observed if the pH value is higher than 10.5.

The yield is also reduced with the extending of cooking time (Figure 3), the reduction of yield is about 1.5 points for each 10 minutes extension of cooking time. In the cooking time range of 0 to 80 min, the yield drops 14 points from 82% to 68%. The decrease of yield with cooking time is due to two possible factors. One might be the high content of water soluble material and 1% NaOH extractive substance in non-wood plant fibre materials; another might be that the extent of chemical reaction between chemical agent and fibre materials increases with cooking time. The second one causes not only the sulpholignin and alkaline lignin to be dissolved in cooking liquor but also the degradation of cellulose and hemicelluloses. Since non-wood fibre material is very different from wood fibre material, the loss of yield in the heating stage (from 20°C to 145°C) is drastic, as indicated by the yield of 82% at zero cooking time.

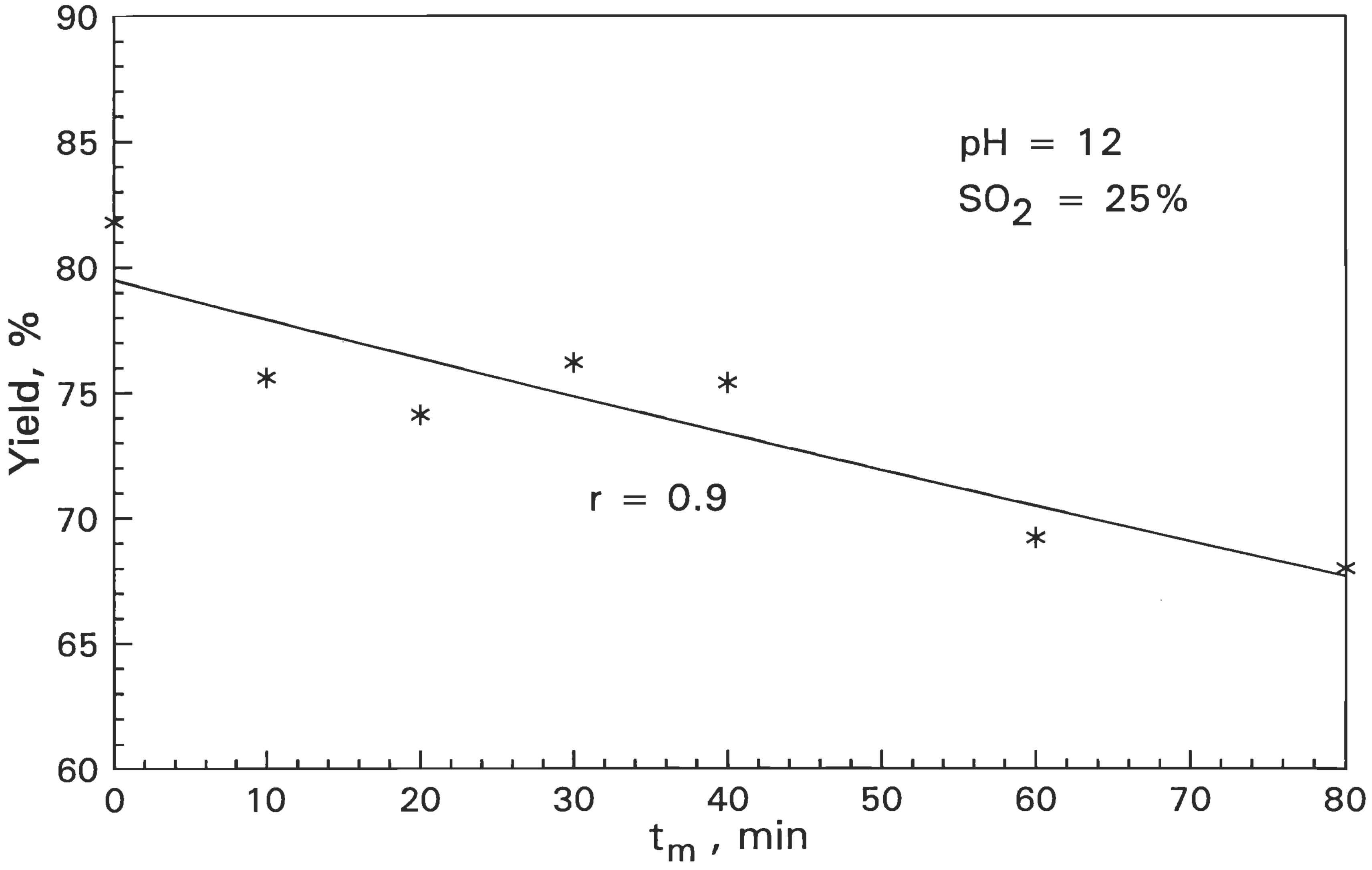


Figure 3 Effect of cooking time on yield.

4.1.2 Effects of cooking variables on pulp properties

For examining pulp characteristics, pulp sample was refined to four or five levels of freeness. After establishing the relationships between pulp properties and freeness, each property was evaluated at either 120 mL or 150 mL CSF, and will be reported afterward, unless otherwise specified.

Preliminary test was carried out to investigate the refining compatibility between two apparatus: a PFI mill and a blender. Test results are presented in Figures A1 to A4, annexed to Appendix. As shown in these figures, the blender used was similar to a PFI mill with regard to refining function, in terms of burst index, breaking length, tear index, and bulk of pulp. This investigation agreed well with the finding of other researchers [45]. Due to the limited availability of PFI mill, the blender was therefore used in the present work for pulp refining.

Effect of pH

In the range studied, Figure 4 shows that when the liquor pH is at lower levels (pH 4.5 and pH 6), the strength properties

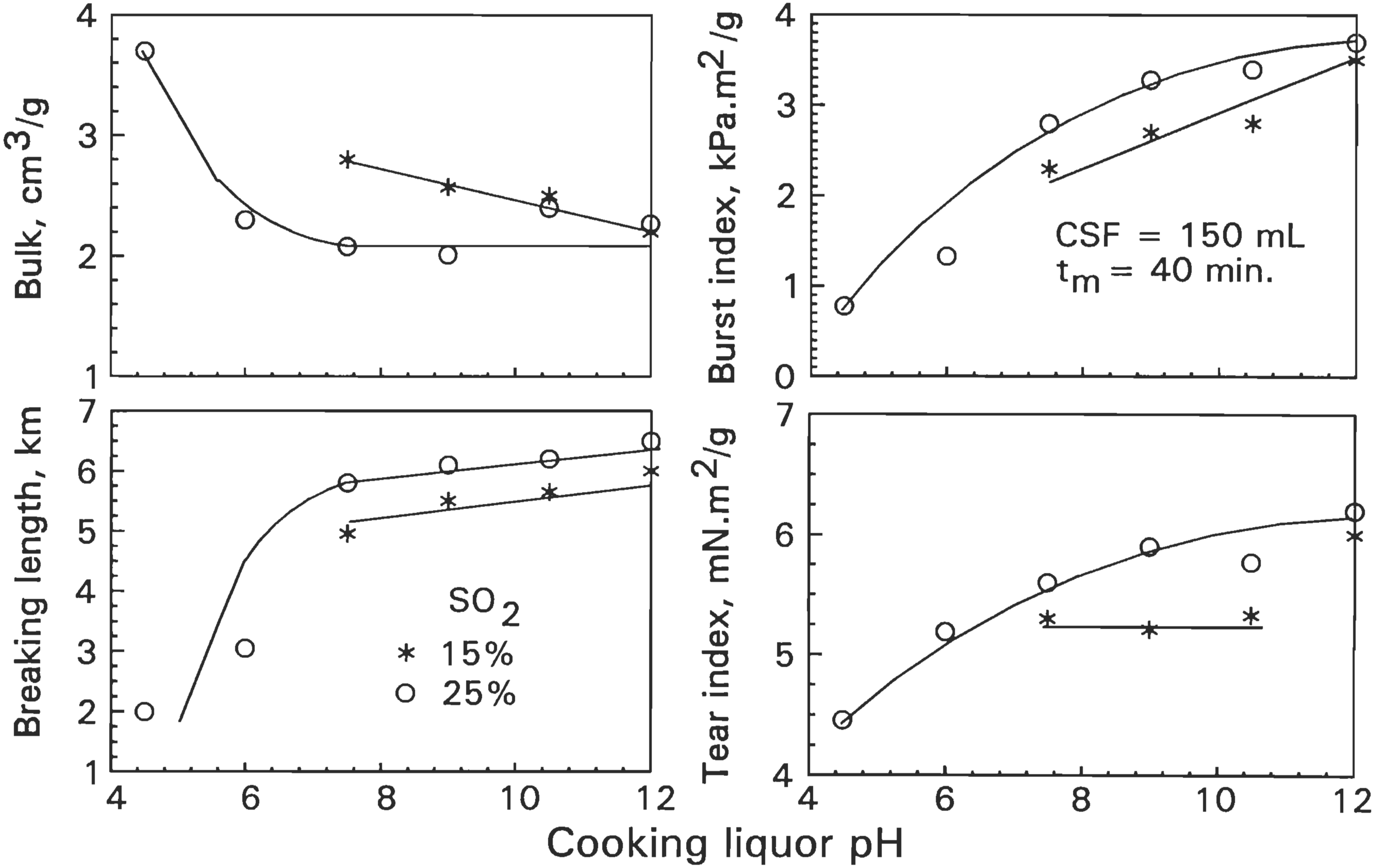


Figure 4 Effects of cooking liquor pH (4.5 - 12) on physical properties.

of the pulps are poor. As shown, physical properties increase significantly with cooking liquor pH, therefore, more experiments were made in the range of pH 7.5 - 12, using SO_2 charge as parameter.

High pH level improves the pulp physical properties, and Figure 5 shows the results. As shown, the physical characteristics, except for tear, are improved with an increase in the pH of cooking liquor. Both burst index and breaking length increase with liquor pH; and at a given pH, they increase with SO_2 charge. The decrease of bulk with increasing pH implies that the pulp bonding increases as cooking liquor pH increases.

The effects of cooking liquor pH on pulp optical properties are presented in Figures 6 and 7. The Elrepho brightness in Figure 6 increases from 36% to 41% as the liquor pH is raised from 7.5 to 12. Figure 7 indicates that the opacity of pulp decreases correspondingly from 94.4% to 92%.

Effect of SO_2 charge

Chemical pretreatment of chips has significant beneficial effects on the resulting pulp strength properties. It improves fibre flexibility, conformability, and interfibre bonding, thus

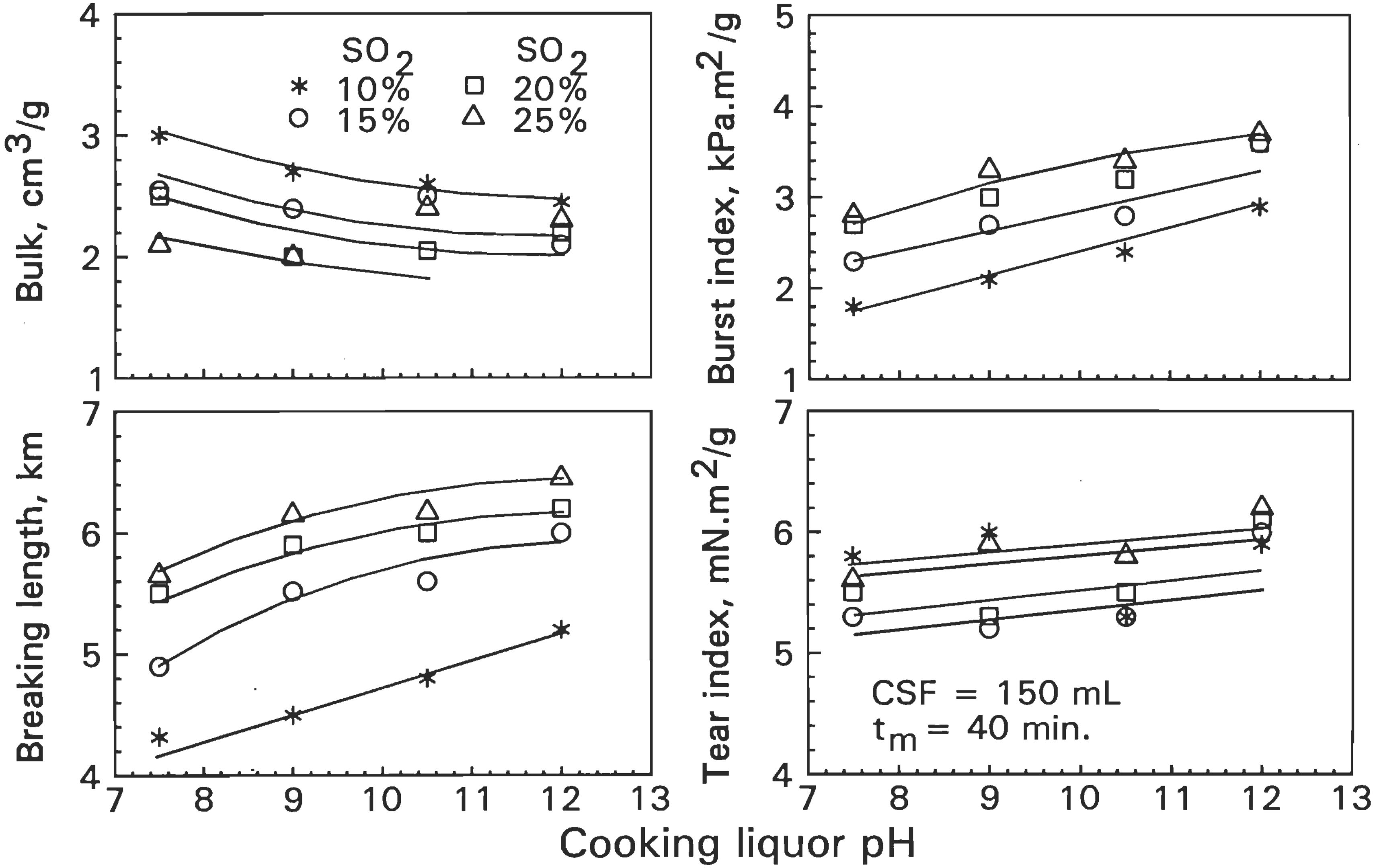


Figure 5 Effects of cooking liquor pH (7.5 - 12) on physical properties.

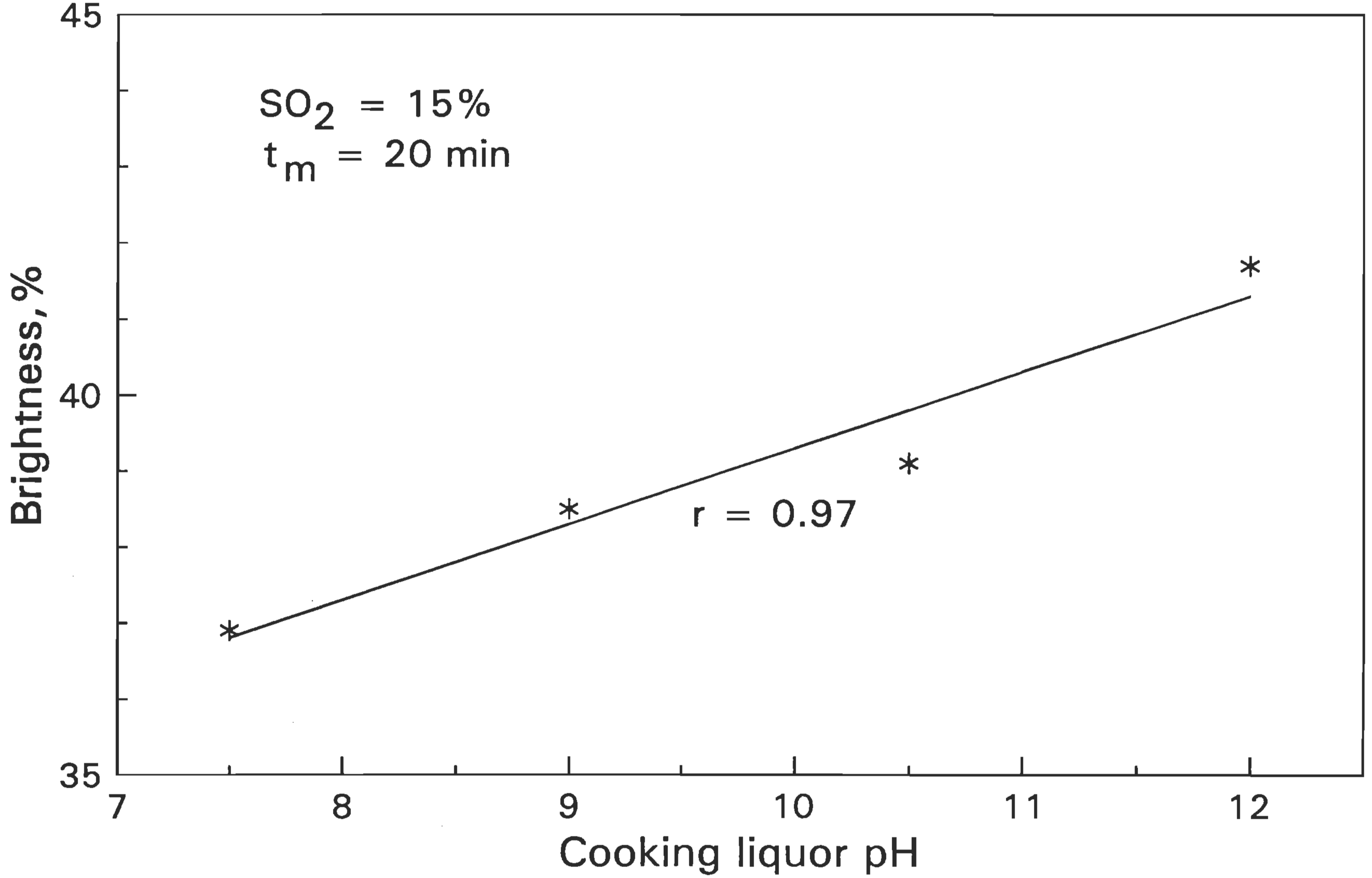


Figure 6 Brightness versus cooking liquor pH

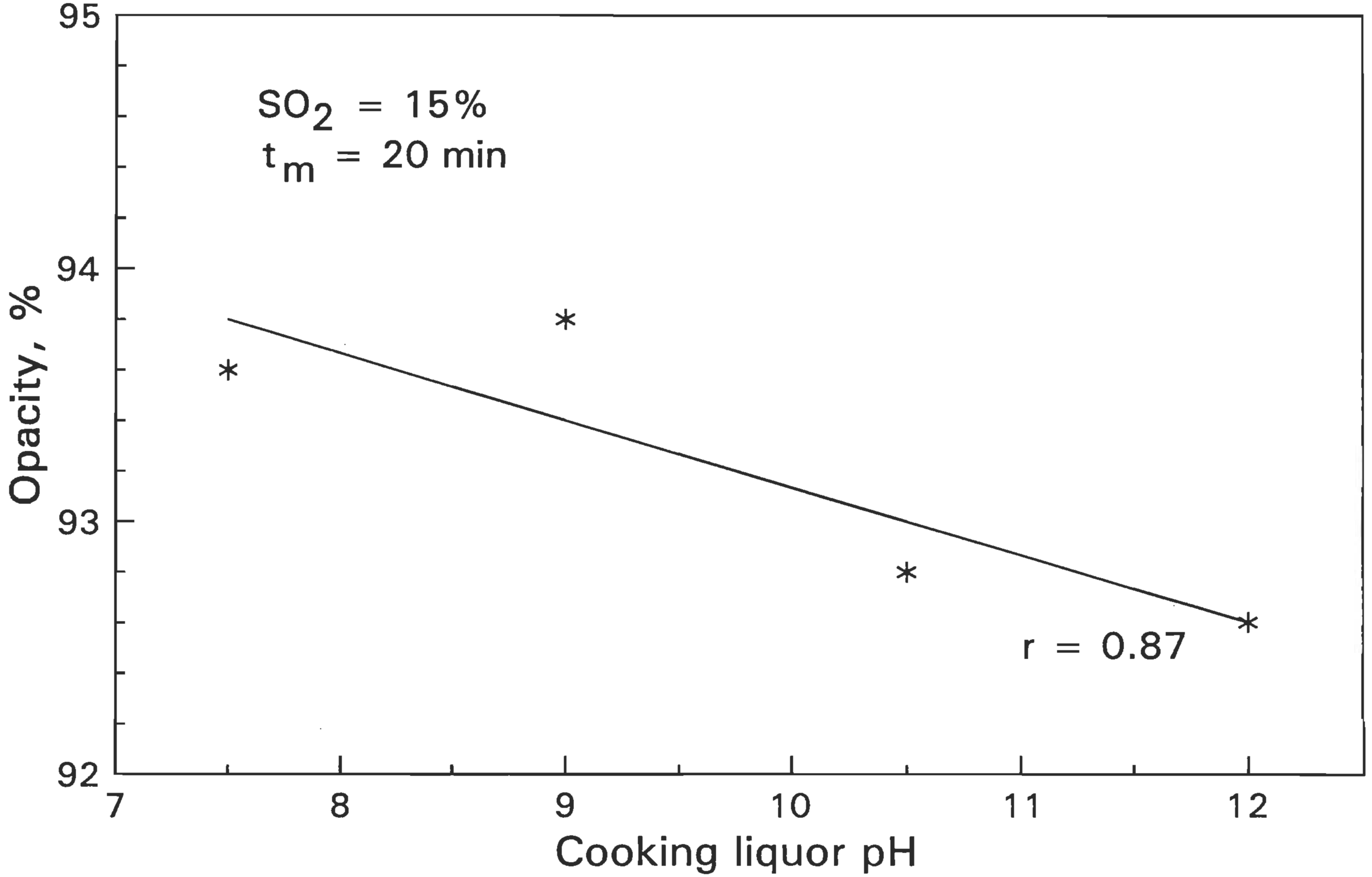


Figure 7 Opacity versus cooking liquor pH.

increasing the strength of a paper [9]. The variations of physical properties versus SO_2 charge are presented in Figure 8. As shown, burst index, breaking length, and tear index are improved with the raising of SO_2 charge. Bulk is decreased with increasing SO_2 charge, suggesting the improvement of interfibre bonding properties. The improvement in burst index, or in breaking length, with increasing SO_2 charge has a similar trend for all pH levels. The highest values obtained for burst index and breaking length were 3.7 kPa.m^2/g and 6.4 km, respectively, under the conditions of pH 12 and 25% SO_2 charge. The improvement in either bulk or tear index is inferior to those for burst index and breaking length.

Figure 9 presents the effects of sulphonation on yield and physical properties. It is interesting to find that, in the case of reed, pulp yield increases as sulphonate content increases; on the other hand, there is no significant effect of sulphonation on strength properties. These results are contrary to the observations in most cases for wood chips, that a low yield pulp displays higher strength properties than its high yield counterpart when produced from the same pulping process. At this moment, before further investigation is made, it can only speculate that the yield loss found with lower sulphonate content is due to hydrolysis of sulphonated lignin groups.

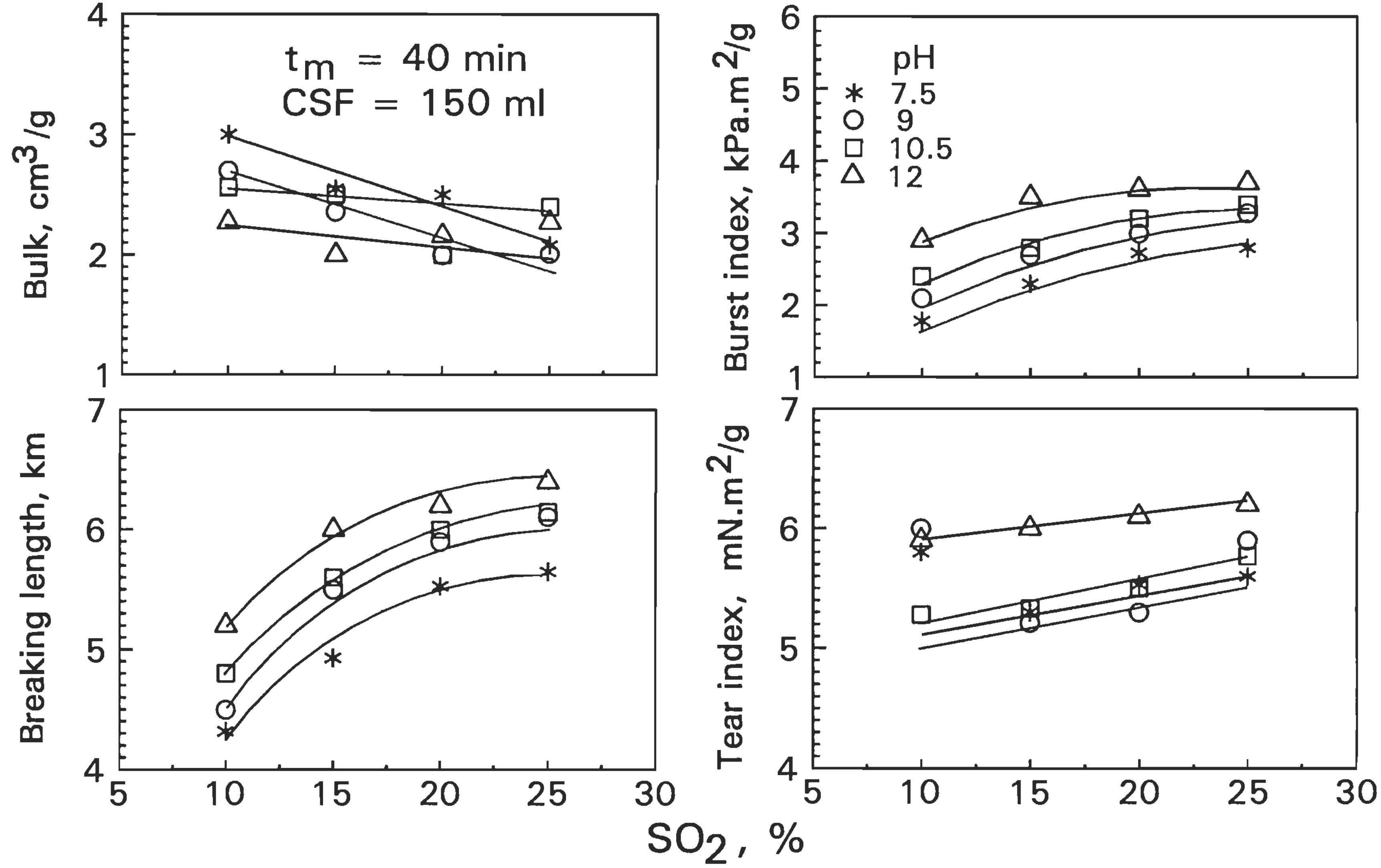


Figure 8 Effects of SO_2 charge on physical properties.

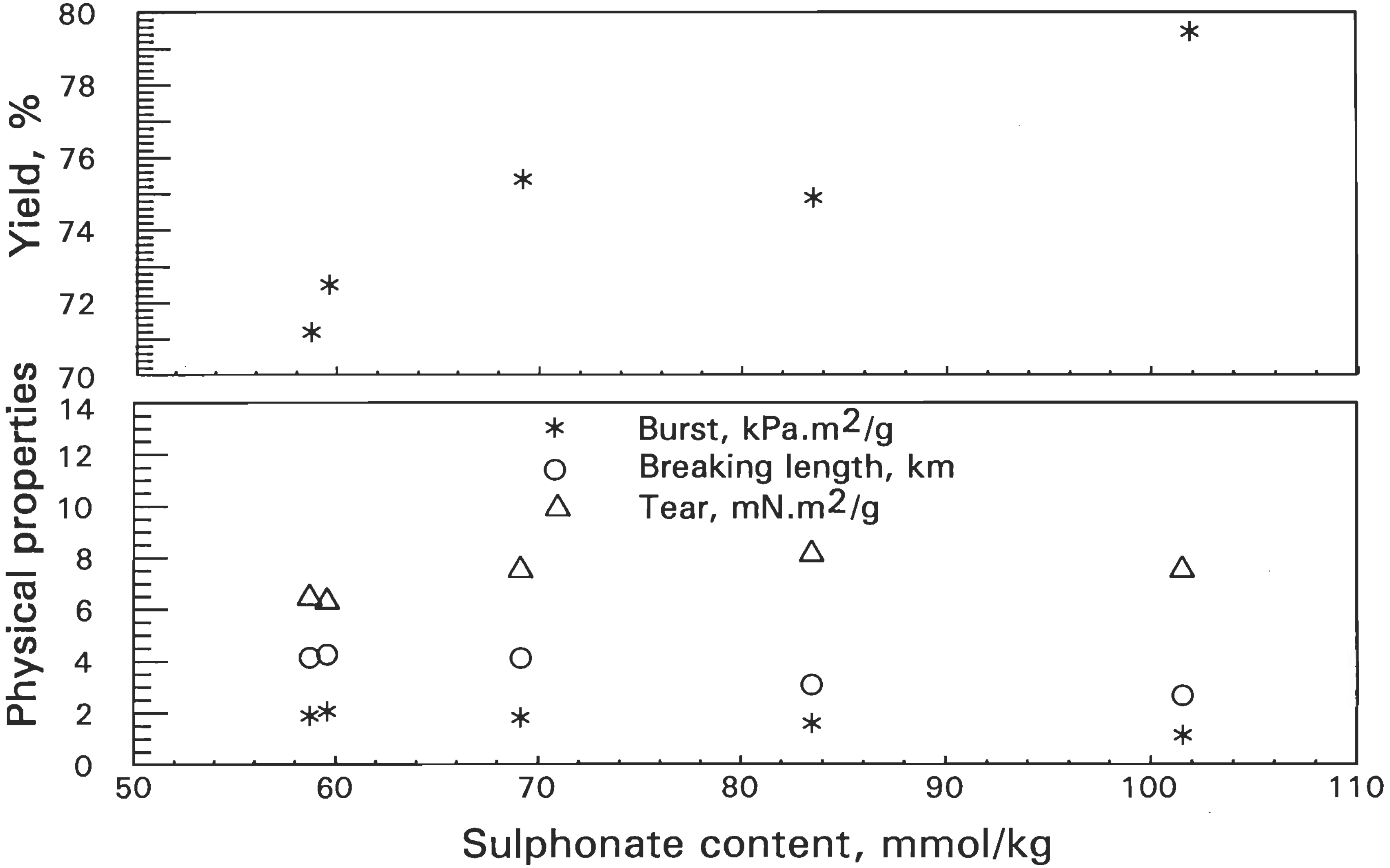


Figure 9 Effects of sulphonation on yield and physical properites.

The effects of SO_2 charge on optical properties are presented in Figures 10 and 11. Under the conditions specified, Elrepho brightness of the pulp is raised from 34.1% to 38.8% as SO_2 charge is increased from 10 to 25% (Figure 10). The opacity of the pulp exhibits a slight drop from 94.4 to 93.2% with SO_2 charge increasing from 10 to 25% (Figure 11). The drop in opacity might suggest a better fibre bonding, leading to a reduction of light scattering area.

Effect of cooking time

Figure 12 presents the variations of physical properties versus cooking time. In general, burst index, breaking length and tear index increase with the prolongation of cooking time, but at the expense of pulp yield (a typical relationship between yield and cooking time has already been shown in Figure 3). For the case of 20% SO_2 shown in Figure 12, when cooking time prolongs from 10 to 40 minutes, burst index increases from 3 to 4 kPa.m^2/g, breaking length from 5 to 6.2 km, tear index slightly from 5.6 to 6.1 mN.m^2/g, and bulk decreases from 2.5 to 2.2 cm^3/g. When SO_2 charge is low, much longer cooking time is required to obtain pulps possessing acceptable properties, as shown by the case of 7.5% SO_2.

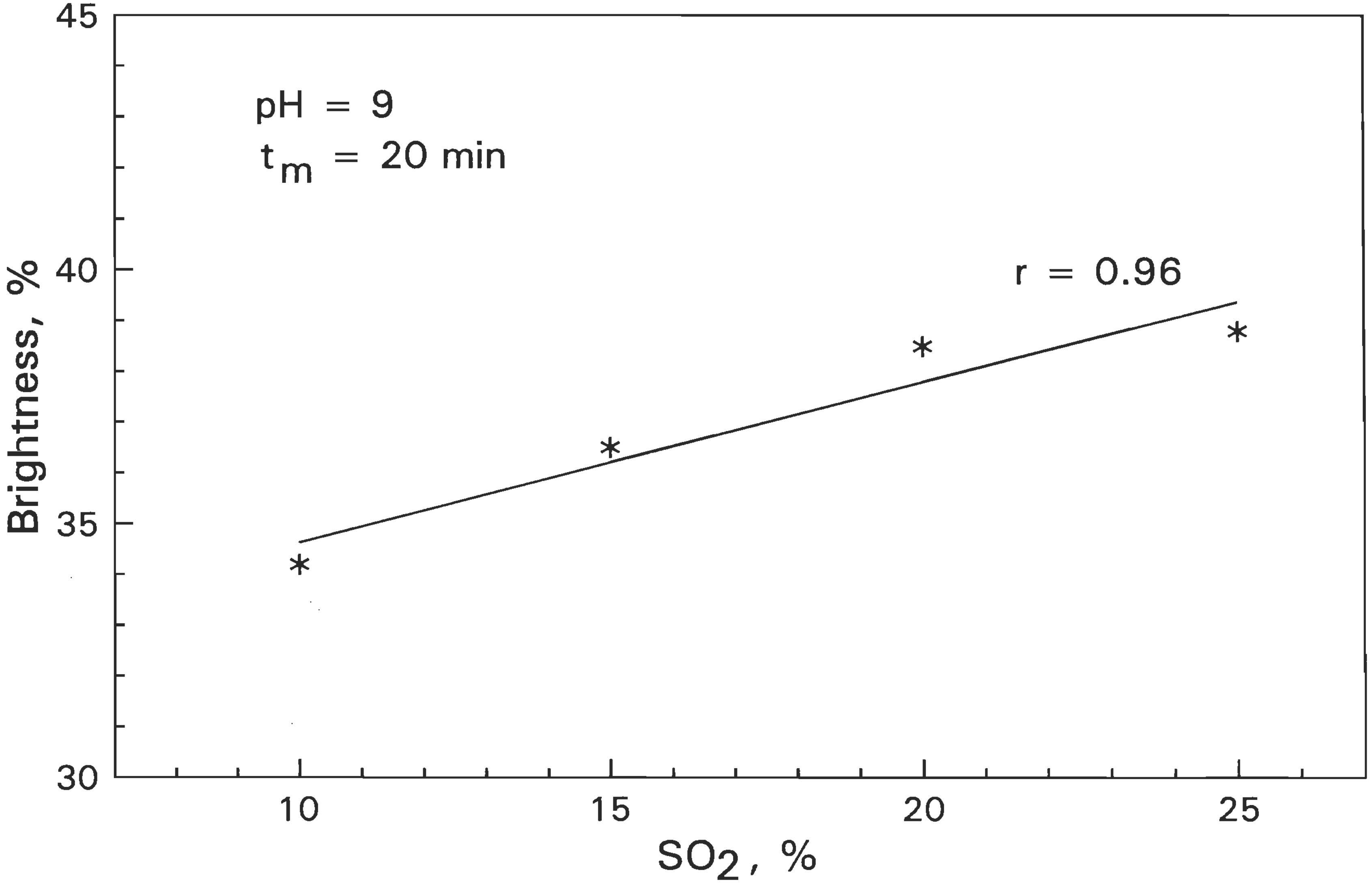


Figure 10 Brightness versus SO_2 charge.

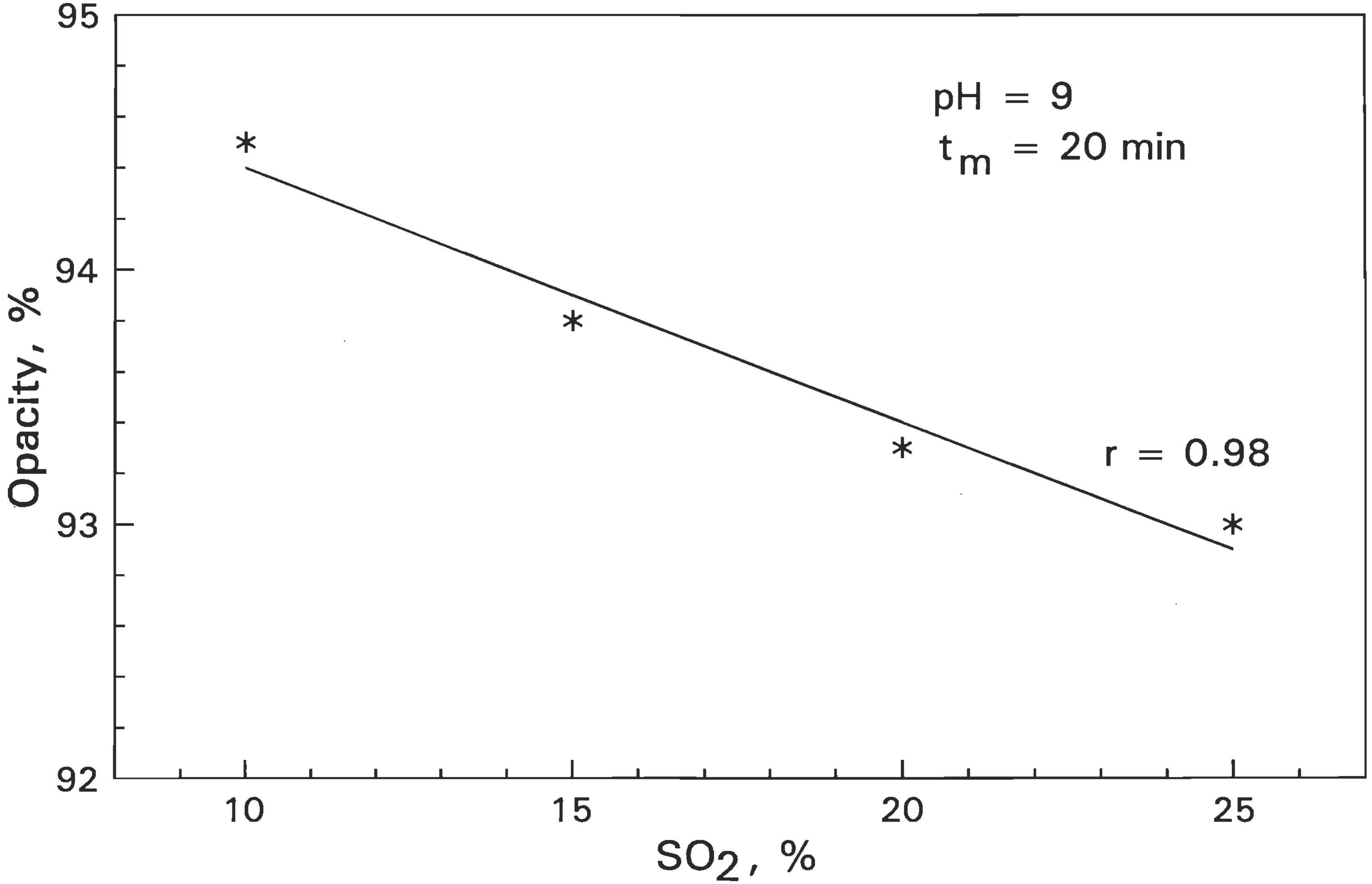


Figure 11 Opacity versus SO_2 Charge.

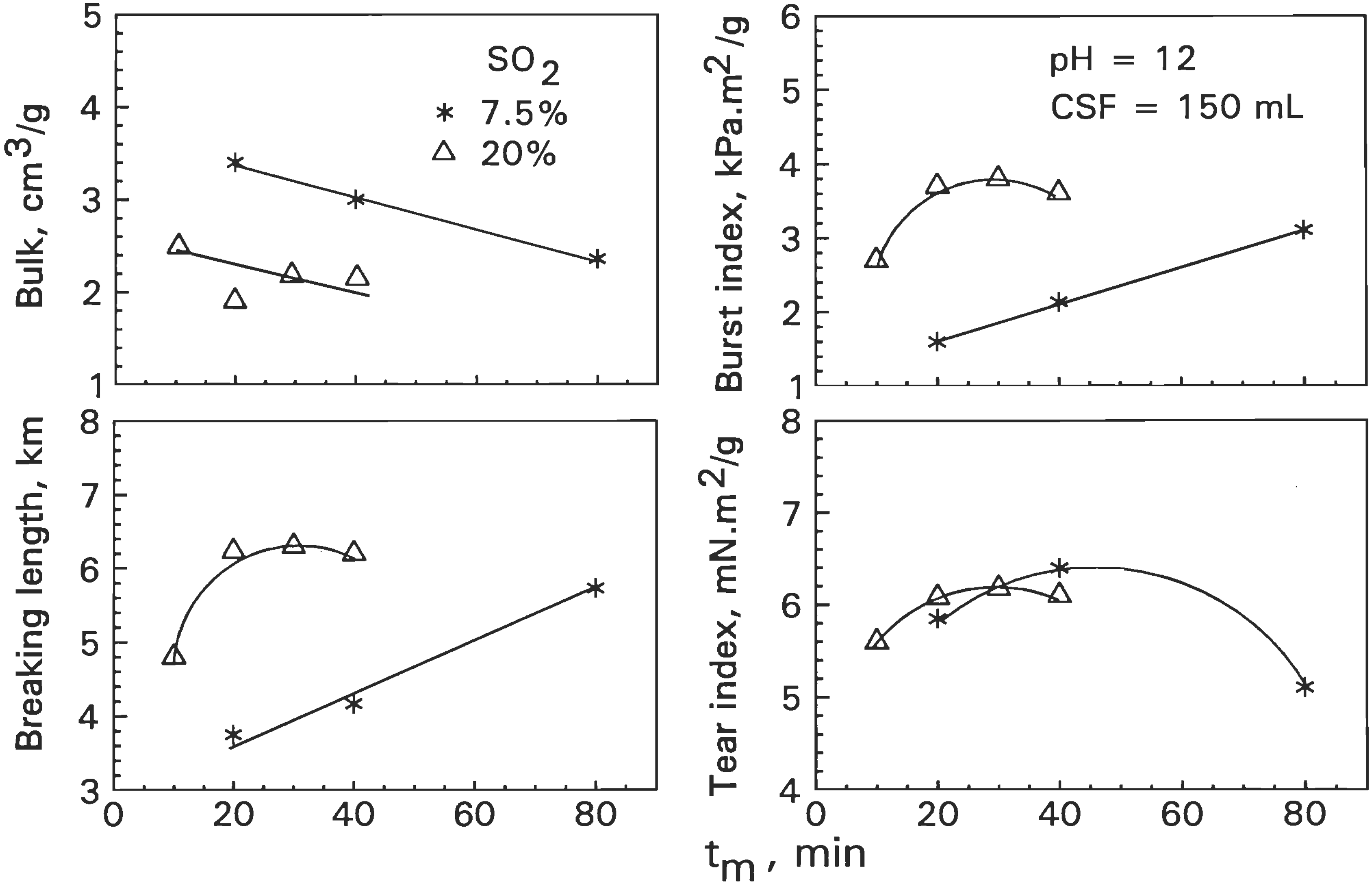


Figure 12 Physical properties versus cooking time.

4.1.3 Relationships between pulp properties

Breaking length versus pulp yield

Figure 13 illustrates the variation of breaking length with pulp yield at CSF 150 mL. As shown, breaking length increases at the expense of pulp yield. The breaking length at the highest yield is 3.3 km; while at the lowest yield is 7.5 km. Breaking length of 5 to 6 km can be obtained in the yield range of 70 to 75%, implying that high-yield pulp with high breaking length can be produced from reed.

Other physical properties versus breaking length

The variations of other physical properties versus breaking length are shown in Figure 14. Burst index, stretch and bulk have good correlations with breaking length. Since all these three properties mainly depend on fiber bonding strength, therefore, they are improved by the increase in breaking length.

Though the relationship between tear index and breaking length seems irregular, an upward trend can still be observed. There appear two regions where breaking length has good correlation with tear index. The first region lies in between

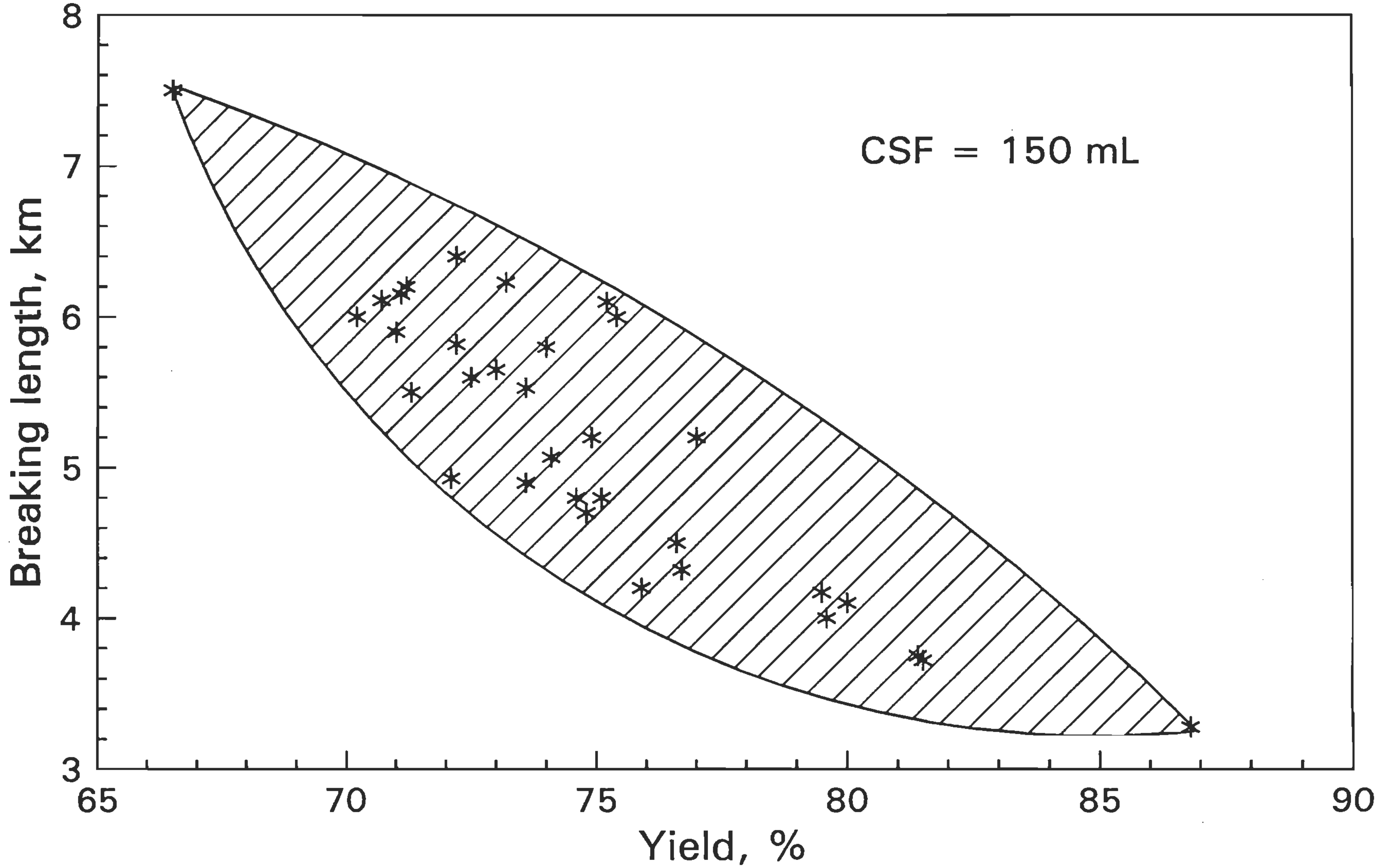


Figure 13 Relationship between breaking length and yield.

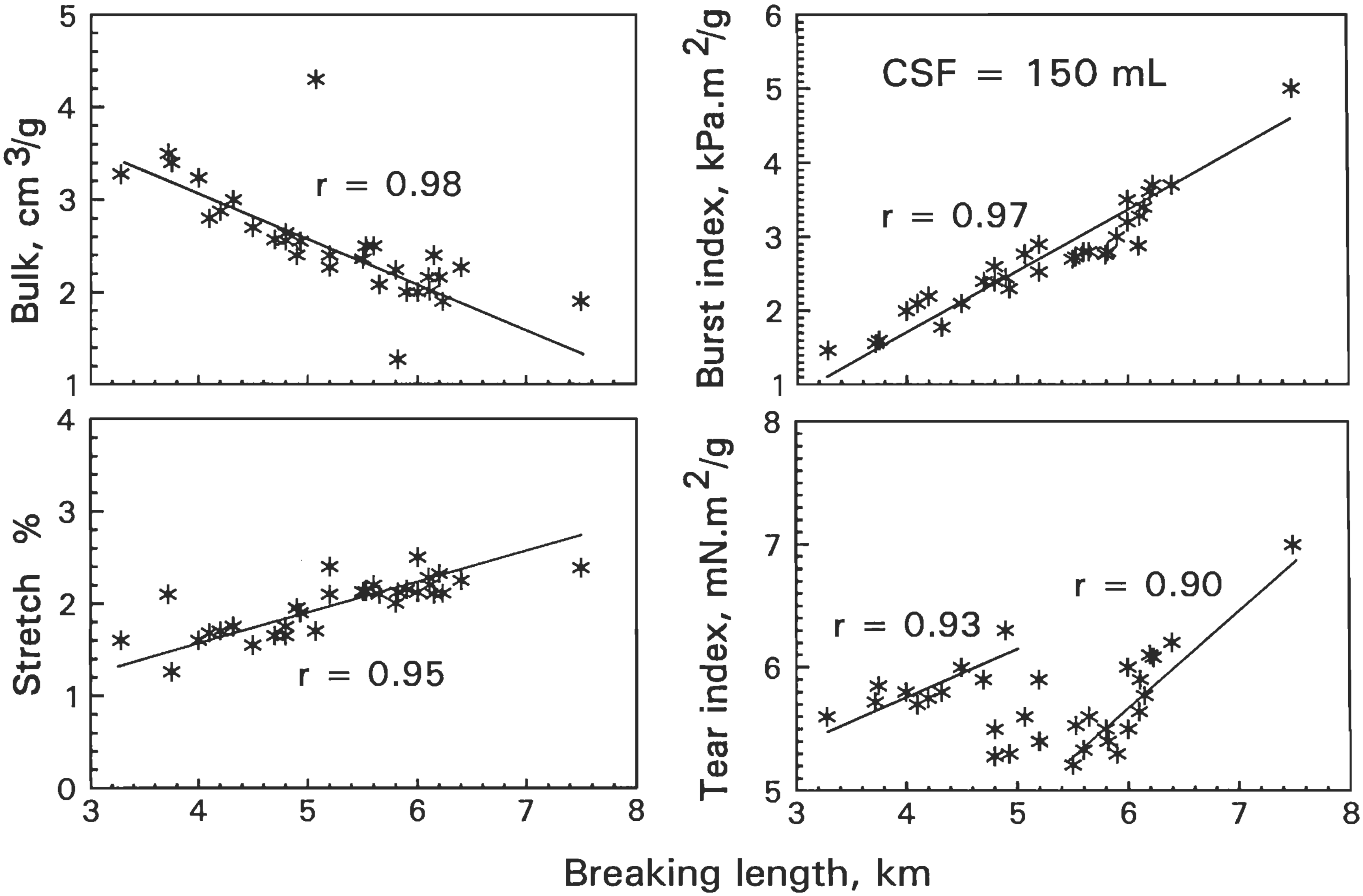


Figure 14 Physical properties versus breaking length.

about 3.3 and 4.7 km, and the second in between 5.6 and 7.4 km. The yield ranges (refer to Figure 13) corresponding to these two regions are approximately 66 - 72% and 77 - 82%, respectively. Good upward-trend correlations between tear and breaking length have also been observed for CM wood pulps [40, 41]. In the region of 5.6 and 4.7 km (corresponding to the yield range of 72 and 77%), the relationship between tear index and breaking length is poor (Figure 14). In this range, tear index varies from 5.3 to 6.5 $mN.m_2/g$ which is considered to be very high for a non-wood pulp with yield of 72 - 77% and having 5.6 - 4.7 km of breaking length.

4.1.4 Refining energy

Non-wood plants have relatively short fibres and high content of hemicelluloses, as compared to wood, so the CM pulp from reed would possess a good refinability. In order to obtain information on refining energy consumption which would be close to industrial practice, a series of refining tests on sulphonated reed chips were carried out with a single-stage Sunds defibrator pilot-plant refiner. The results are presented in Table 9, together with refining conditions.

The results in Table 9 show that reed chips can be readily

Table 9 Specific refining energy for liquid-phase reed CM pulp

Code	#1	#2	#3	#4	#5	#6
Effective charge kW	8	12	13	19	21	22
Clearance of disk mm	0.6	0.5	0.4	0.3	0.25	0.2
Average production kg/min	0.77	0.58	0.63	0.82	0.64	0.55
Consistency, %	11.4	11.2	11.7	12.2	10.6	10.0
Specific energy MJ/kg	0.63	1.3	1.2	1.4	2.0	2.4
CSF, mL	121	94	70	53	45	36

pH = 9; SO_2 = 15%; T_m = 145 °C; and t_m = 40 min.

refined to 120 mL CSF level with a specific refining energy of 0.63 MJ/kg; the refining energy required to reach a 50 mL CSF level would probably not exceed 1.5 MJ/kg. It is obvious, that like most non-wood plants, reed is easier than wood to be refined, because of its open structure.

Effects of fresh liquor pH and SO_2 charge on refining energy

The variation of specific refining energy with fresh liquor pH is presented in Figure 15. As shown, the drop in refining energy with a raise of pH in low pH range (4.5 to 7.5) is very fast, from 9.3 to less than 1 MJ/kg. In the pH range of 9 to 12, liquor pH has no effect on the specific refining energy consumption which is low and at about 0.4 MJ/kg, indicating that pH higher than or at least equal to 9 should be used to carry out chip sulphonation.

The effect of SO_2 charge on specific refining energy for pH 9 is presented in Figure 16. At this pH, a SO_2 charge higher than 15% does not affect the specific refining energy which remains at a level about 0.35 MJ/kg. The specific energy would be doubled when the charge is decreased from 15 to 10%. The results imply that a SO_2 charge of at least 15% should be used for chip sulphonation to economize energy consumption.

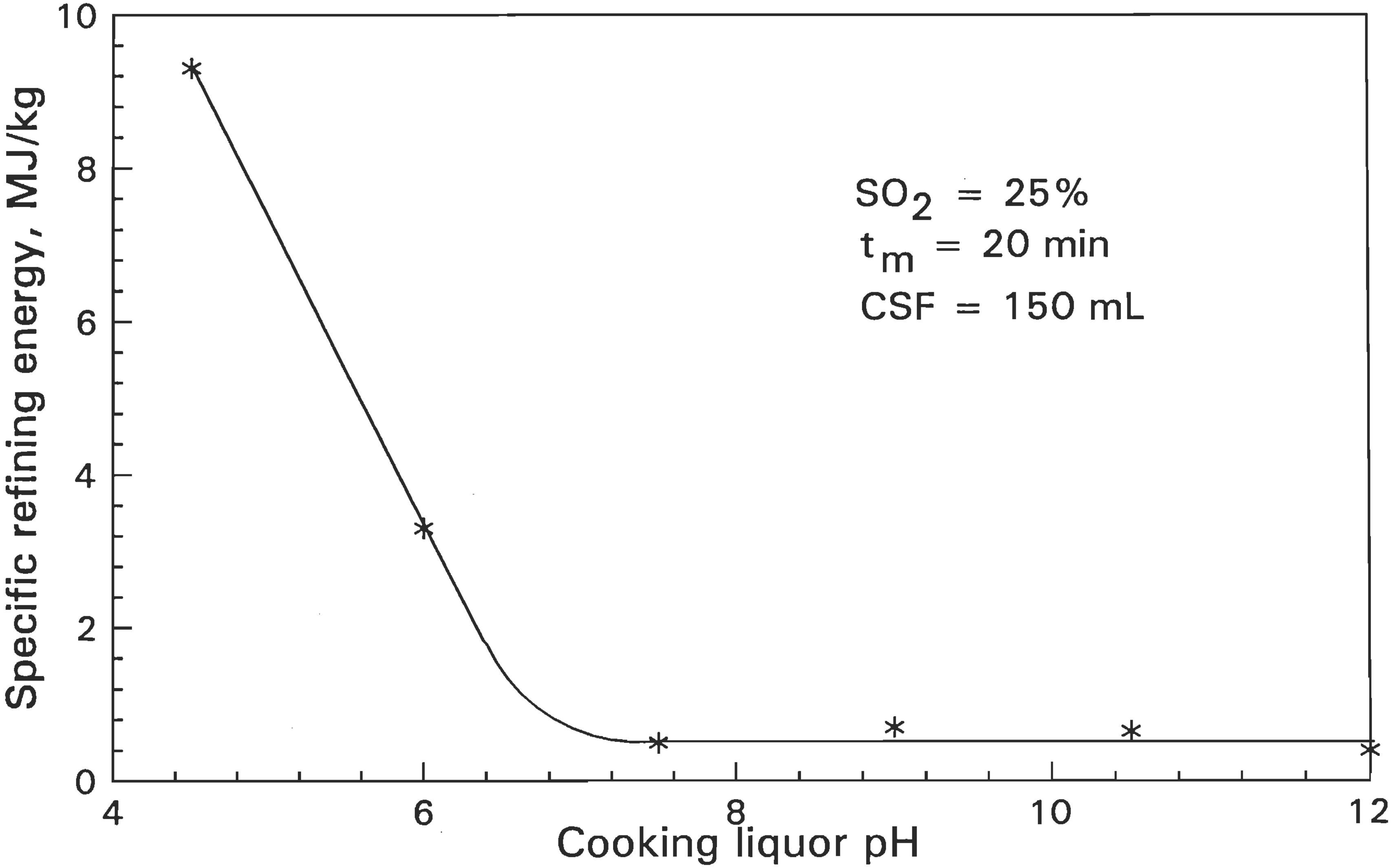


Figure 15 Effect of fresh liquor pH on specific refining energy.

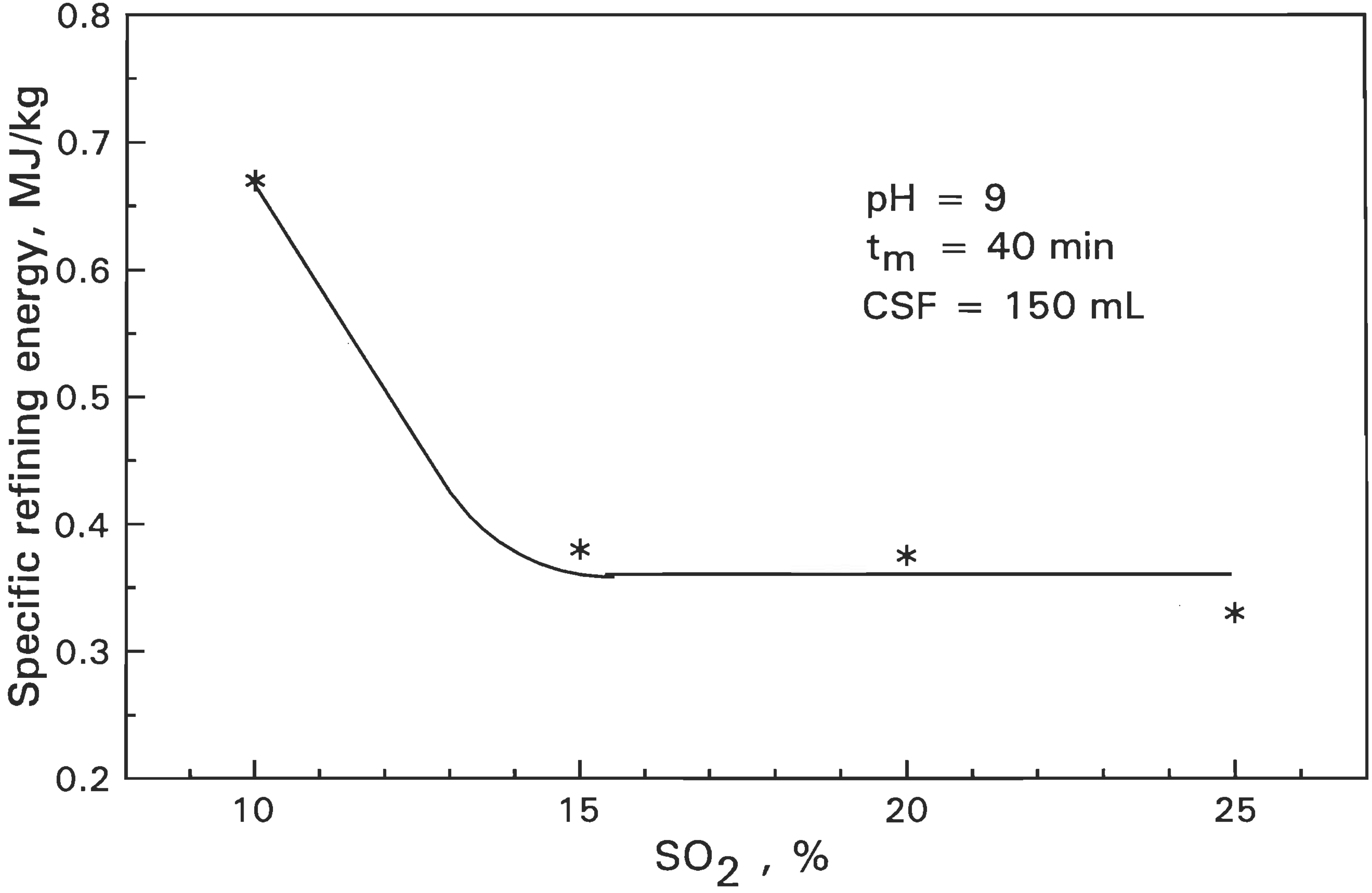


Figure 16 Specific refining energy versus SO_2 charge.

CSF versus specific refining energy

Figure 17 presents the variation of CSF versus specific refining energy, for pulps cooked under the conditions which are considered to be optimal, as discussed in the last two paragraphs. The curve in this figure illustrates the usual relationship between them, i.e., CSF decreases with increasing specific refining energy. As observed, the energy requirement for refining a pulp to 300 - 100 mL CSF, which is usually used in the production of paper products, is low and amounts to 0.3 - 1.2 MJ/kg. The CM pulp from reed at this CSF range possesses acceptable physical properties, that will be presented in the following sub-sections.

Physical properties versus CSF

Refining plays a very important role to improve the physical characteristics of mechanical pulp. During refining, fibres are subjected to be cut, swelling, collapse, and fibrillation, so more bonding area is generated; and at the same time fiber becomes more flexible and has much better conformability. CSF is usually used to express the degree of refining. The variations of physical and optical properties of two reed CM pulps versus CSF are presented in Figures 18 - 21, for the

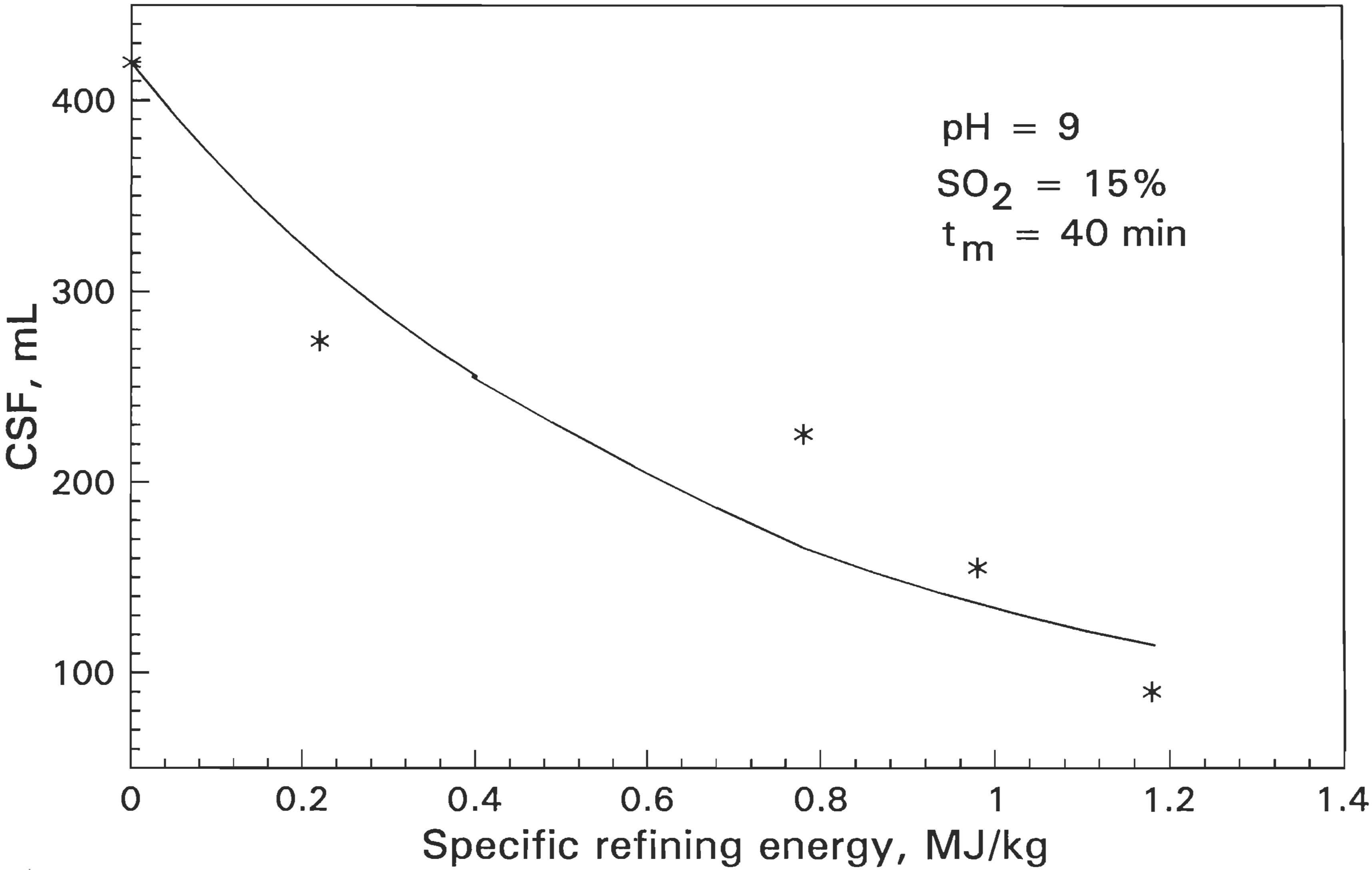


Figure 17 CSF versus specific refining energy.

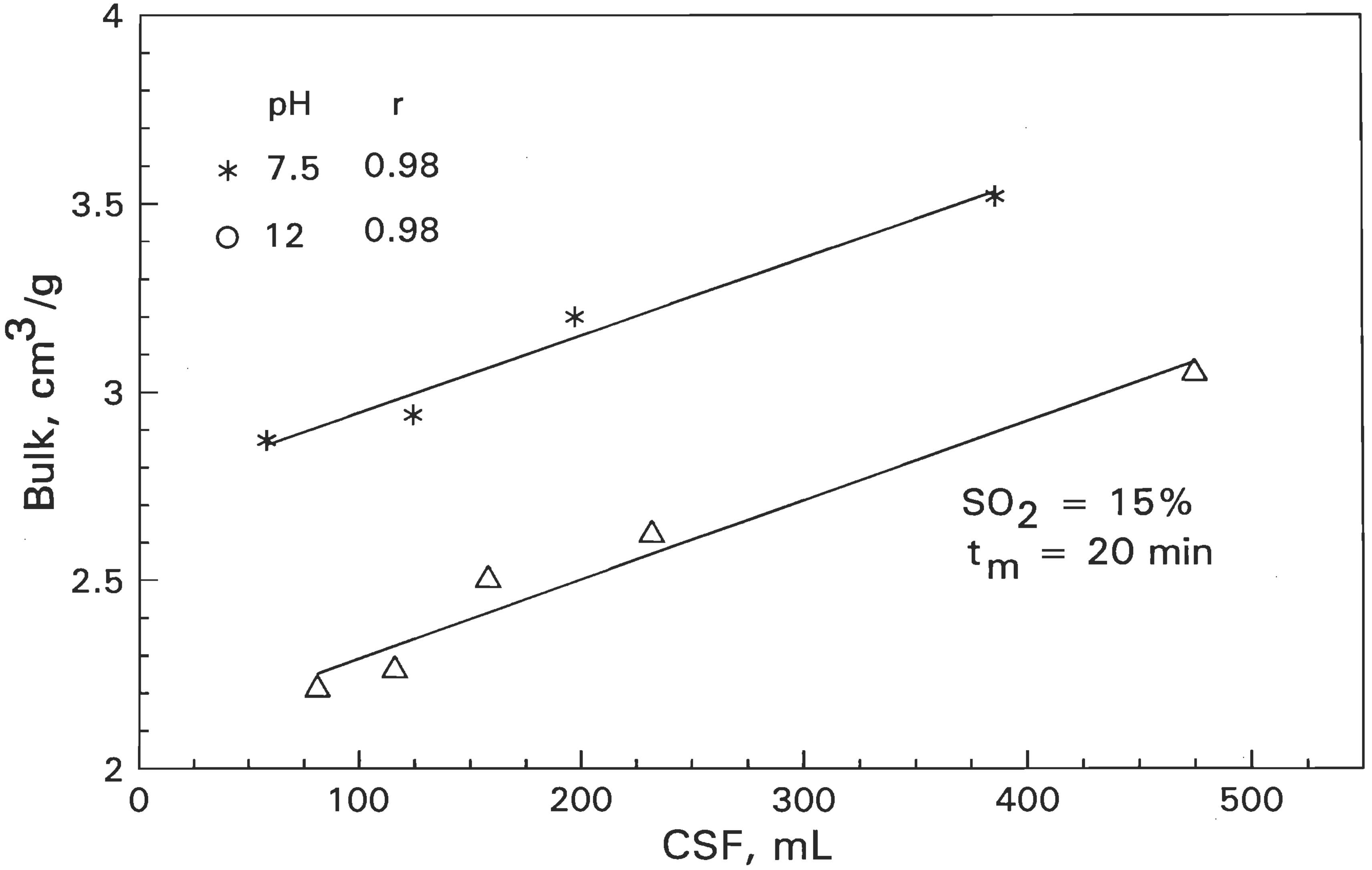


Figure 18 Bulk versus CSF.

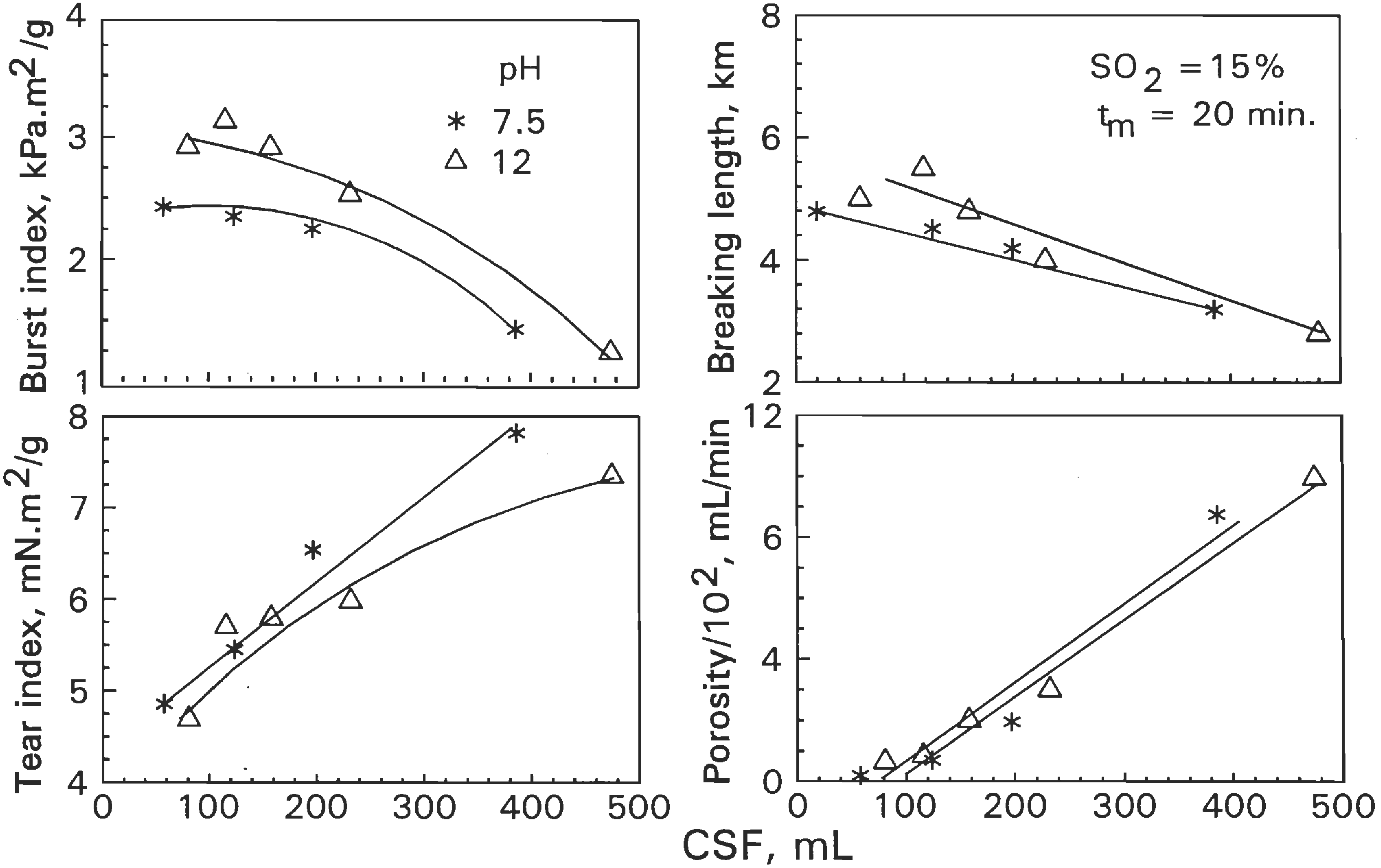


Figure 19 Relationships between physical properties and CSF.

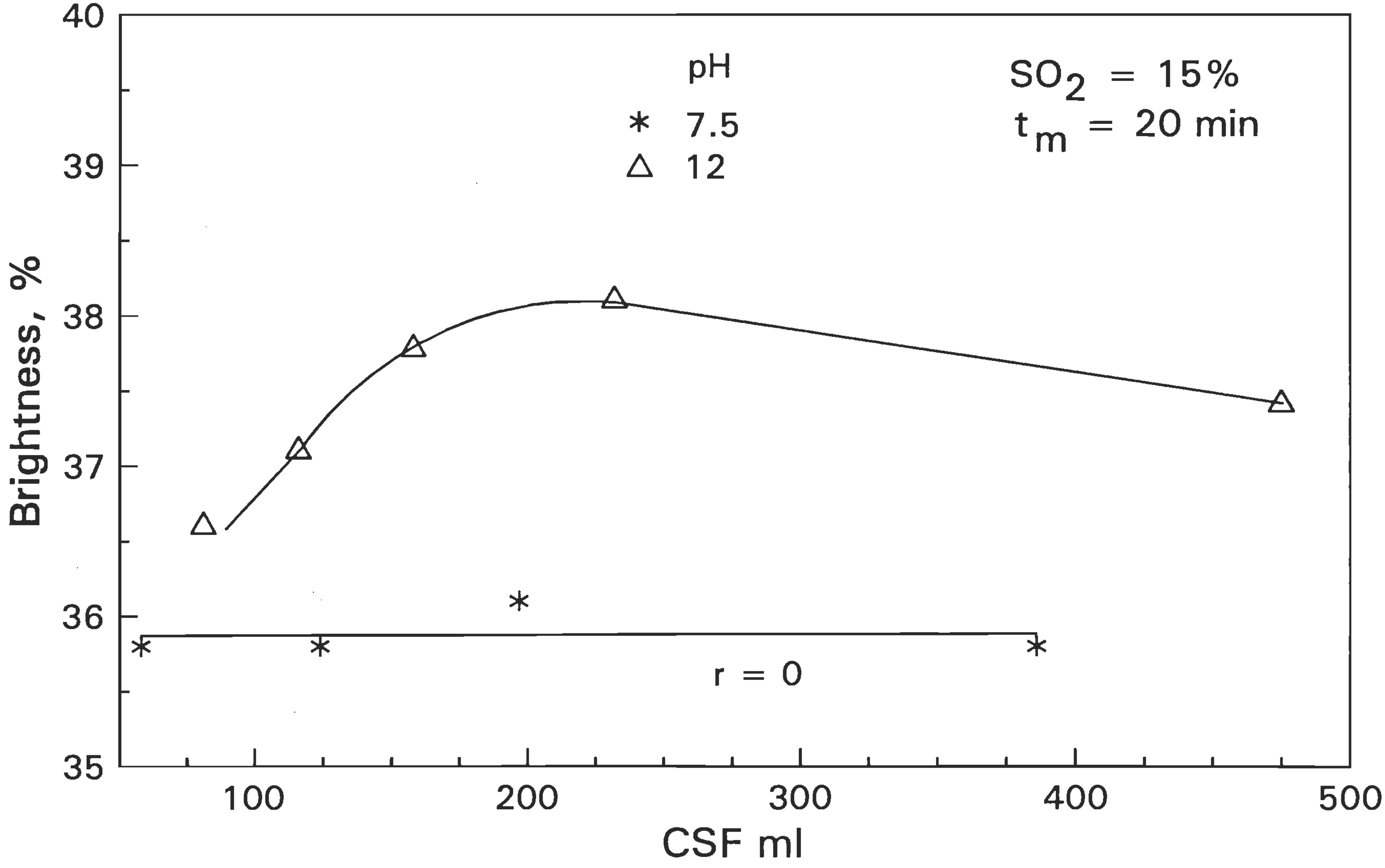


Figure 20 Brightness versus CSF.

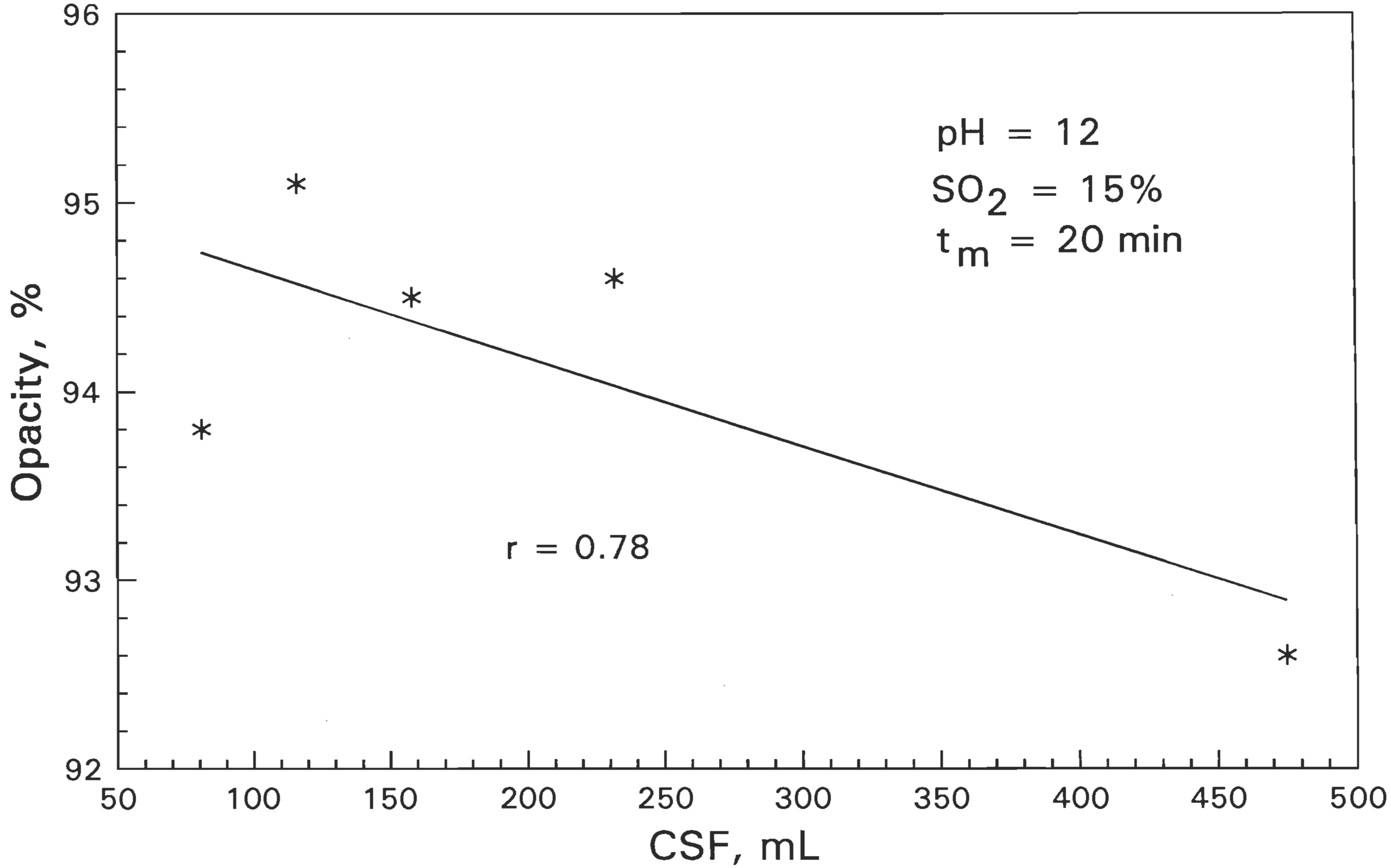


Figure 21 Opacity versus CSF

purpose of showing the effect of refining.

The decrease in bulk (Figure 18) and porosity (Figure 19) suggests that the bonding properties of the pulps are improved by refining. As shown, the bulks of both pulps decrease slightly and the porosities drop very significantly with decreasing CSF. High bulk is one of the characteristics of mechanical pulp. As it is known that porosity is strongly affected by the fine content in sheet, and that fine content normally increases with decreasing CSF, therefore, porosity decreases significantly with decreasing CSF.

For the data presented in Figure 19, the magnitudes of gain in burst index due to refining, expressed by CSF, are about 1.5 and 2 units (kPa.m_2/g), respectively for pH 7.5 and 12; while the magnitudes of gain in breaking length are about 2 and 2.5 units (km). Both properties depend on fibre bonding and long fibre fraction. Tear index drops very sharply with decreasing CSF, suggesting further fibre-cutting during refining since tear depends strongly on long fibre fraction,

For the two sets of cooking conditions (pH = 7.5 and 12, SO_2 charge =15%) presented in Figure 18, satisfactory physical properties can be developed by refining the reed CM pulp to the

CSF level of 300 - 100 mL. The physical properties of pulp at that level would be: breaking length, 4 - 5 km; burst index, 2 - 3 kPa.m^2/g; tear index, 5 - 7 mN.m^2/g; and bulk, 2.2 - 3.2 cm^3/g.

Optical properties versus CSF

At pH 7.5 (Figure 20), refining introduces no effect on brightness of the CM pulp from reed. At pH 12, the effect of refining on brightness is significant, inducing a maximum reduction of about 2 points at about 100 mL CSF.

Shown in Figure 21 is the effect of CSF (or degree of refining) on pulp opacity. As illustrated, opacity increases with refining. This might be explained as follows. The initial opacity (92.6%) at 475 mL CSF is low, due to some bundles and shives existing in the unrefined pulp, thus reducing the light scattering area. As refining proceeds, fine fraction would increase with refining which contributes to the increase of opacity.

4.1.5 Effect of SO_2 charge on residual SO_2

Figure 22 presents for two pH's, 9 and 12, the relation-

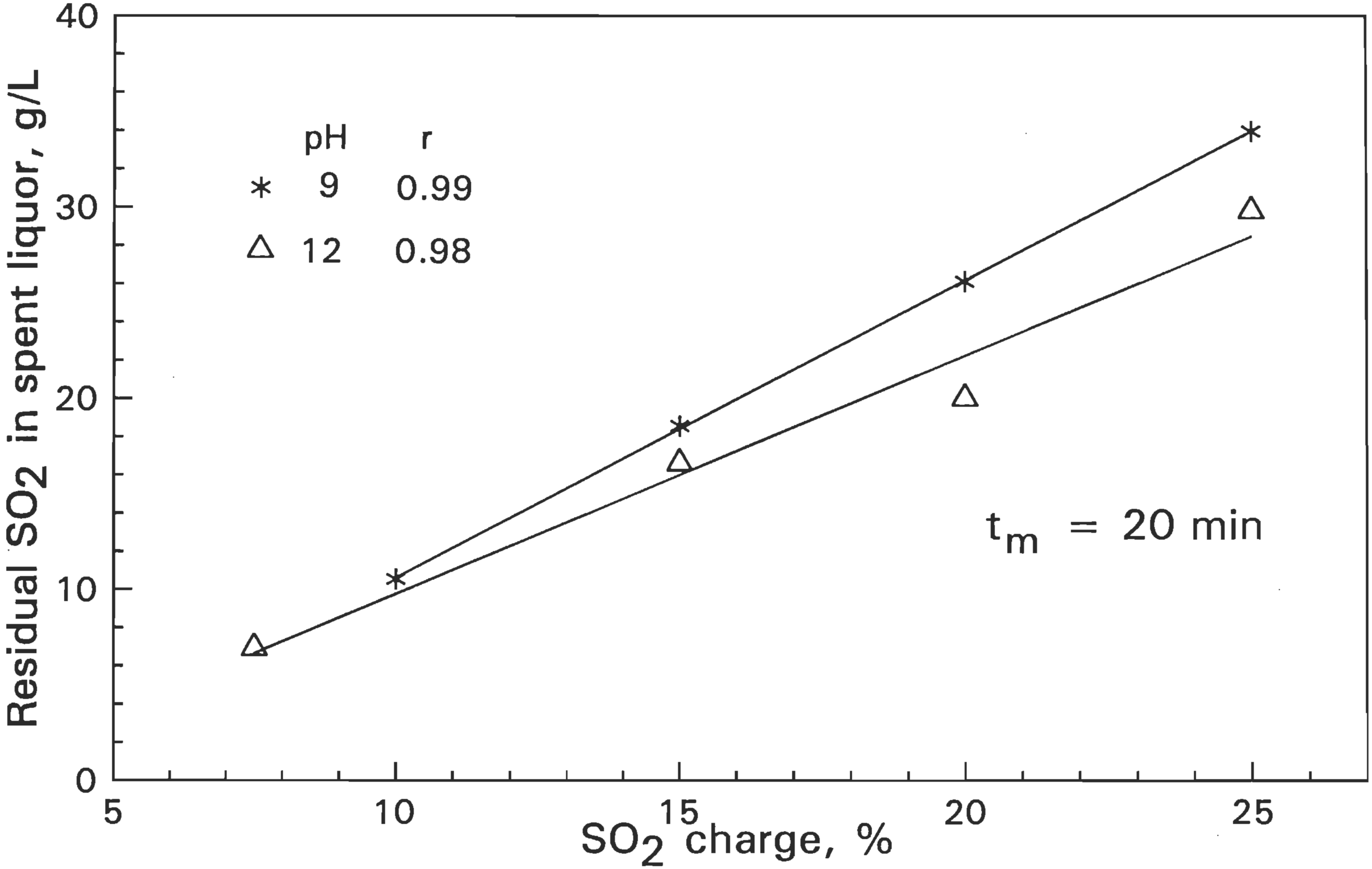


Figure 22 Residual SO_2 versus SO_2 charge at two levels of pH.

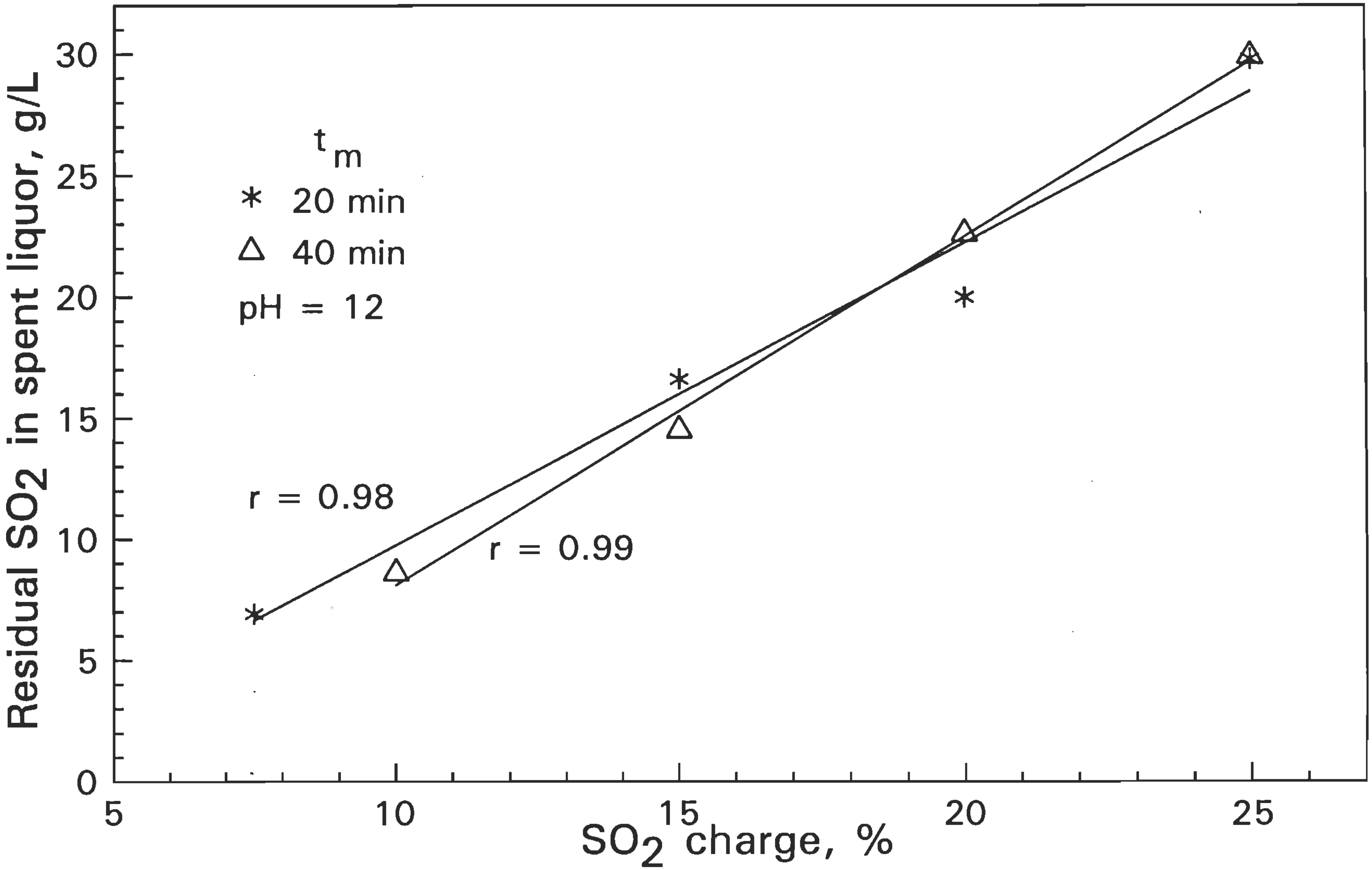


Figure 23 Residual SO_2 versus SO_2 charge at two levels of cooking time.

ships between the residual SO_2 in the spent cooking liquor and the SO_2 charge for the cook. For both cases, the residual SO_2 increases linearly with the increase in SO_2 charge. At a given SO_2 charge, the case of pH 9 leaves more residual SO_2 in the spent liquor than the case of pH 12. At high pH, high concentration of OH^- ions leads to more active sites for reaction, so more SO_2 is consumed for chip sulphonation. especially at high SO_2 charge.

Figure 23 shows that, for a given pH, increase in cooking time has no effect on the residual SO_2 in the spent liquor, for all the SO_2 charges studied. Therefore, over extending of cooking time is unnecessary, because it can not further increase the extent of chip sulphonation, since there is a limitation of maximum sulphonation (2 - 2.4% on o.d. pulp) [19]; and it will cause further loss in pulp yield. At high SO_2 charge, 25%, the residual SO_2 reaches 30 - 35 g/L (Figure 23), amounting a heavy loss in cooking chemicals. To recover this huge loss, the work on vapor-phase cooking with recycling of spent impregnation liquor was thus initiated.

4.2 VAPOR-PHASE CM PULPING OF REED

4.2.1 Cooking without spent liquor recycling

Listed in Table 10 are the cooking conditions, together with the corresponding yields and physical properties of pulps. As shown in the table, pulp yield ranges from 73.5 to 86%, and it is significantly influenced by the maximum cooking temperature, cooking time, and sightly by liquor pH and SO_2 charge. The physical properties obtained under the conditions studied are: burst index, 1.6 -2.6 kPa.m^2/g; breaking length, 3.8 - 5.2 km; tear index, 5.7 - 6.4 mN.m^2/g; and bulk, 2.8 - 3.3 cm^3/g. The optical properties are: brightness, 38 - 39.4%; and opacity, 92.6 - 94.8%. Compared with liquid-phase cooking (reported previously in Section 4.1), pulps obtained from vapor-phase cooking display inferior properties and higher yield when identical operation conditions are applied. When the maximal temperature, T_m, for vapor-phase cooking was maintained at 155°C (i.e., 10°C higher than that for liquid-phase cooking) and other conditions kept unchanged, the outcomes from both modes of cooking then became comparable.

When taking into consideration the pulp yield and strength properties and chemical charges, a set of cooking conditions, listed under the code RV-8 in Table 10, was chosen for the subse-

Table 10 Vapor-phase CM pulping without recycling of spent impregnation liquor

Code	RV-1	RV-6	RV-8	RV-9	RV-10	RV-11	RV-12	RV-13
Max. temp., T_m, ^oC	145	155	155	145	145	145	155	155
Time at T_m, t_m, min	40	20	40	20	20	40	20	40
Liquor pH	12	12	9	9	12	9	9	12
SO_2/o.d. chip, %	15	15	15	15	25	25	25	25
Bulk, cm^3/g	3.3	3.8	2.8	3.3	3.2	3.2	2.8	2.8
Burst, kPa.m^2/g	1.9	1.8	2.2	1.9	2.1	1.6	2.6	2.6
Breaking length, km	4.1	4.3	4.8	5.1	4.5	3.8	4.5	5.2
Tear, mN.m^2/g	5.9	6.2	5.9	5.9	6.4	5.9	5.7	5.8
Brightness,	38.7	37.9	36.5	38.6	38.2	38.7	39.1	39.4
Opacity, %	94.0	93.6	94.2	94.8	92.6	93.1	94.2	94.1
Yield, %	79.2	74.6	74.9	86.0	78.6	79.4	76.1	73.5

Impregnation temperature, T_i : 100 ^oC; Time at T_i : 20 min; Liquor/o.d. chip : 6
Pulp properties evaluated for CSF of 120 mL.

quent experiments with recycling of spent impregnation liquor.

4.2.2 Cooking with spent liquor recycling

The spent liquor recovered from chip impregnation was recycled 17 times; the cooking conditions were the same as those for the experiment RV-8 (Table 10). The cooking yields and physical characteristics of pulps thus produced will be presented in corresponding figures in the following sub-sections, which indicate the outcomes as a function of NR (number of recyclings).

4.2.2.1 Pulp yield and refining energy

As shown in Figure 24, the pulp yield varies from 74.5 to 75.3%, with an average of 74.8%, all along the 17 times of recycling. Seeing that the variation is small and that the average yield is practically the same as the one obtained without spent liquor recycling (74.9%, RV-8 in Table 10), one can conclude that the recycling of spent impregnation liquor has no effect on pulp yield.

Figure 25 illustrates that the specific energy required to refine the pulp to 150 mL CSF declines slightly, as NR increases from 0 to 17. This tendency assures that the vapor-phase cooked reed chips will be easy to be refined.

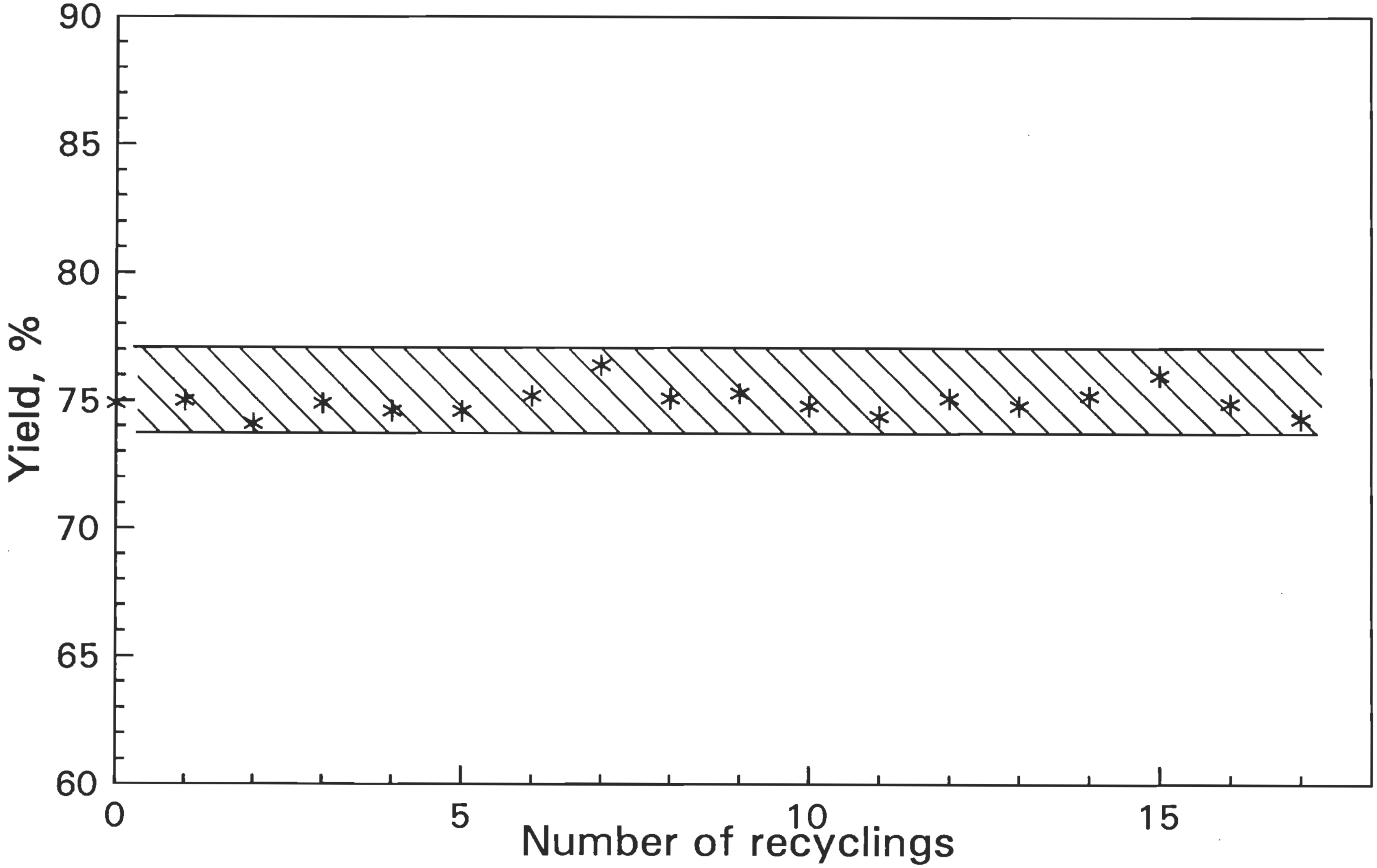


Figure 24 Relationship between yield and number of recyclings.

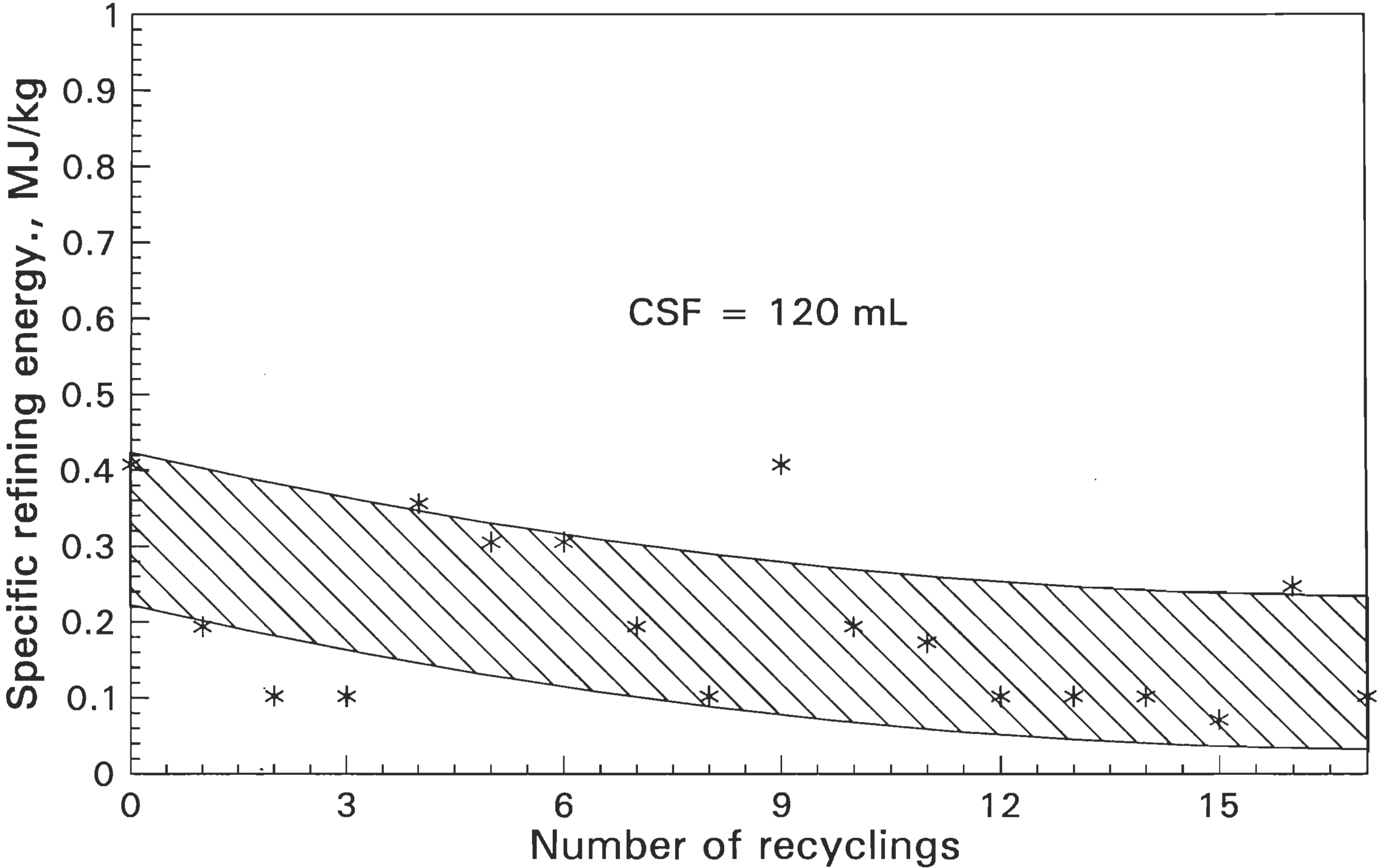


Figure 25 Specific refining energy versus number of recyclings.

Shown in Figure 26 is the relationship between CSF and specific refining energy. The CSF rapidly decreases from its initial level of 420 mL to about 200 mL with only a small quantity of refining energy in the order of 0.1 MJ/kg o.d. pulp.

Indeed, high-yield reed pulps have a good refinability, one of the major reasons for this is that, having characteristics of non-wood plant material, reed pulps possess a higher content of hemicelluloses and shorter fibres than wood pulp. Besides, non-wood plant material has a looser structure than wood; therefore, the specific energy consumption for refining the reed CM pulp to a reasonable CSF range (e.g. 300 - 100 mL) is only 0.1 to 0.5 MJ/kg -- a value about 1/10 to 1/50 of that required for a wood CM pulp refining.

4.2.2.2 Characteristics of handsheets

Figure 27 shows that, within the NR range studied, there is no significant variation in pulp characteristics, no matter what the NR is. The average values of these properties are: bulk, 3.1 cm^3/g; burst index, 1.9 $kPa.m^2/g$; breaking length, 4.6 km; and tear index, 6.1 $mN.m^2/g$.

Figures 28 and 29 show that recycling of spent impregnation

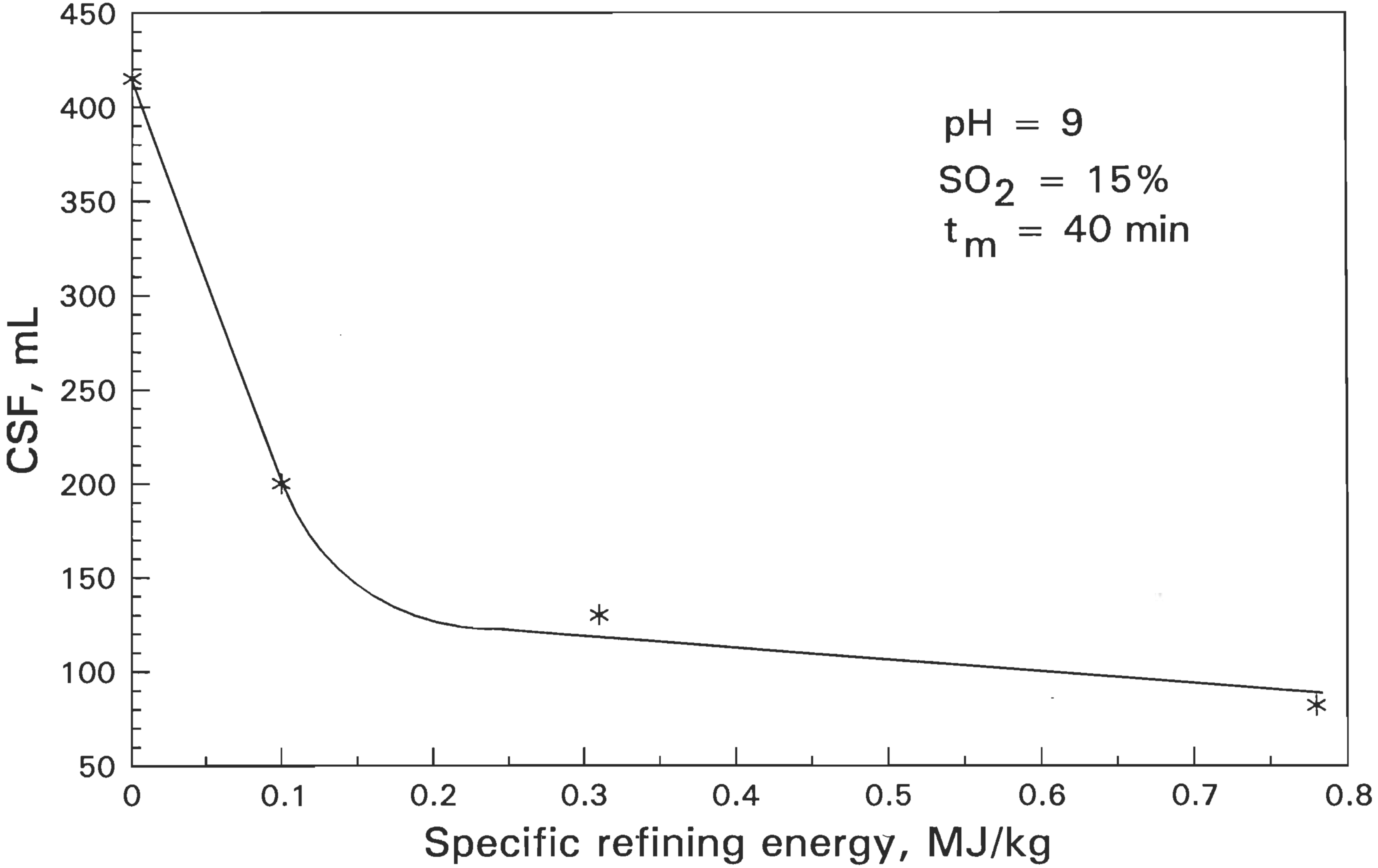
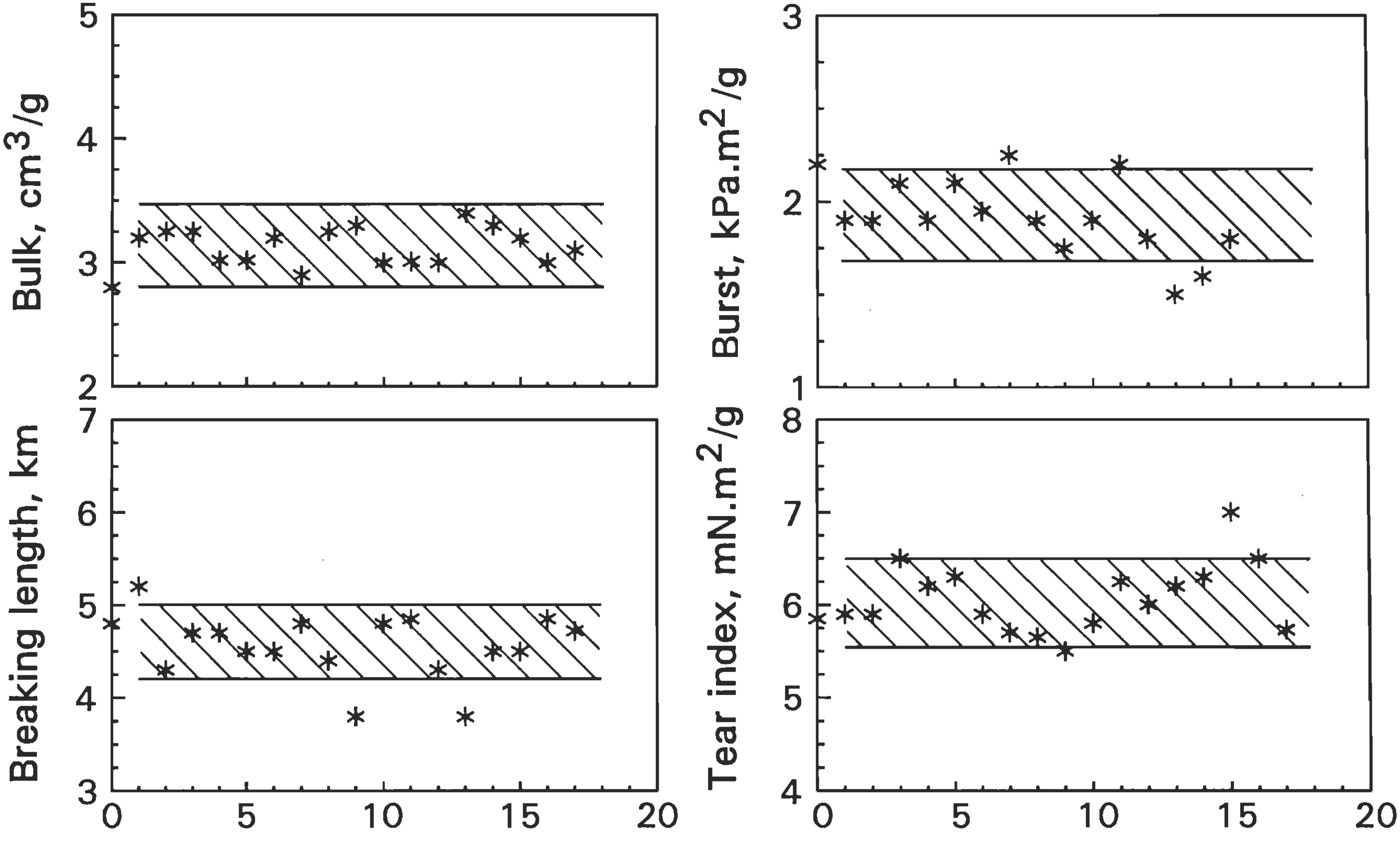


Figure 26 CSF versus specific refining energy.



Number of recyclings.

Figure 27 Physical properties versus number of recyclings.

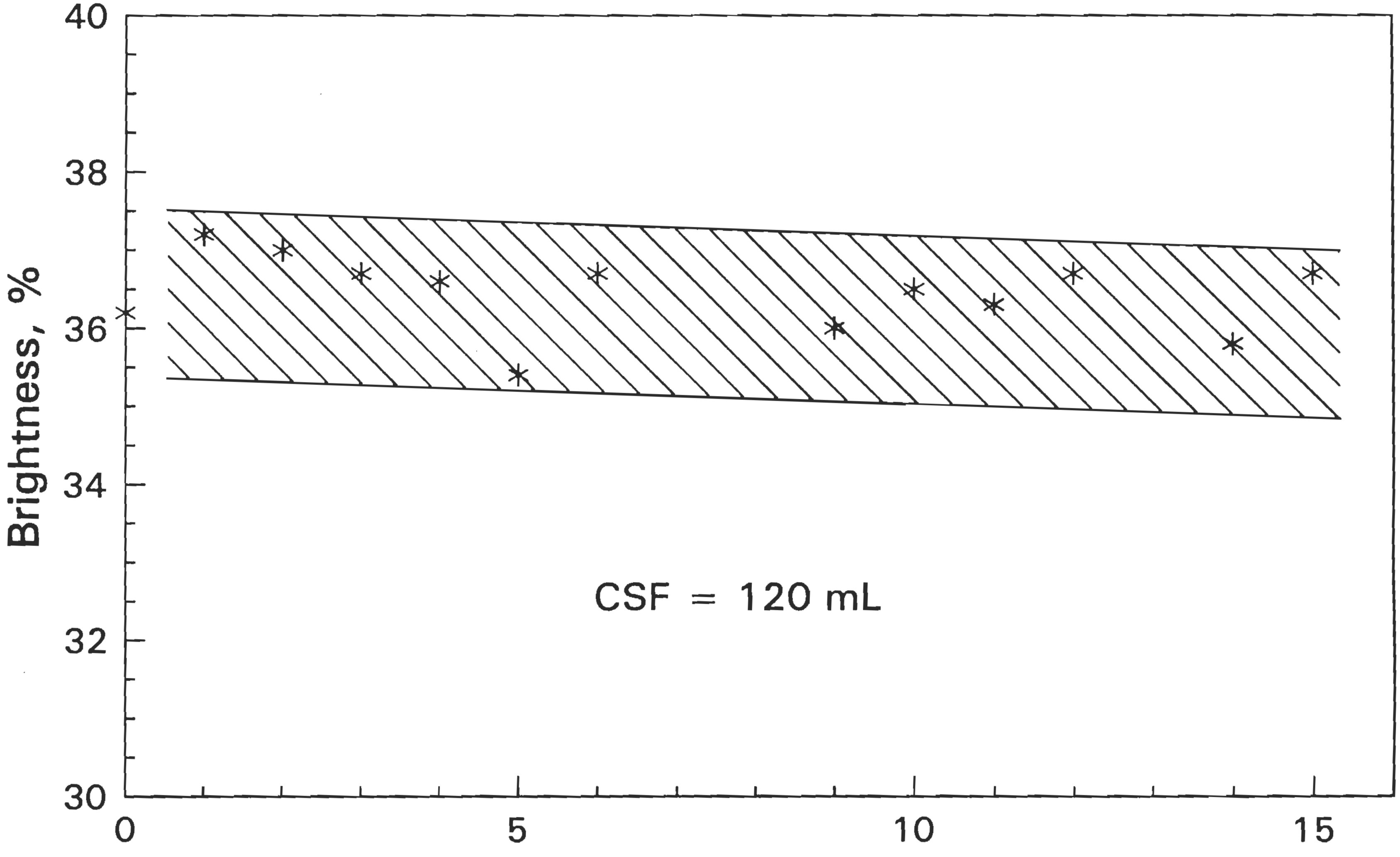


Figure 28 Brightness versus number of recyclings.

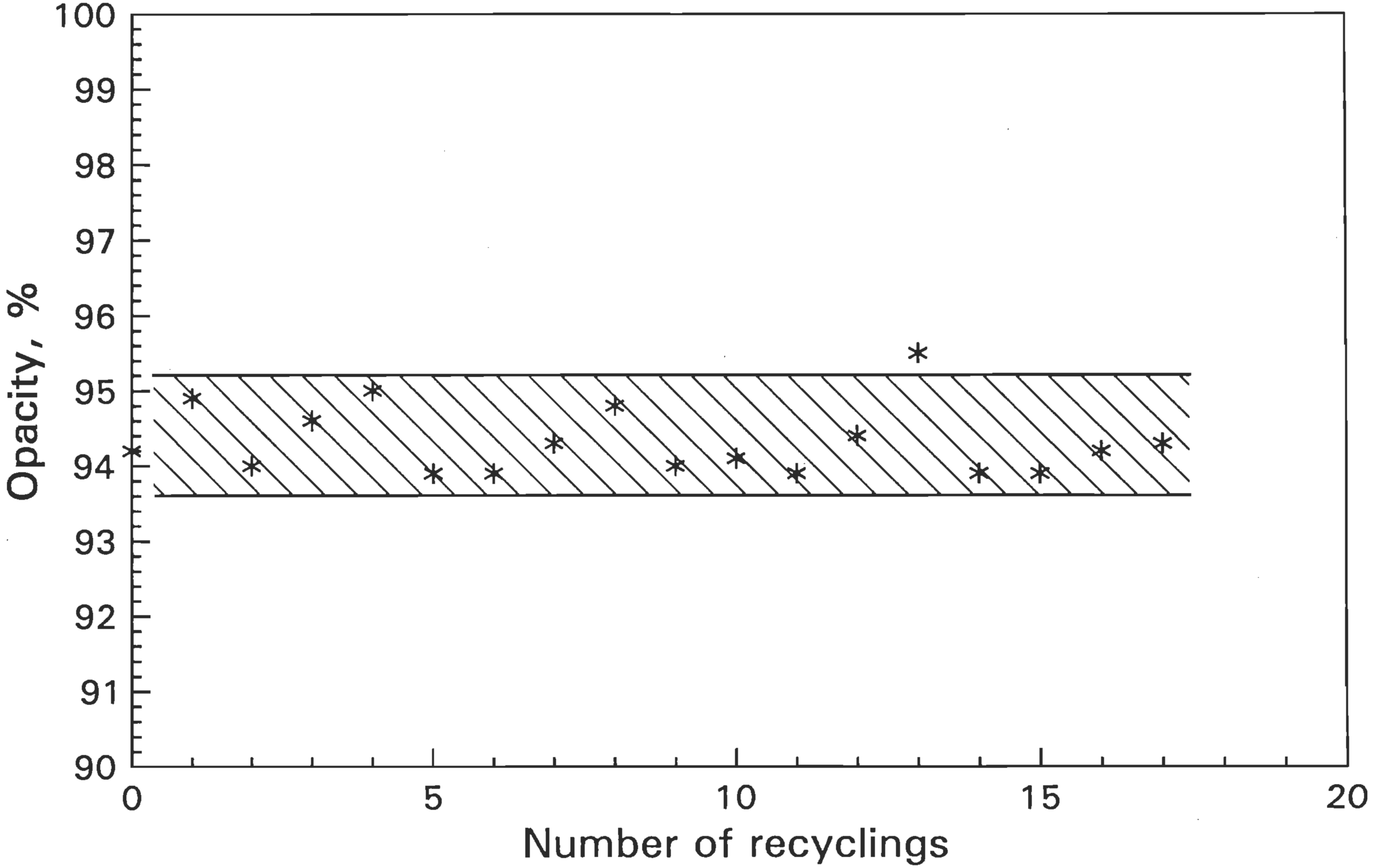


Figure 29 Opacity versus number of recyclings

liquor has no influence on the optical properties of reed CM pulps. The brightness varies between 36% and 37%, and opacity is in the range of 93.5% to 95%.

4.2.2.3 Effects of refining energy on physical properties

The effects of refining on the pulp physical properties are presented in Figure 30. With the CSF range studied, a linear correlation between each of the properties and CSF can be seen. As refining could improve the flexibility and conformability of fibers, as well as the interfiber bonding strength, one can see from Figure 30 that bulk decreases, while burst index and breaking length are increased with decreasing of CSF. Tear index decreases with CSF, probably partly due to the decrease in long fiber fraction and partly due to the increase in tensile strength resulting from the refining.

From the results presented in Figures 24 to 29, one can conclude that the pulp produced with spent liquor recycling has similar yield, strength characteristics and optical properties, as compared to the pulp produced with a fresh impregnation liquor (i.e., the number of recycling equal to zero).

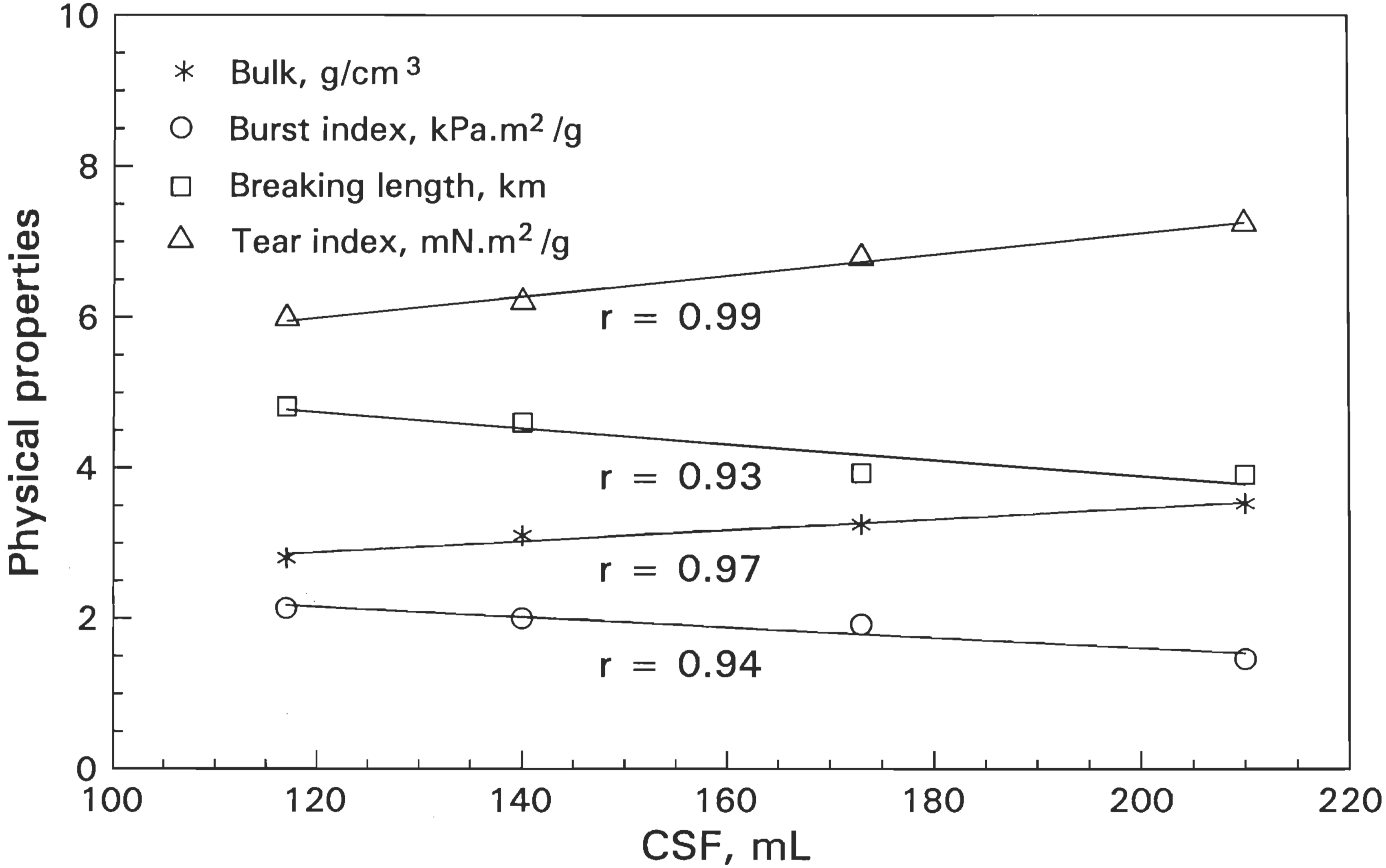


Figure 30 Physical properties versus CSF.

4.2.2.4 Spent impregnation liquor characteristics

Liquor pH

Figure 31 shows that the spent liquor pH is quite constant (8.2 - 8.3) as the number of recyclings increases from 0 to 17. Since the liquor pH starts from 9 and ends around 8 during the chemical pretreatment (impregnation), the equipment needs not to be constructed with highly acid-resistant materials; in other words, any conventional equipment can be used for chemical pretreatment in this process.

Liquor density

When it comes to the density of spent liquor, one would expect that the spent liquor becomes thicker due to the increase of dissolved solids in the liquor along with the increase of NR. It is true when NR is small (e.g., NR < 9, as shown in Fig. 32). However, when NR is large, the density attains a plateau whose value is about 1.075 kg/m^3; no further increase can be obtained with higher NR. This observation suggests that, at the fixed impregnation conditions (T_i = 100°C, t_i = 40 min, etc..), there is a quasi-saturation point of dissolved solids in liquor. This point corresponds to a stoichiometrical concentration of reed components

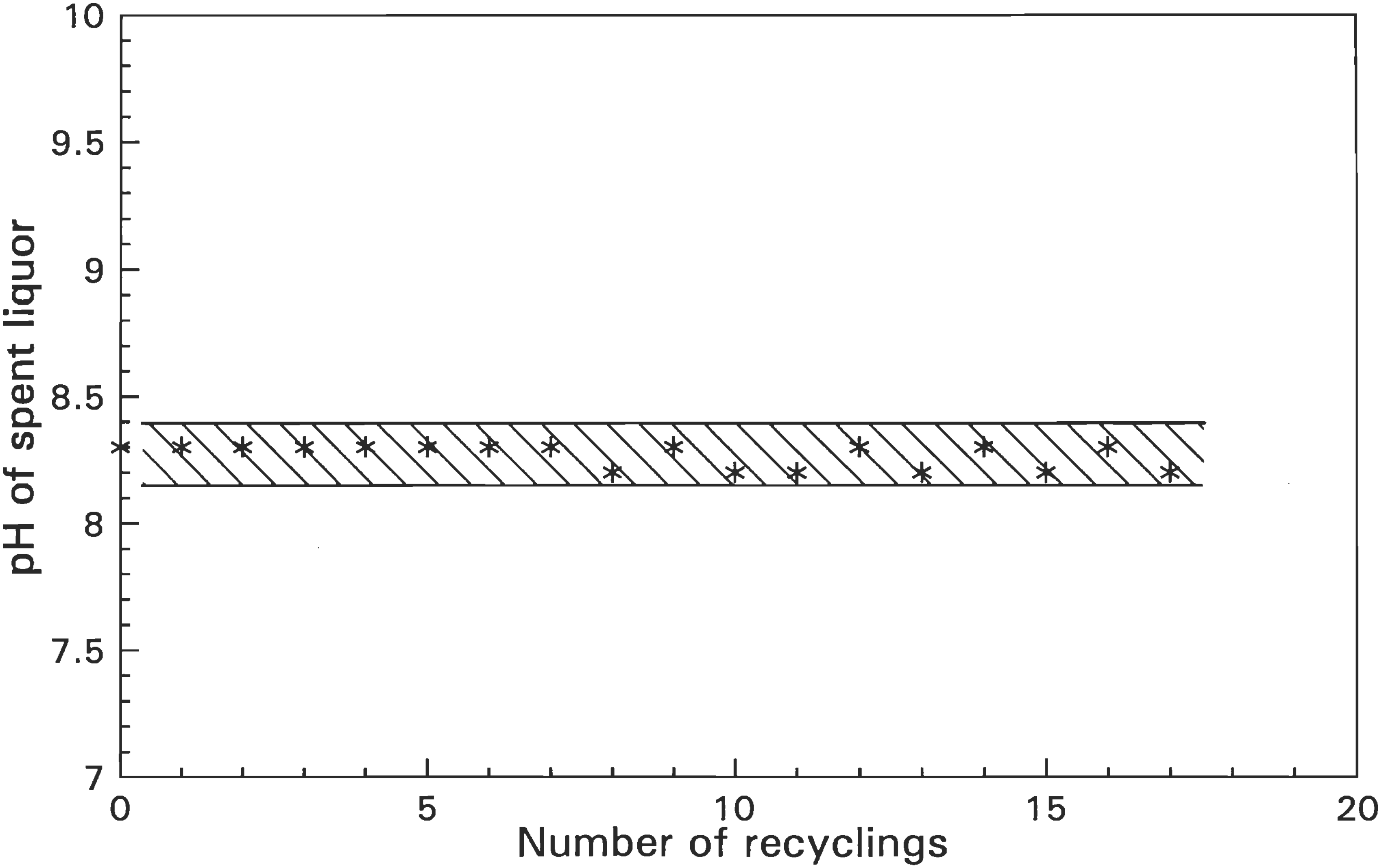


Figure 31 Relationship between spent liquor pH and number of recyclings.

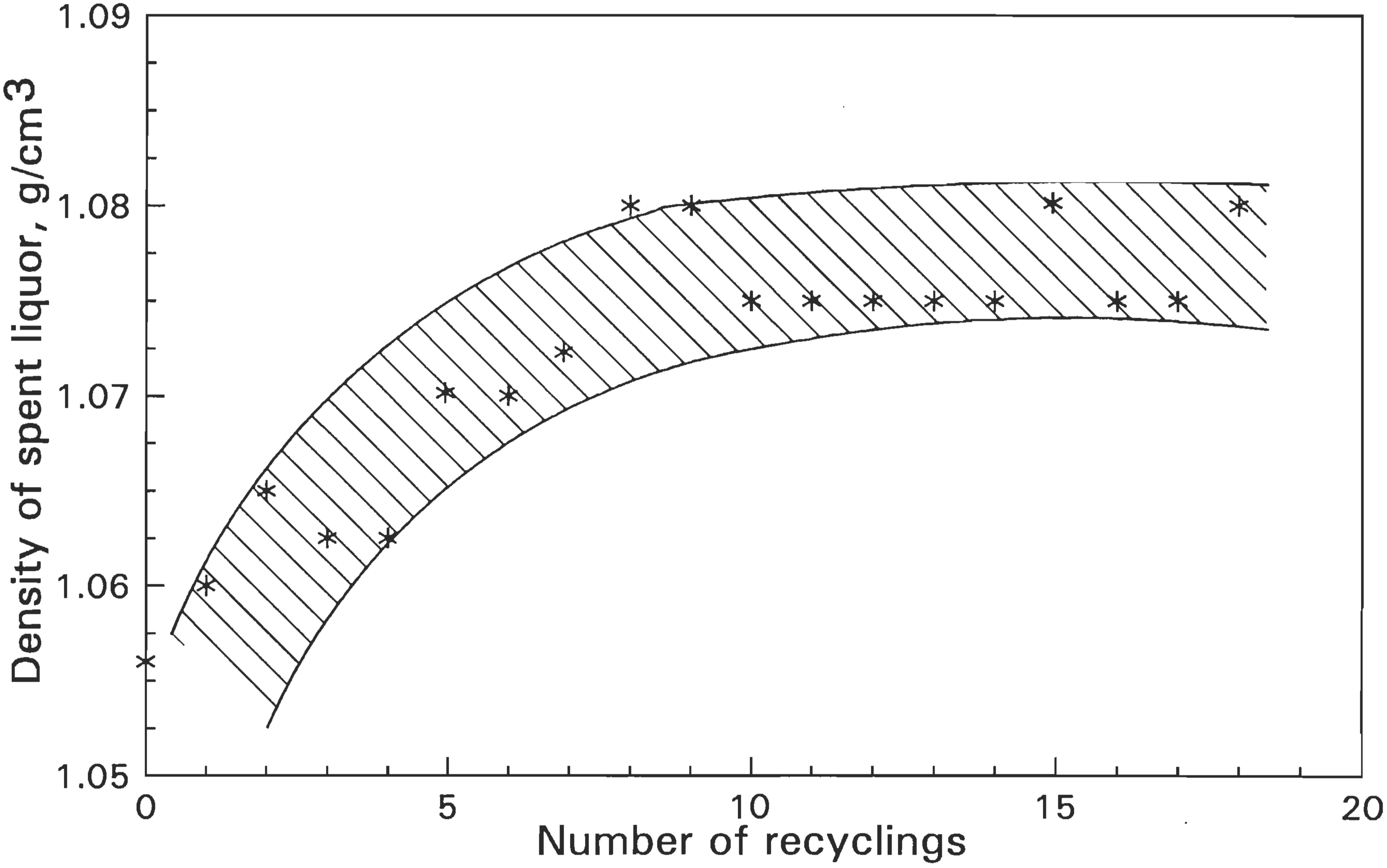


Figure 32 Relationship between spent liquor density and number of recyclings.

that can be dissolved into the liquor during impregnation. Since the "fresh" impregnation liquor is prepared by adding the necessary make-up chemicals and water into the recovered spent liquor, the concentration of dissolved solids is lowered at the beginning of impregnation, and the liquor can thus dissolve again a certain quantity of reed components. At the end of each impregnation, only one part of spent liquor is recovered; in other words, the recovered liquor contains only one part of the newly dissolved materials, another part is contained in the unrecovered liquor that is retained in the chips and will be finally washed away from the chips after cooking.

The above results indicate that the recycled spent liquor possesses eventually constant characteristics, and that there is no significant effect of NR on pulp properties. One can thus conclude that it is possible to produce reed CM pulp by using batch-wise vapor-phase cooking with unlimited times of spent liquor recycling.

Spent liquor volume and SO_2 recovered

Figure 33 shows that the average volume of the spent liquor recovered after each impregnation was about 2.4 liters. This volume corresponds to 67% of that employed in each cook for chip impregnation.

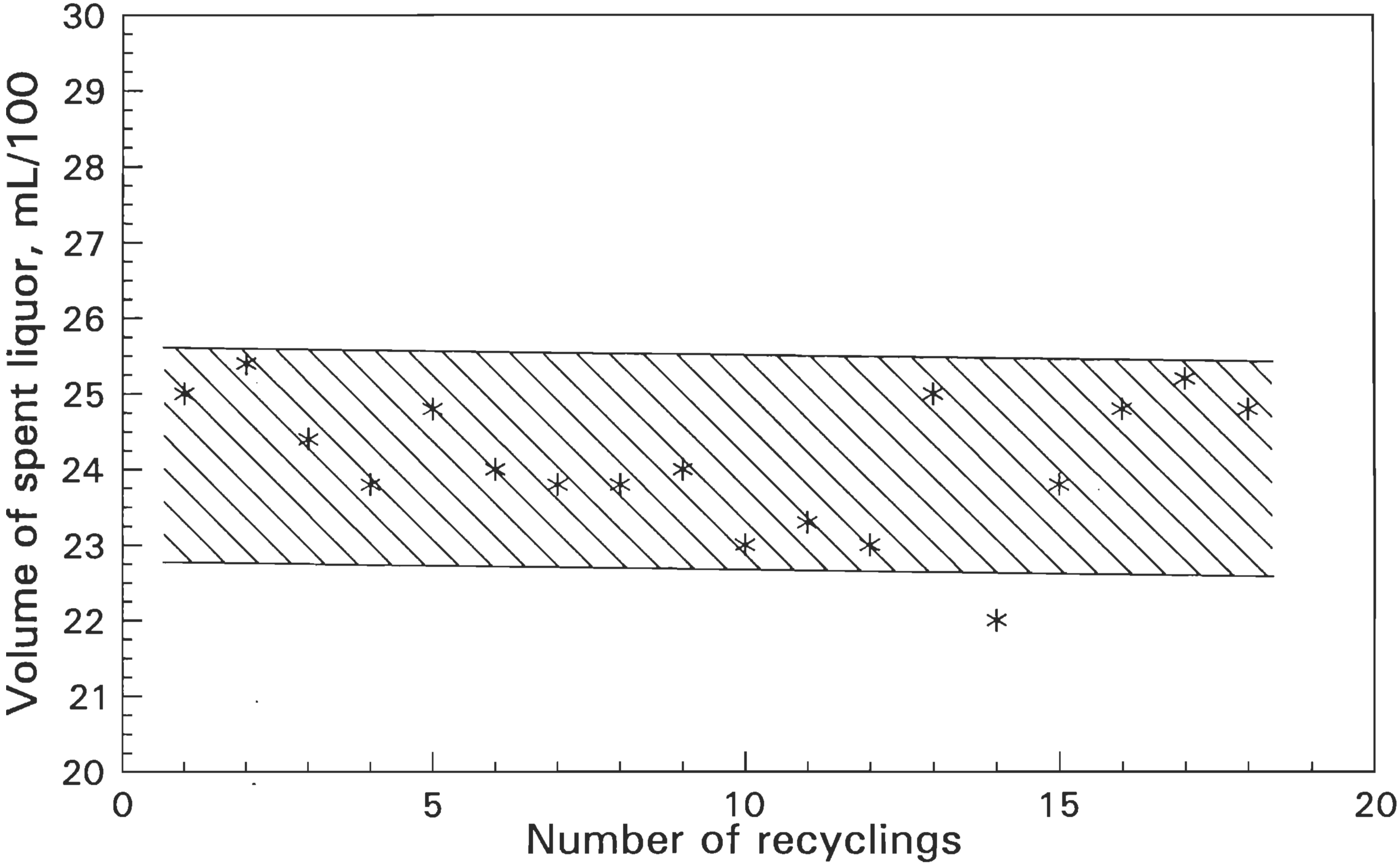


Figure 33 Relationship between spent liquor volume and number of recyclings.

After the concentration of residual SO_2 in spent liquor had been determined, the amount of SO_2 was then calculated, and the results are shown in Figure 34 where the percentage recovery is plotted against NR. It is interesting to notice that one can recover as much as about 65% of the SO_2 initially charged for chip impregnation, and there is no significant influence of NR on the recovered quantity. These results reveal one important advantage of vapor-phase cooking in chemicals saving from the liquor recovery, as compared with the liquid-phase cooking practiced in China.

Cooking condensate

The condensate formed during cooking was collected after each cooking, its volume was in the range of 350 to 600 mL for 0.6 kg o.d. chips, as shown in Figure 35. The variation in the collected quantity might be due to the packing of chips in the digester, thus affecting the drainage of cooking condensate. Nevertheless, the average volume of cooking condensate was small. The mass of condensate could serve to estimate the quantity of the steam required per cook; as for the present study, the average steam consumption was 0.8 kg per kg o.d. reed chips.

During cooking, certain quantity of SO_2 was stripped by steam condensate from the chemically impregnated chips. The amount of

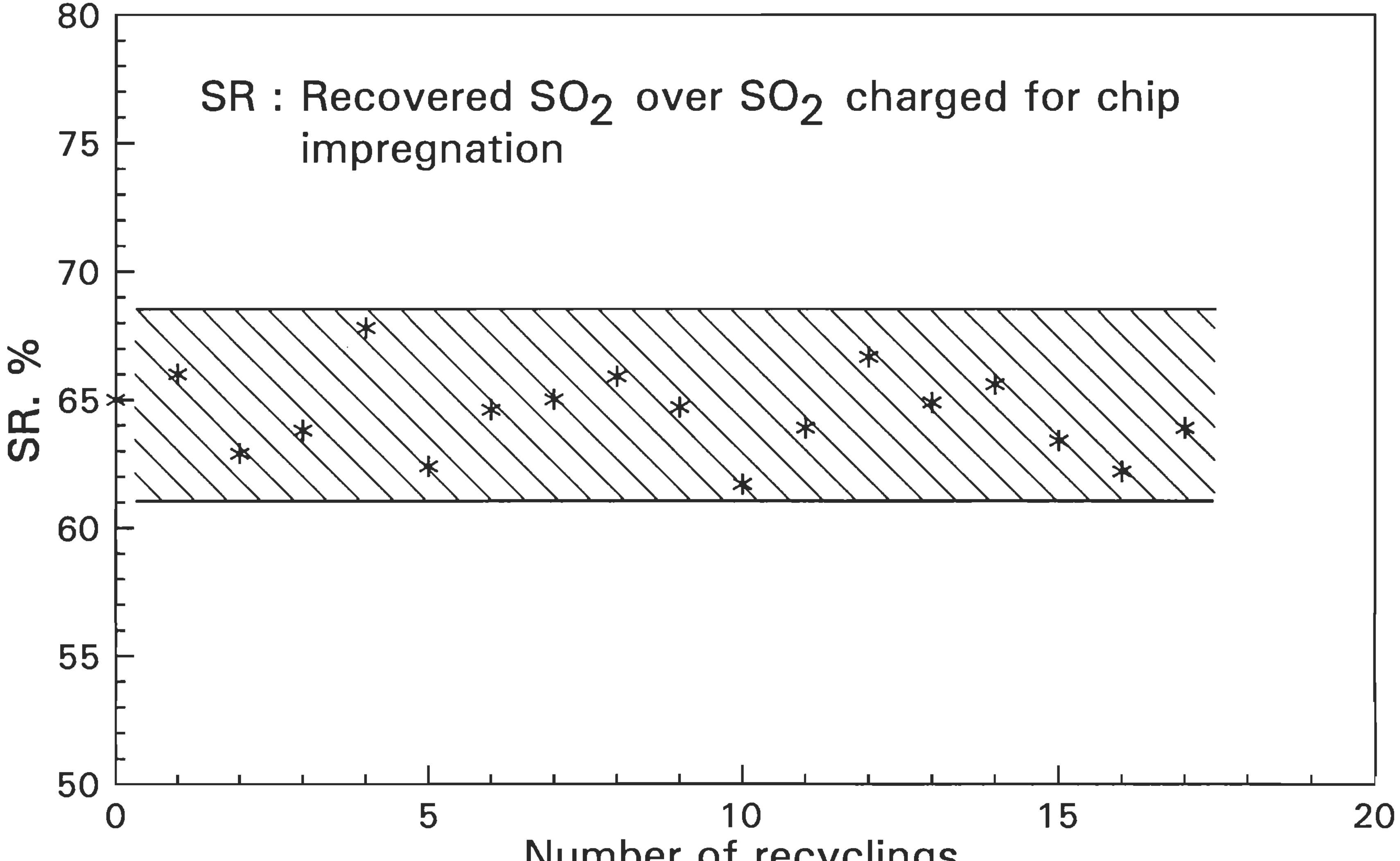


Figure 34 Percent of the SO_2 charge recovered versus number of recyclings.

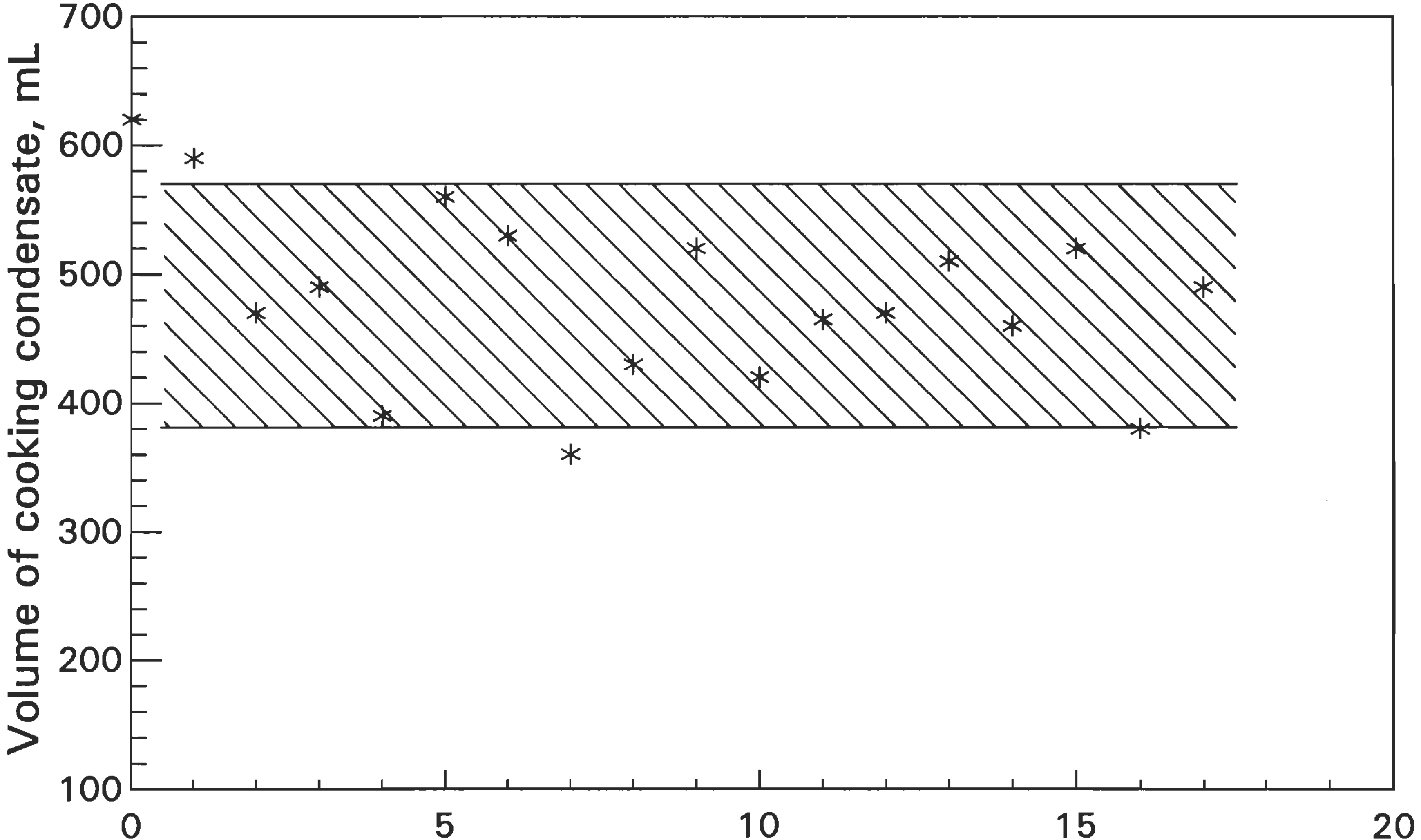


Figure 35 Relationship between cooking condensate volume and number of recyclings.

SO_2 in the condensate was about 1.5-3% of that initially charged for impregnation (Figure 36). It was equivalent to 2.8 - 5.6 g per litre of cooking condensate (Figure 37). The pH of condensate was fairly constant and equal to about 7.8 (Figure 38).

4.2.2.5 Pollution

In the case of liquid-phase cooking, which was conducted under the same conditions as vapor-phase cooking, the volume of spent liquor drained from the digester after each cooking was about 4.0 liters and contained about 100 g of SO_2 for one kg of o.d. chips. Without recycling and any treatment, this liquor would certainly cause serious water pollution, if discharged directly to a river.

In the case of vapor-phase cooking, it was evident that the spent liquor (referred to the condensate in this case) produced from each cooking was rather small (0.8 litre versus 4.0 liters), as well as the quantity of SO_2 contained in the spent liquor (3.75 g versus 100 g). Besides, the pH of the condensate approached to the neutral level. Provided that this cooking condensate be rejected directly into receiving water, the environmental impact would be relatively low.

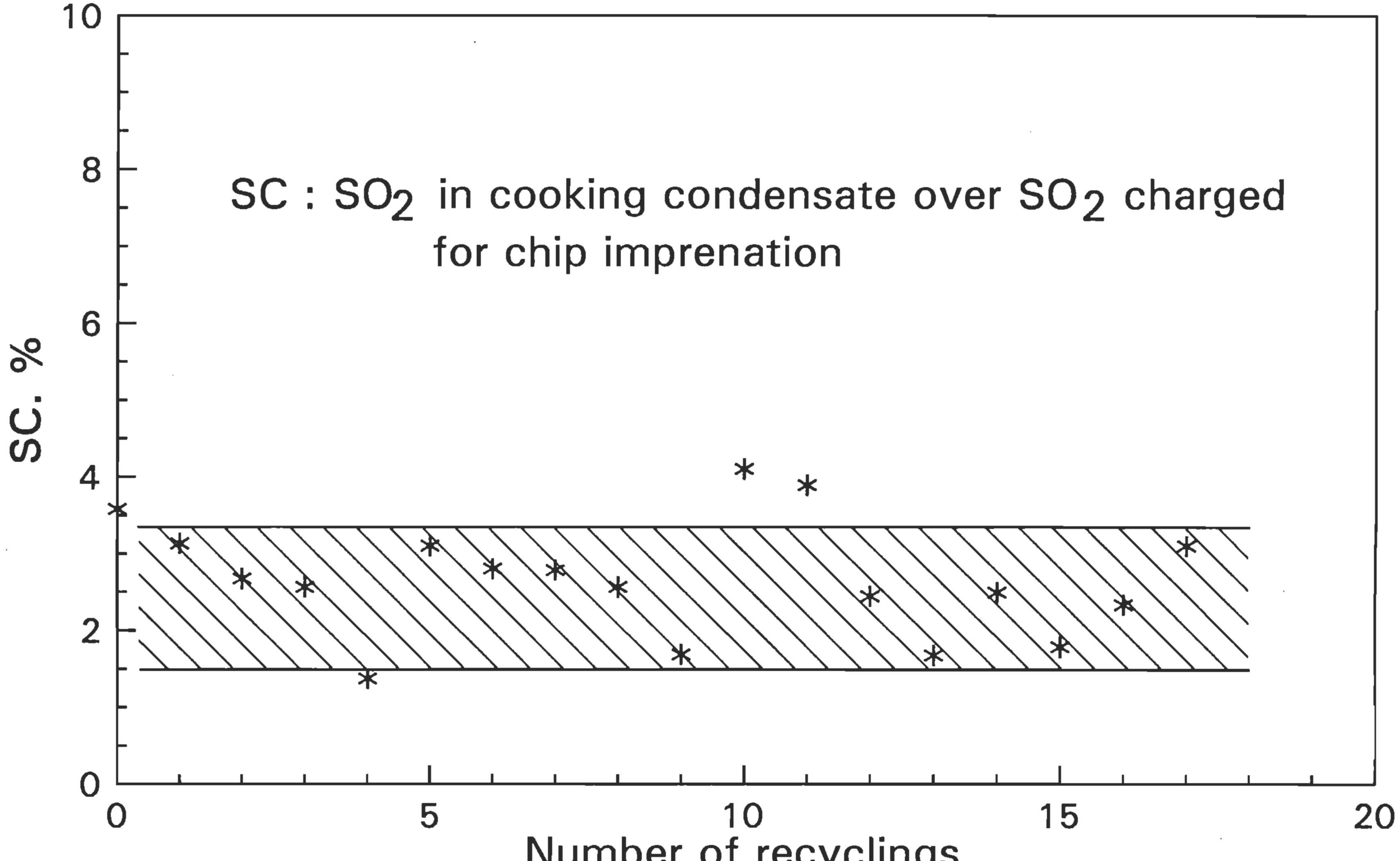


Figure 36 Percent of the SO_2 charge appearing in cooking condensate versus number of recyclings.

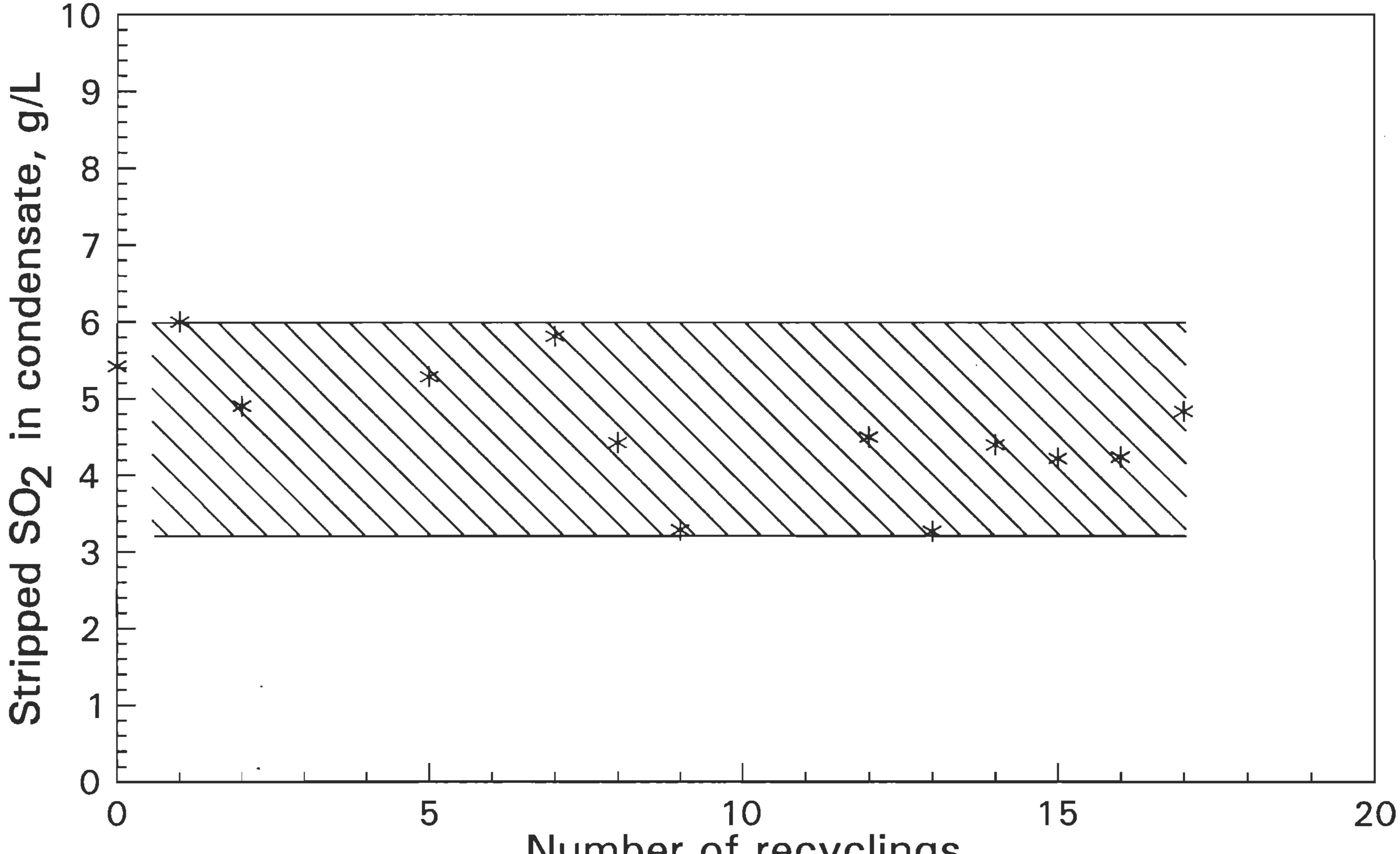


Figure 37 Stripped SO_2 in condensate versus number of recyclings.

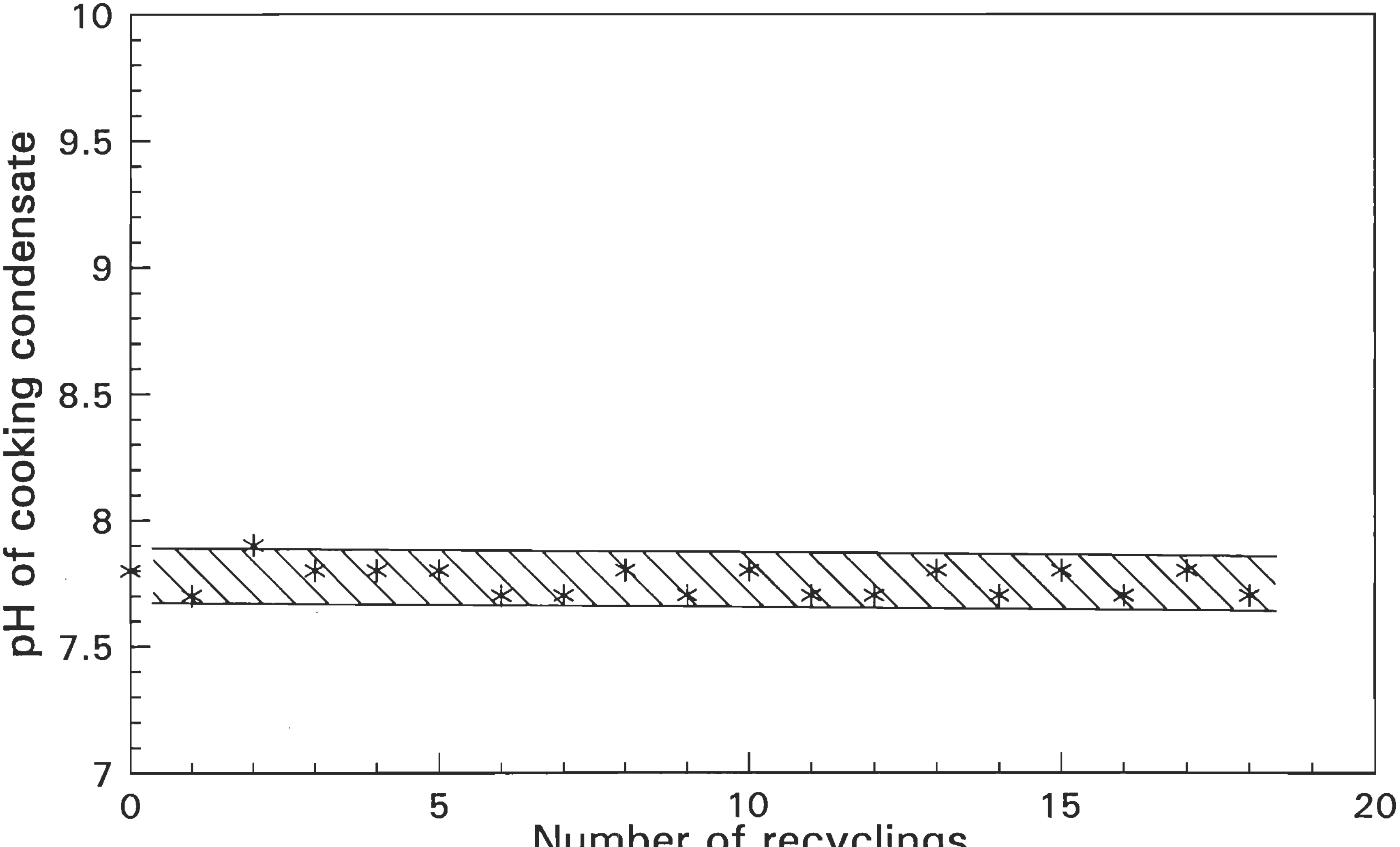


Figure 38 Relationship between cooking condensate pH and number of recyclings.

4.2.2.6 Comparisons of pulps produced from different processes

Table 11 presents a comparison between the pulp obtained in this study and two industrially produced reed pulps: one from neutral sulfite process and the other from soda process, both were obtained from China. The data for vapor-phase CM pulp represent the average characteristics of pulps that were produced with recycling of spent impregnation liquor from 0 to 17 times.

As seen from the table, vapor-phase reed CM pulp displays acceptable properties that are almost equal to those of liquid-phase CM pulp, and comparable with those of reed soda pulp. Though the properties of liquid-phase and vapor-phase CM pulps appear to be inferior to those of neutral sulfite pulp, the yield of the former is much higher than that of the latter.

Table 11 Comparisons of reed CM pulps with reed pulps produced from other processes

Process	Liquid-phase CM pulp[1]	Vapor-phase CM pulp[1]	Neutral sulfite[*,2]	Soda[2]
Yield, %	74.8	74.4	50	38
Bulk. cm^3/g	2.57	2.8	1.88	1.73
Burst, $kPa.m^2/g$	2.4	2.2	2.84	2.21
Breaking length, km	4.7	4.8	5.95	4
Tear, $mN.m^2/g$	5.9	5.85	7.04	5.15
Brightness, %	35.7	35.3	67.5	40.6
Opacity, %	95	93.4	88.3	90.7

CSF 150 mL
* : Semi-bleached pulp
1 : Lab
2 : Mill

4.3 BLEACHING OF REED CM PULP

Preliminary trials for pulp bleachability were conducted using the following bleaching methods : 1) single-stage using peroxide (P) ; 2) two-stage with hypochlorite (H) in first stage and followed by peroxide in the second stage; 3) two-stage with first stage using peroxide and followed by hydrosulfite; and 4) three-stage with a sequence of chlorination (C), extraction (E), and hypochlorite.

The pulp used to study the bleaching response was produced from a liquid-phase cooking conducted at pH 9 and at a maximal cooking temperature of 145°C for 40 minutes with a SO_2 charge of 15%. The initial brightness after cooking was 32%. From the results of those trials, as summarized in Table 12, it was found that the reed CM pulp responded better to HP bleaching than to the other processes under study. The two-stage HP sequence was thus thought to be an adequate bleaching process for reed CM pulp; the operation parameters which would affect the bleaching outcomes were examined and are presented hereafter.

4.3.1 Effects of peroxide and total alkalinity charges

It has been well known that peroxide charge and total alka-

Table 12 Bleaching of reed CM pulps with various processes

Process	Peroxide CM pulp 1*		Hypochlorite Peroxide 2*		Peroxide Hyposulfite 3*		CEH 4*	
Chemical charge, %, o.d. pulp								
$Na_2S_2O_4$					1	1		
Tripolyphosphase					0.5	0.5		
H_2O_2	1	4	2	2	1	4		
NaOH	1	2	1	1	1	2		
Silicate (41'Be)	4	4	4	4	4	4		
Epsom salt	0.5	0.5	0.5	0.5	0.5	0.5		
Cl_2 (available Cl^2)							6	10
NaOH							3	5
NaClO (available Cl_2)			4	6			1.6	1.6
Characteristics								
Yield, %	99.1	96.6	93	93.1	98.2	95.6	87.8	86.7
Brightness, %	44.9	58.7	65.2	69.8	48.5	61.2	41.6	44.4
Opacity, %	86.5	84.1	77.8	74.4	86	75.5	81.3	80.6

1* 70°C, 90 min, Consistency : 12 %.
2* Stage H : 30 °C, 45 min, Consistency 12%; Stage P : 70 °C, 120 min, Consistency 12%.
3* Stage P : 70 °C, 120 min, Consistency 12%; Stage H : 70 °C, 60 min, Consistency 4%.
4* Stage C : room temp., 45 min, Consistency 4%; Stage E : 70 °C, 120 min, Consistency 12%; Stage H : 30 °C, 45 min, Consistency 12%.

linity could have interaction effect on brightness. A number of experiments were carried out to investigate the interaction. For presenting a clear picture, two series of experiments showing the effects of these two parameters are presented in Figures 39 and 40.

Figure 39 shows the results obtained by using 6% of hypochlorite in first stage, and 2% of peroxide with various NaOH charges (in turn, the total alkalinity) in the second stage. It indicates that the brightness is initially increased with NaOH charge but passes through a maximum value and then goes down. The maximum corresponds to the optimum ratio of NaOH/H_2O_2. Prior to the maximum, perhydroxyl ions (OOH^-), which provide the bleaching action, increase with NaOH charge. During bleaching, high pH could favour the equilibrium of H_2O_2 and OH^- system toward perhydroxyl ions but also accelerate the decomposition of hydrogen peroxide to water and oxygen [26]. The use of excess alkali leads to a decrease of brightness, especially for a low peroxide charge. It is essential that peroxide bleaching should be conducted at optimum alkalinity. For this series of experiments, a 1.5% of NaOH appears to be adequate for 2% of H_2O_2, giving a ratio of NaOH/H_2O_2 of 0.75.

A second series of HP bleaching experiments were carried out by using 12% of hypochlorite in first stage and a ratio of

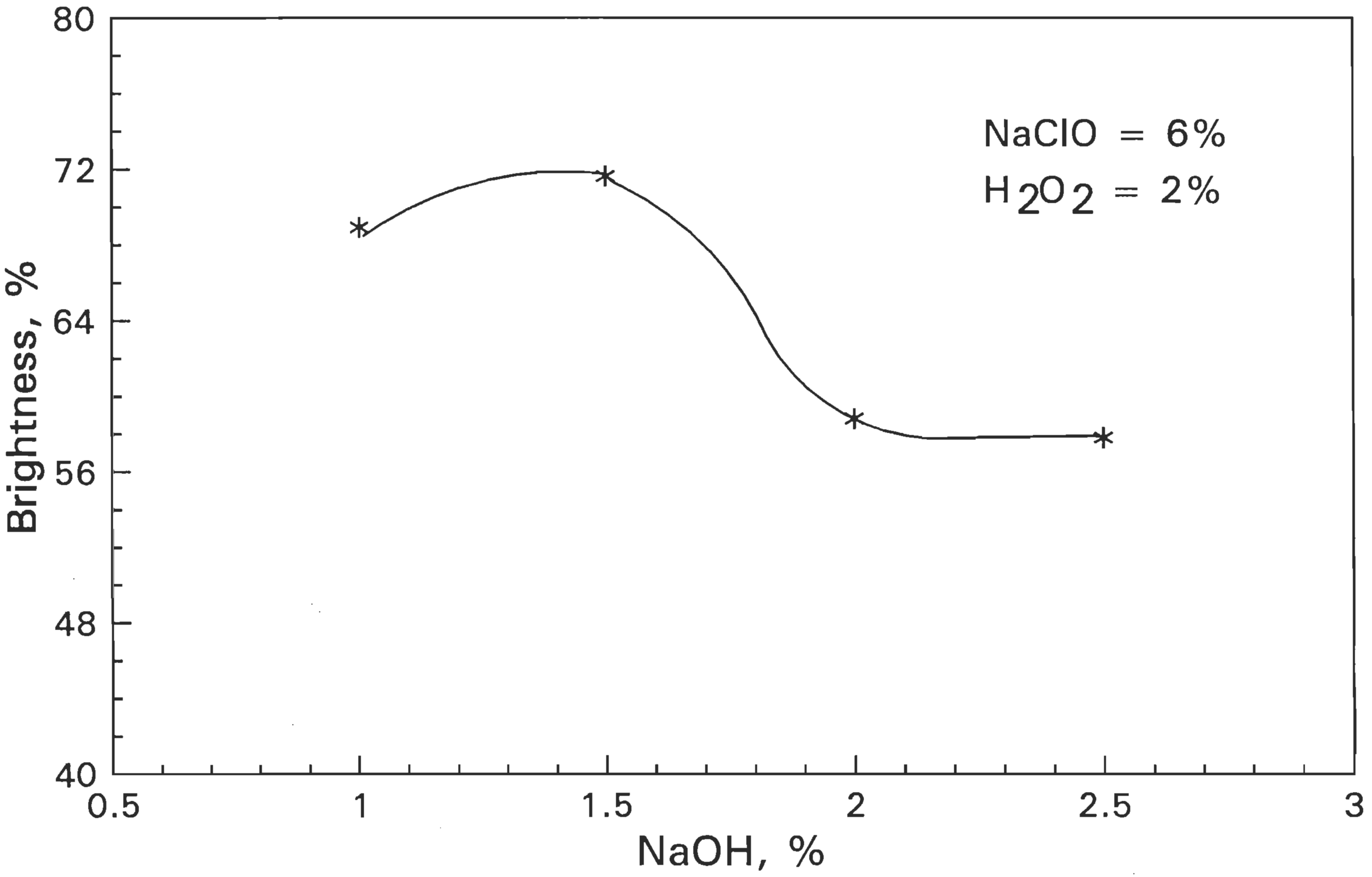


Figure 39 Effect of NaOH charge on brightness.

0.75 for NaOH/H_2O_2 in the second stage; the results are displayed in Figure 40. At the given hypochlorite charge and ratio of NaOH/H_2O_2, the brightness first increases with peroxide to a maximum and declines afterward.

It appears that the selected ratio of NaOH/H_2O_2 = 0.75 is suitable for peroxide charge up to 2% but unsuitable for higher peroxide charge. According to other investigators [24, 43], there is an optimal alkali concentration for each peroxide charge. The optimal alkali concentration tends to increase with the increasing of peroxide charge, but the optimal ratio of NaOH/H_2O_2 tends to decrease with the increasing of peroxide charge.

The outcomes in this series of experiments present an evidence that the ratio NaOH/H_2O_2 = 0.75 is too high for 3% peroxide charge. When alkali concentration exceeds the optimal value, it could stimulate faster the formation of chromophores than the generation of peroxide ions for eliminating the chromophores [43]; a decrease in brightness would consequently occur. Nevertheless, the results of both sets of experiments show a concordance that this ratio is optimal for 2% peroxide charge.

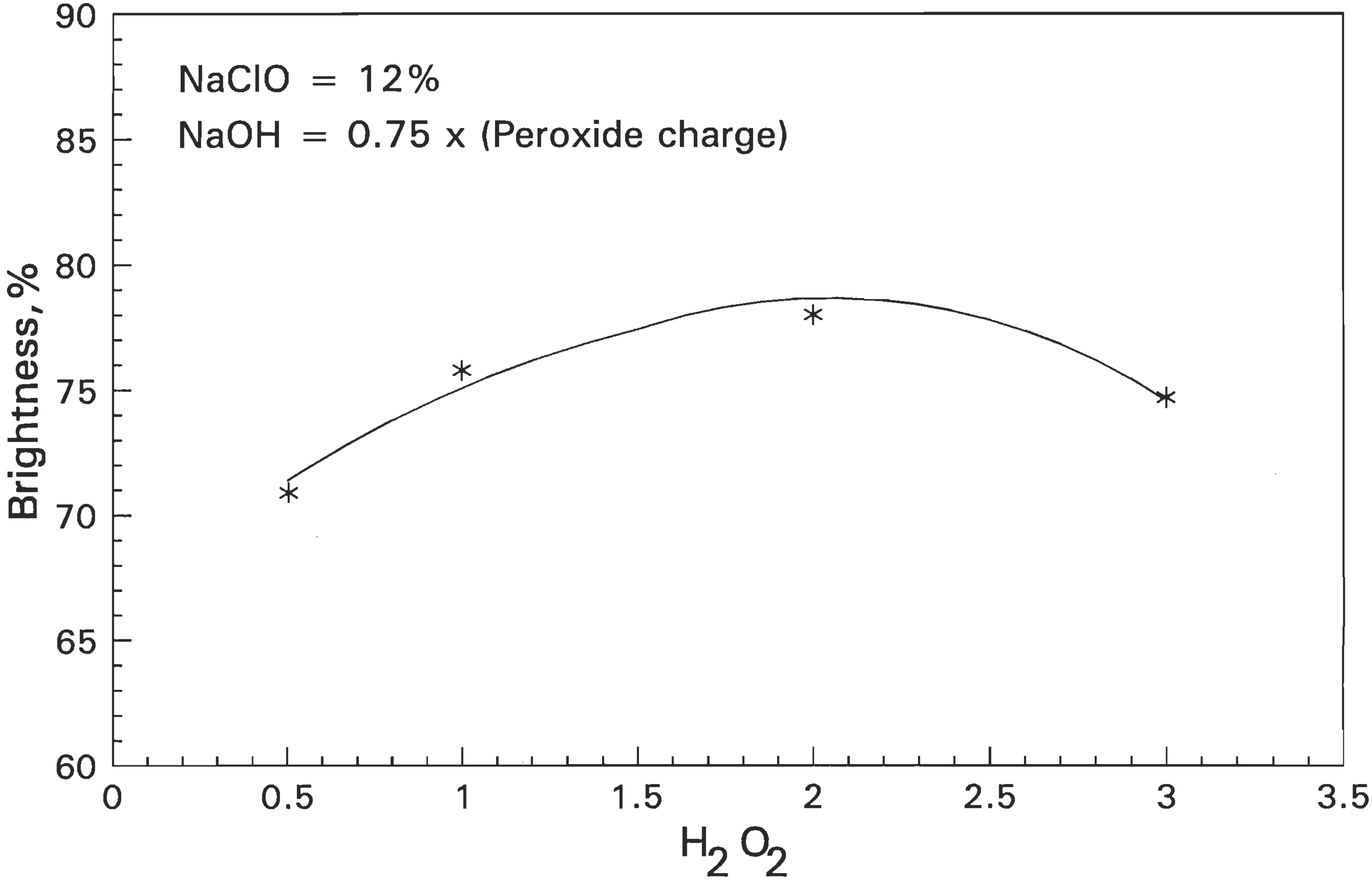


Figure 40 Effect of peroxide charge on brightness.

4.3.2 Two-stage HP bleaching

Figure 41 shows the general trend in two-stage HP bleaching of reed CM pulp as the charge of bleaching agents varies. The lowest curve represents the results obtained from only one stage bleaching using hypochlorite. It can be seen that the brightness raises rapidly from 50 to 65.5% when the NaClO charge (in terms of available Cl_2, on o.d. pulp) is increased from 4% to 8%. Then the increasing rate of brightness with the increase of hypochlorite charge diminishes when the latter is over 8%, and a plateau appears around 10%. For further improvement in brightness, a second stage bleaching with peroxide is thus necessary. The brightness gain in second stage depends on the bleaching results obtained in first stage, its magnitude diminishes with the increase of brightness obtained in the first stage; a further gain ranging from 10 to 20 points could be obtained. At a given NaClO charge, the brightness generally increases with peroxide charge, but is affected by the ratio of $NaOH/H_2O_2$. It can be seen from the two upper curves, with 2% peroxide charge, the brightness gain is higher when using a $NaOH/H_2O_2$ ratio of 0.75:1 than a ratio of 0.5:1. For the range studied, with two-stage HP bleaching, a final brightness of 78% can be attained.

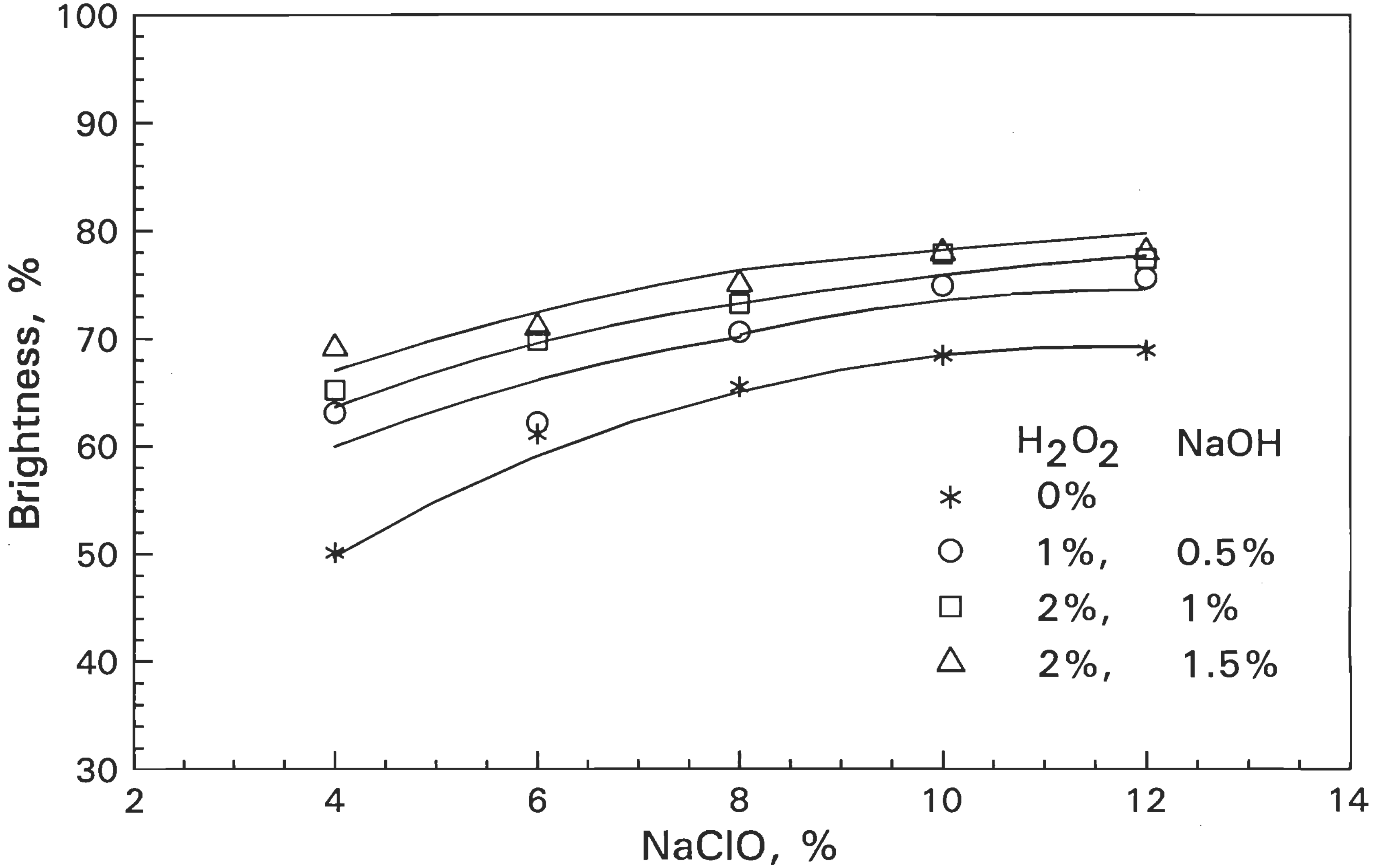


Figure 41 Effect of NaClO charge on brightness.

4.3.3 Effect of bleaching on pulp yield

The variations of pulp yield versus one-stage bleaching, hypochlorite or peroxide, and the two-stage HP bleaching are shown in Figures 42 to 44, respectively. Hypochlorite displays a stronger influence on bleaching yield (as shown in Figure 42), as compared to peroxide (Figure 43). The difference in yield after bleaching, when applying different bleaching processes, is mainly due to the fact that hypochlorite brightens pulp by removing a part of the lignin remaining in the pulp, while peroxide only oxidizes the chromophore groups and preserves the lignin in pulp. As a consequence, the yield decreases with the increasing of hypochlorite charge; with a charge in the range studied (4 to 12%), a decrease up to 4 points in yield has been observed (Figure 42). As the function of hydrogen peroxide on pulp is different from other bleaching agents, the influence of peroxide charge on yield is rather small due to the lignin-preserving characteristics of the peroxide. The yield loss is less than 2% when peroxide charge is 4% on o.d. pulp (Figure 43).

The variation of bleaching yield versus hypochlorite charge used in the two-stage HP bleaching is shown in Figure 44, using 2% H_2O_2 and 1.5% NaOH in the second stage. The bleaching yield decreases from 92% to 89% with the increase of hypochlorite

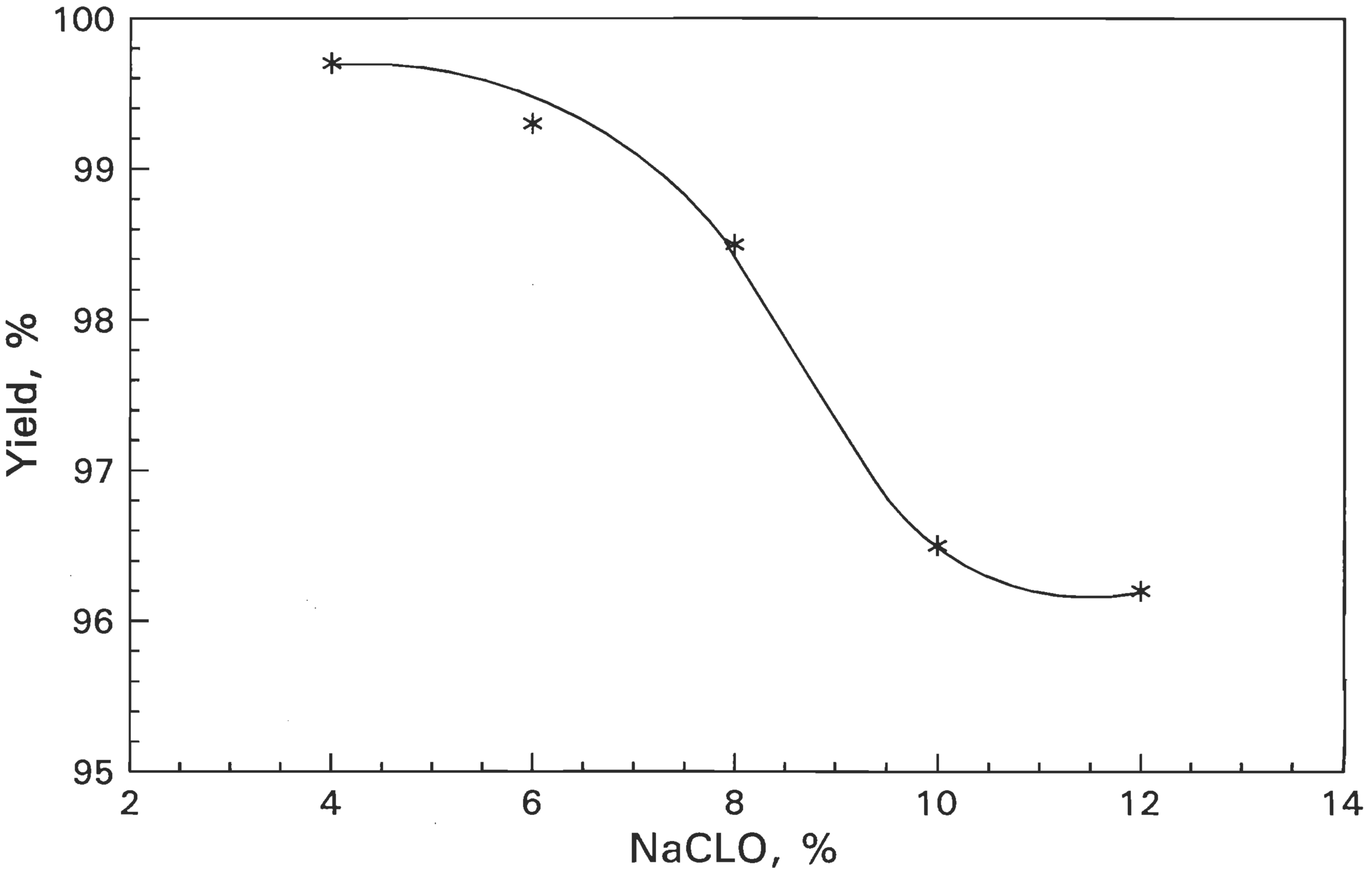


Figure 42 Effect of NaClO charge on yield.

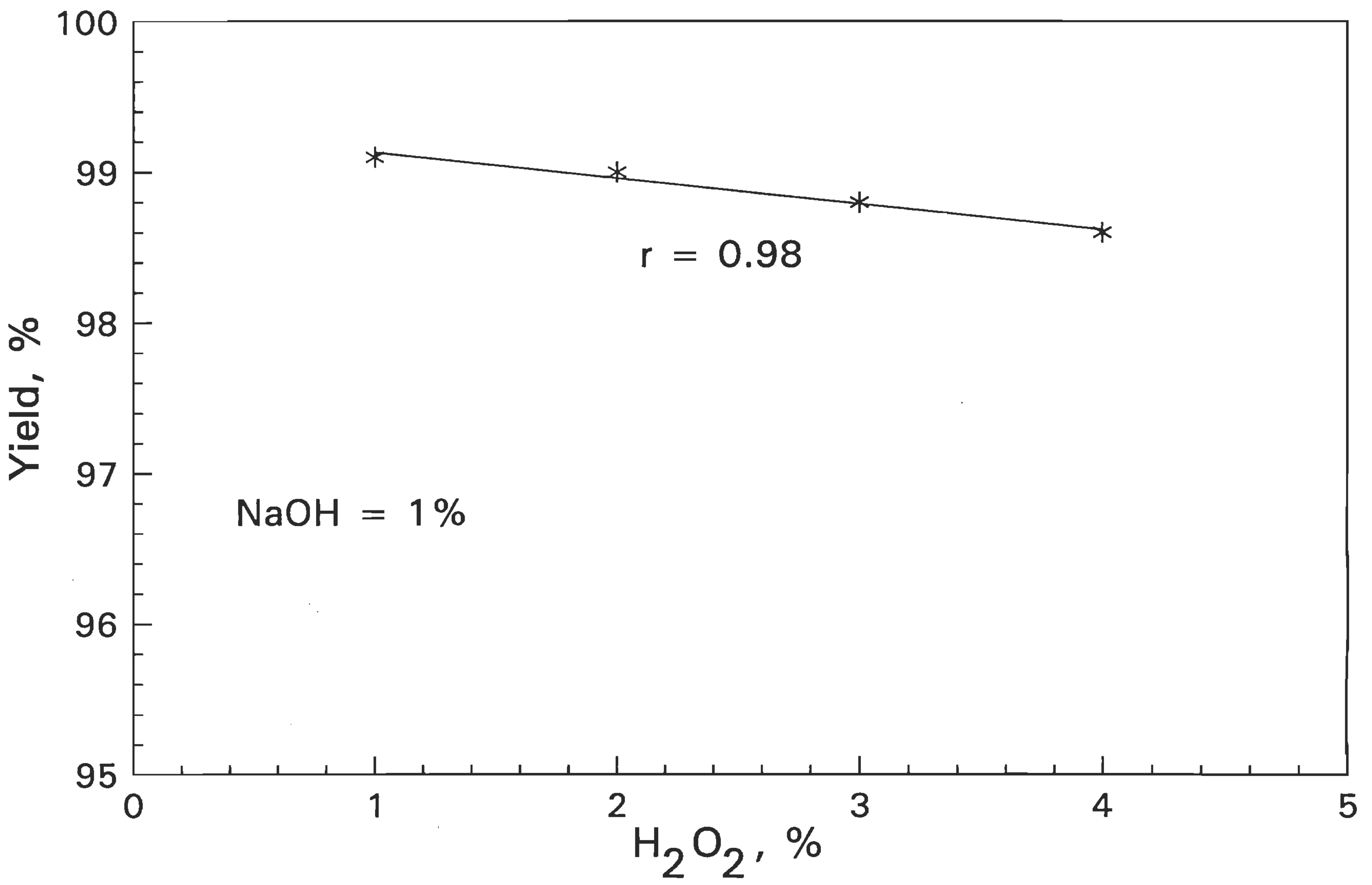


Figure 43 Effect of peroxide charge on yield.

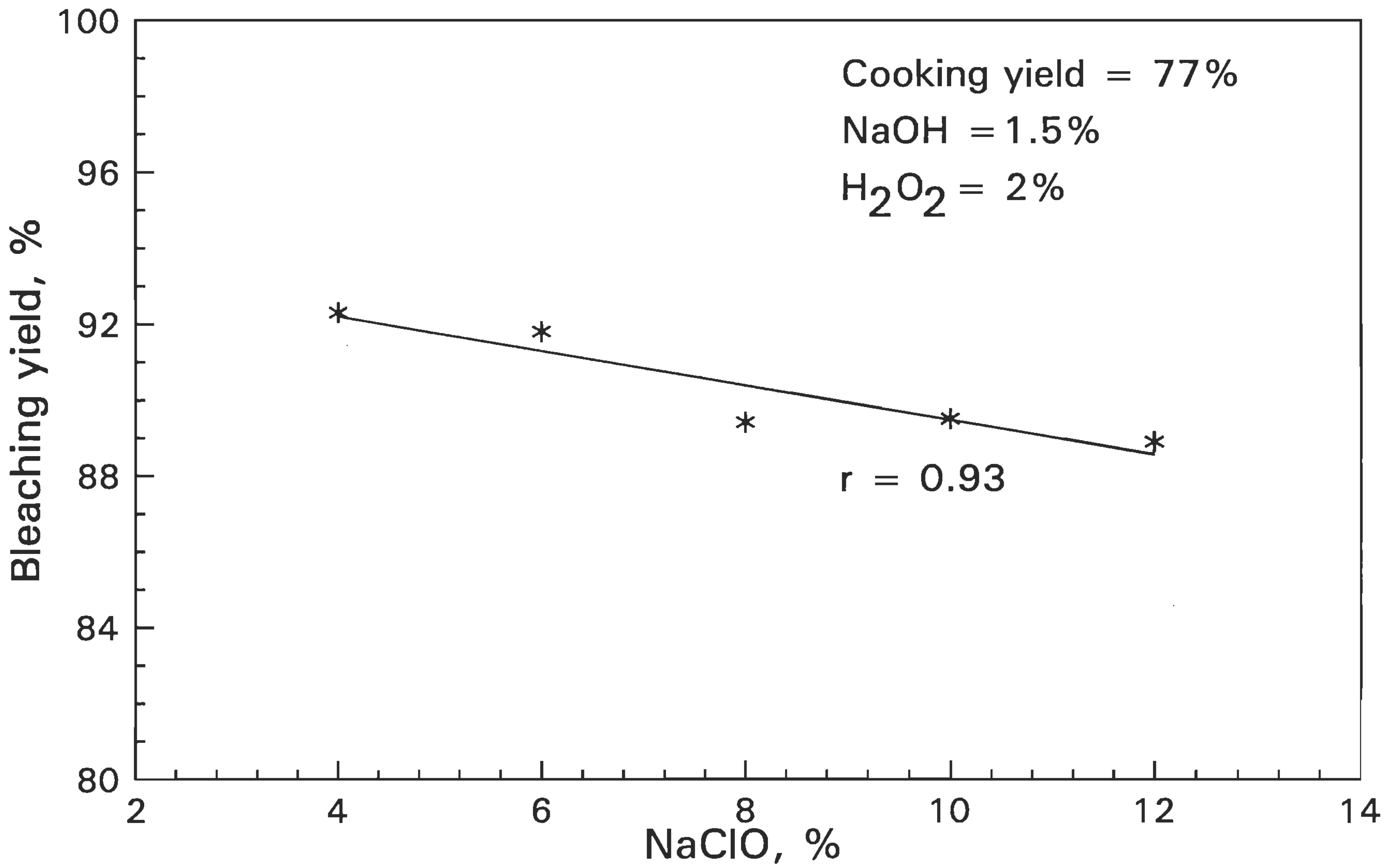


Figure 44 Bleaching yield versus NaClO charge at a given H_2O_2 charge.

charge from 4 to 12%. Under optimal bleaching conditions (first stage : 10% NaClO; second stage: 2% H_2O_2 and 1.5% NaOH, shown in Figure 41), the brightness of pulp could be increased from 32% to 78% (initial brightness of pulp : 32%). Since the bleaching yield could be maintained around 90% (Figure 44), the overall pulp yield (with respect to o.d. reed chip subjected to cooking and bleaching) is in the order of 70%. From the view point of the overall pulp yield and final brightness, the results were thought to be well acceptable.

4.3.4 Pulp opacity after bleaching

Figures 45 and 46 present, respectively, the effects of hypochlorite charge in one-stage bleaching and in HP two-stage bleaching on the opacity of pulp. During two-stage bleaching, a given peroxide charge (2%) was used in the second stage. Figure 45 shows that the opacity of pulp is influenced very significantly by hypochlorite charge. Pulp opacity drops drastically from its initial value of 95% to about 75%, with a rate of 2.5 points per % hypochlorite charge when the charge is increased from 0 to 8%. A further increase of hypochlorite generates no further drop in the bleached pulp opacity.

Figure 46 indicates that, when combined with the results

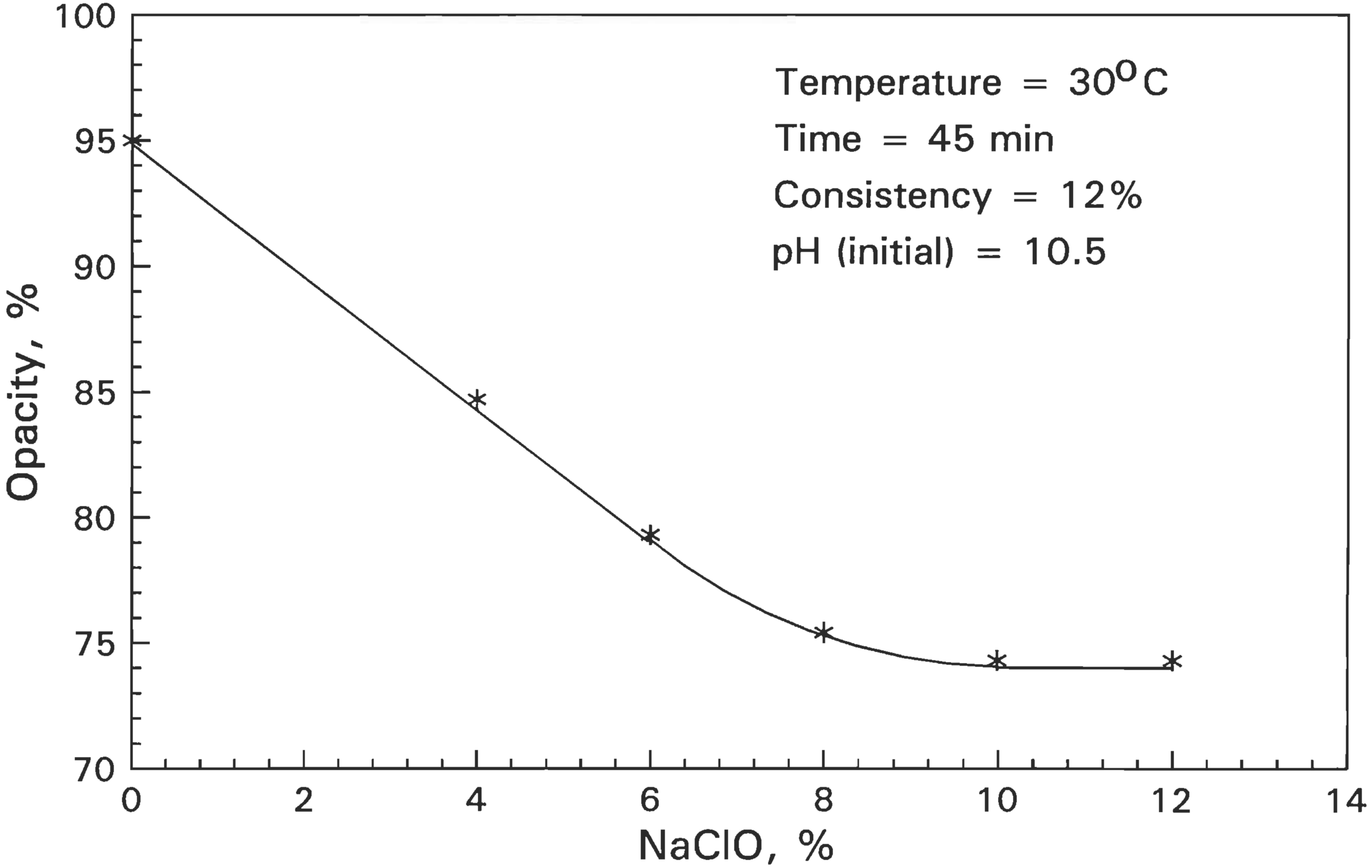


Figure 45 Effect of NaClO charge on opacity.

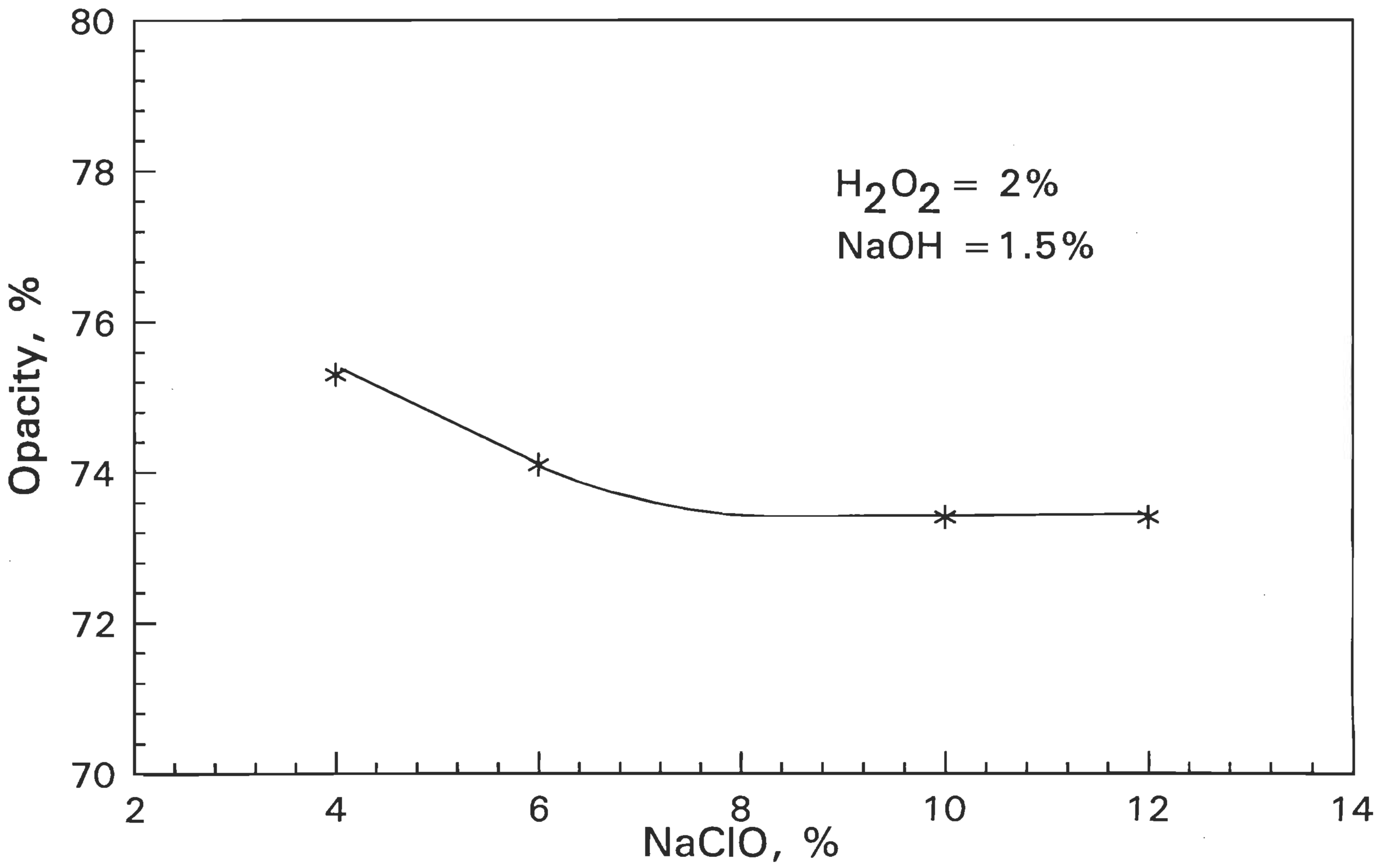


Figure 46 Opacity versus NaClO charge for 2% H_2O_2 and 1.5% NaOH.

shown in Figure 45, peroxide bleaching would introduce a much bigger drop in pulp opacity per % charge (5 points at 4% hypochlorite charge and 3 points at 6% hypochlorite charge), when the hypochlorite charge used in the first stage is in the range of 4 to 6%. Beyond that range, the opacity becomes stabilized. The decrease in opacity is caused by the loss in light scattering ability through bleaching. Furthermore, an increase in handsheet density (i.e., a decrease in bulk) after bleaching would also lead to a decrease in opacity. The opacity of pulp obtained under optimal bleaching conditions is 74%.

4.3.5 Effects of HP-bleaching on physical properties

Presented in Figure 47 are the physical properties of the pulp bleached with 2% H_2O_2 and 1.5% NaOH in the second stage, and with different charges of NaClO in the first stage. As mentioned in the preceding section 4.3.4, bulk could be decreased by strengthening the bleaching conditions, resulting in less light scattering and lower opacity. These might be explained by the drastic reduction of shives after bleaching, the bonding areas are thus increased, leading to an improvement in bonding strength and a decrease of handsheet bulk. One can see that breaking length is increased significantly as the bleaching reaction becomes more severe.

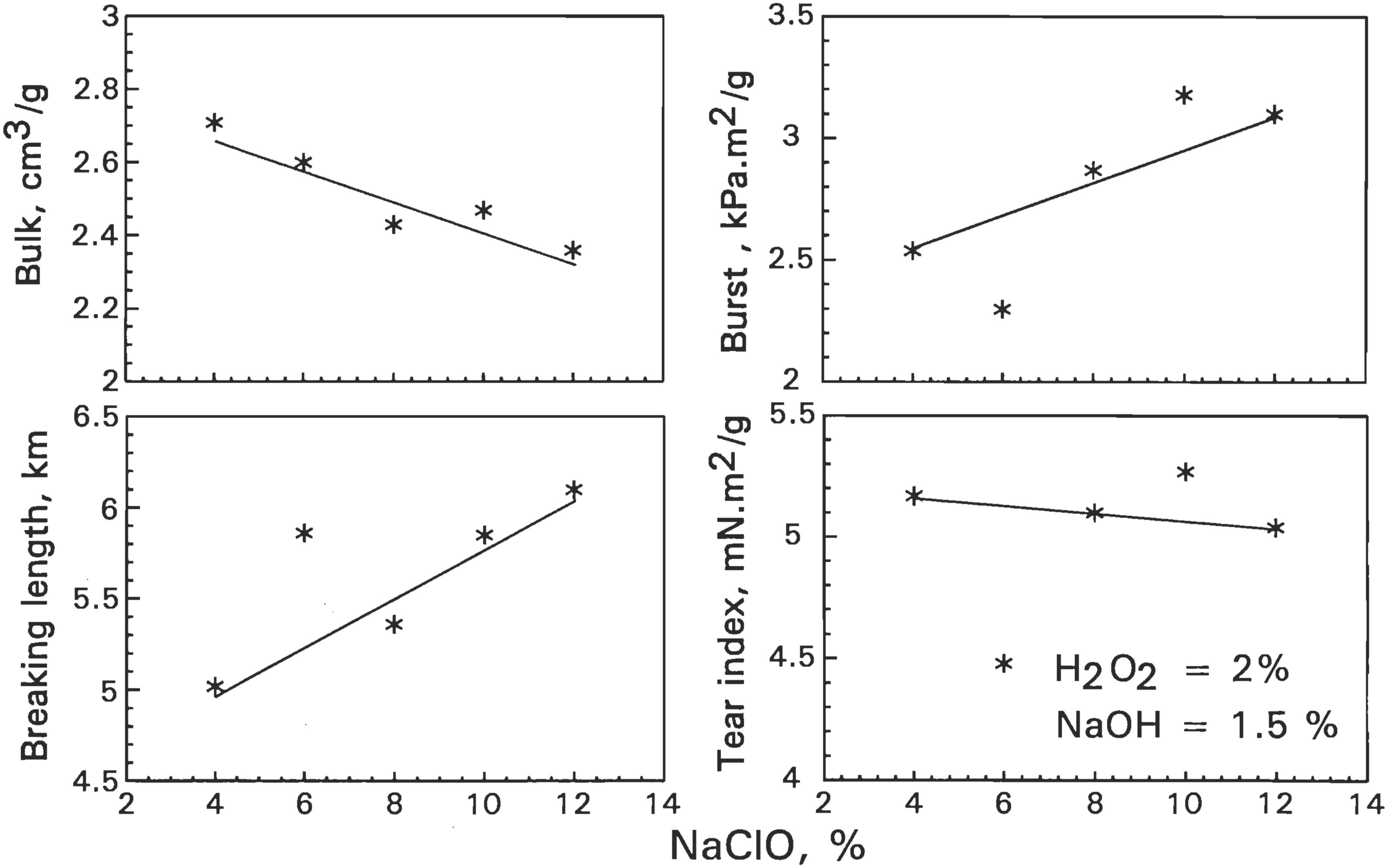


Figure 47 Physical properties versus NaClO charge.

As for tear index, a slight decrease with bleaching severity is observed. It was suspected that degradation of cellulose might happen during the first stage bleaching with hypochlorite, for sodium hypochlorite could display stronger oxidative power than H_2O_2. The correlation between tear index and breaking length appears to follow the general trend, i.e., the former varies inversely with the latter.

A comparison of the physical properties between a bleached pulp and an unbleached pulp is presented in Figure 48. The pulp was bleached with 10% hyphchlorite in first stage, and 2% H_2O_2 and 1.5% NaOH in second stage. It can be seen that bulk decreases 0.5 unit after bleaching, implying a better bonding strength that is then confirmed by a 100% increase in burst index and a 50% increase in breaking length.

4.3.6 Effects of cooking liquor pH and SO_2 charge on brightness

In addition to the species (wood or non-wood) and bleaching conditions, the response of pulp to bleaching depends greatly on pulping history. Figure 49 presents the effect of the cooking liquor pH on bleaching brightness; pulp samples were prepared with 15% SO_2. Under the bleaching conditions specified (first

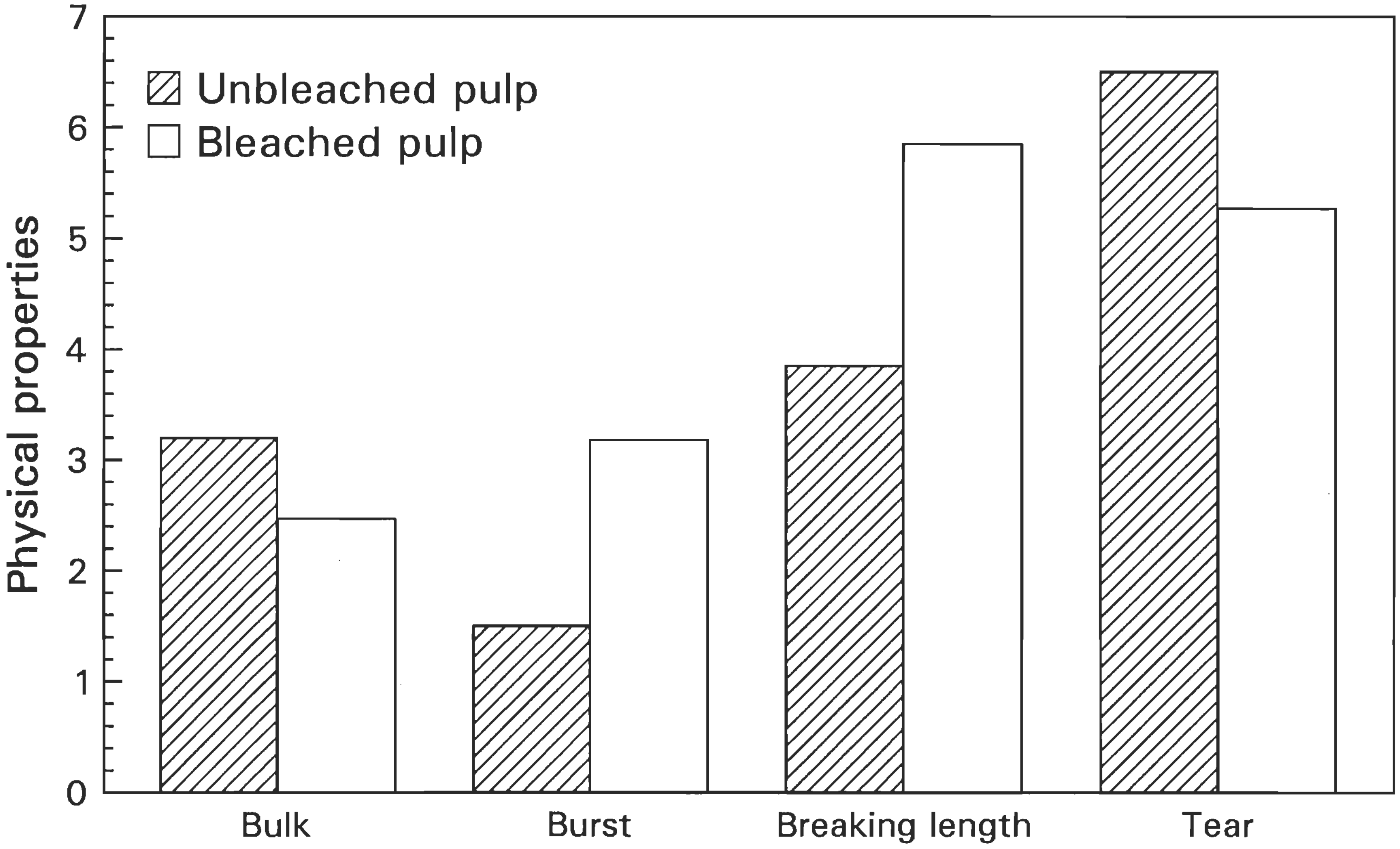


Figure 48 Comparisons of physical properties between bleached and unbleached pulps.

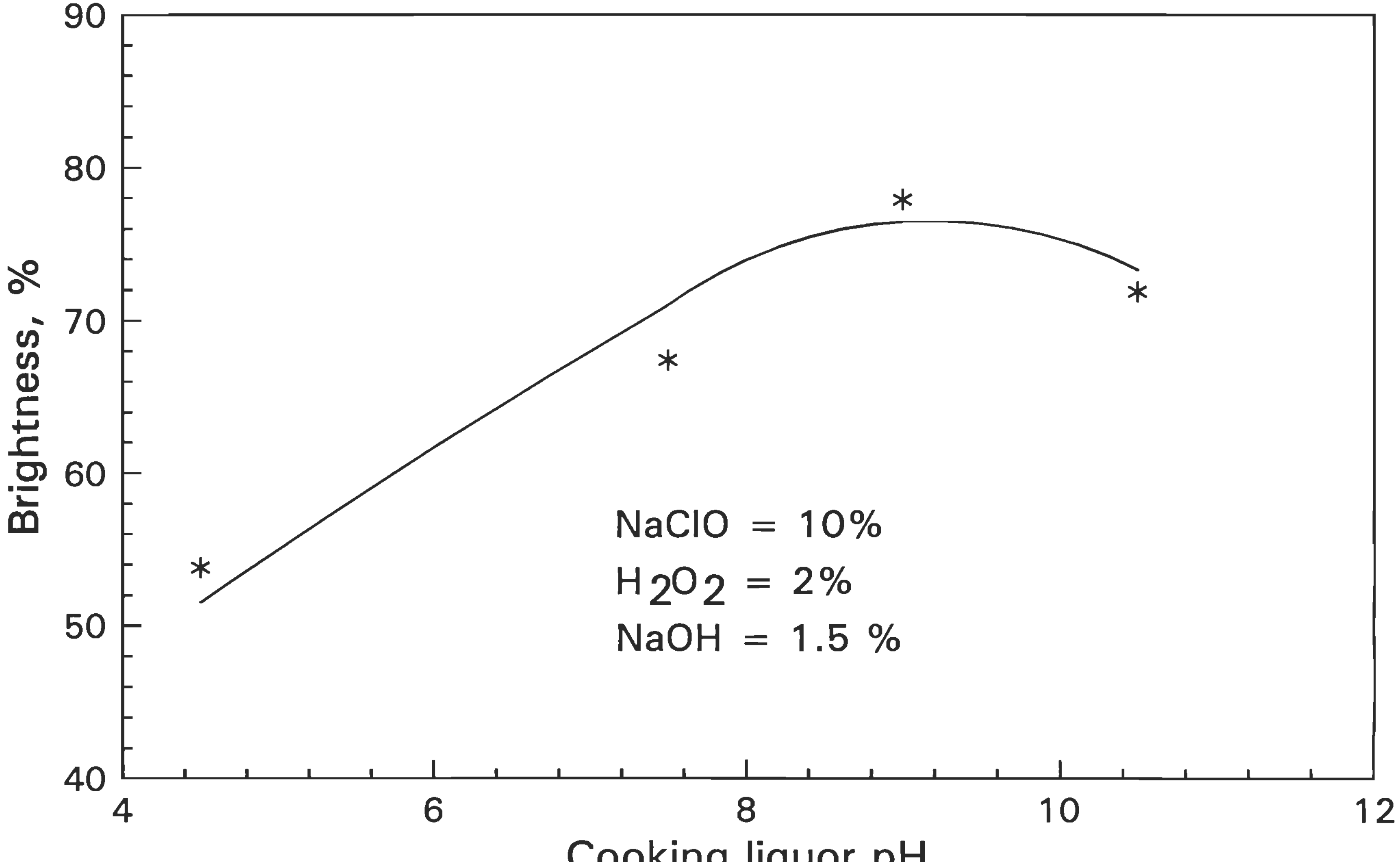


Figure 49 Brightness versus pH of cooking liquor.

stage : 10% NaClO; second stage : 2% H_2O_2 and 1.5% NaOH) a maximum value of brightness (about 78%) is reached when bleaching pulp from chips cooked with a cooking liquor of pH 9. At lower pH, the pulp might contain more lignin and is more resistant to be bleached to a high brightness level. When the cooking pH is higher than 9, the light scattering coefficient of the pulp is decreased and the brightness declines consequently. The difference in resulting brightness is very large that more than 20 points could be observed between pH = 4.5 and pH = 9. These results suggest that for reed CM pulping, it is necessary to adjust the cooking liquor to a pH around 9 in order to assure a good pulp bleachability and to obtain the satisfactory strength properties.

Furthermore, the SO_2 charge also show a significant influence on bleaching brightness, as shown in Figure 50; the pulp samples were prepared with a cooking liquor of pH 9. A maximum appears around 15% SO_2 charge. Two factors might be attributed to the final brightness : the residual lignin content and the extent of pulp sulphonation. On the upward side, residual lignin content has a predominant effect on bleaching result; on the downward side, sulphonation exhibits a determinant influence on final brightness. From the above-mentioned results, a conclusion could be drawn that for obtaining the best

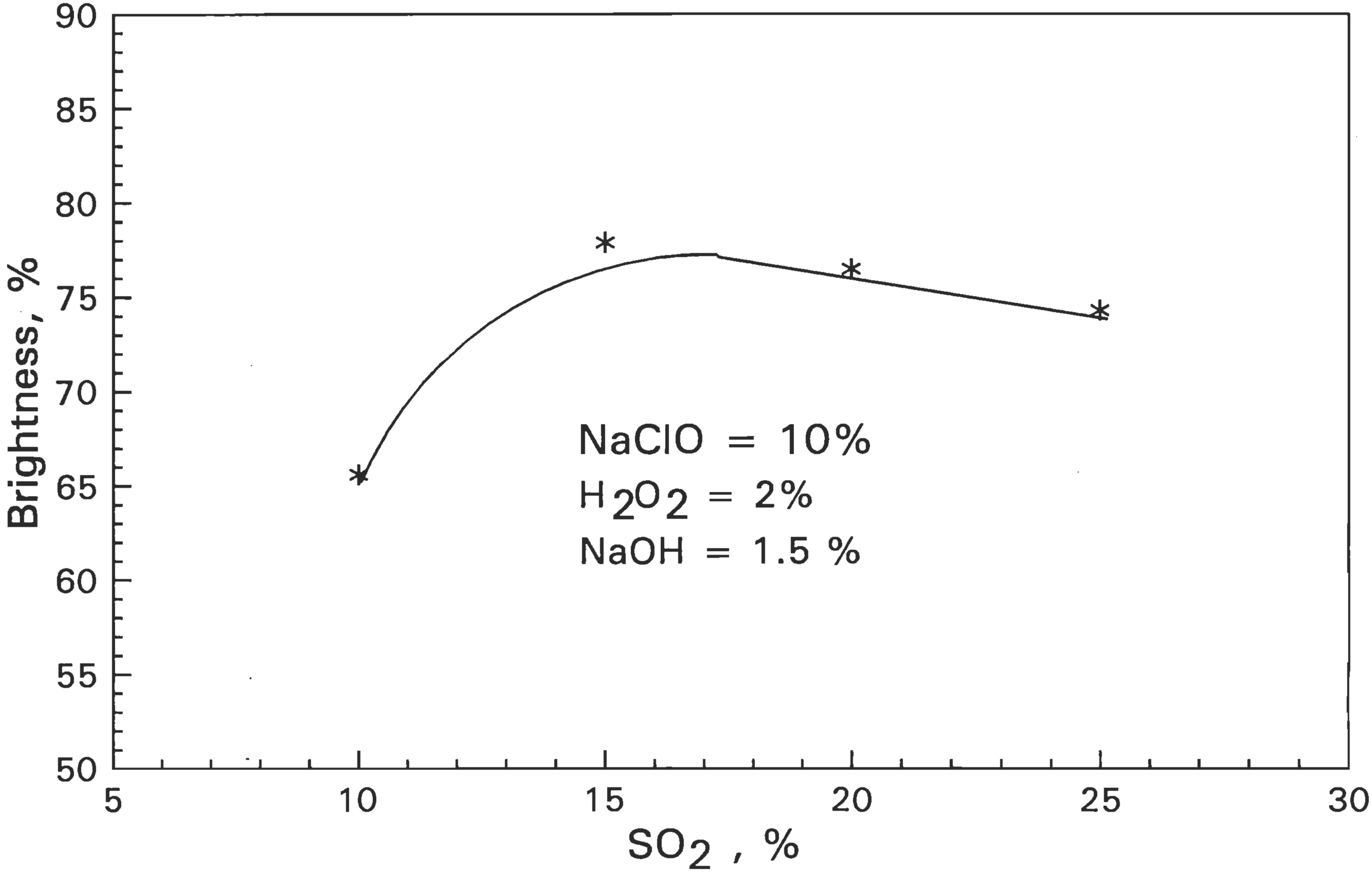


Figure 50 Brightness versus SO_2 charge in cooking liquor.

bleaching brightness, reed pulp should be prepared from chips cooked with a cooking liquor of pH 9 and with SO_2 charge in the range of 15% to 20%.

CHAPTER 5 CONCLUSIONS

The results obtained in this work demonstrate the possibilities of using a non-wood fibre raw material, reed straw, for CM pulping, and the resulting pulp possesses characteristics that meet the requirements for production of printing, writing, and fine papers.

5.1 LIQUID-PHASE CM PULPING OF REED

Liquid-phase cooking produces reed pulps having much higher yield and about the same strength properties, in comparison with soda pulping process. At about 75% yield, the pulp of 150 mL CSF possesses the following properties: breaking length, 5 to 6 km; burst index, 2 to 2.5 $kPa.m^2/g$; tear index, 5.2 to 6.2 $mN.m^2/g$; brightness, 32 to 38%; and opacity, 93 to 95%. The pulp has a good refinability; specific refining energy consumption is in the range of 0.43 to 0.61 MJ/kg, much lower than that for wood pulp.

Cooking liquor pH has important effects on pulp characteristics, especially at low pH. The strength properties of pulp are extremely poor when the liquor pH is lower than 7, and can be increased with increasing pH. As pulping and bleaching response are concerned, it is recommended to use a cooking liquor at pH 9.

The strength properties of the pulp are also improved as the ratio of SO_2 to o.d. chip increases. However, when taking into account the operation factors related to pulp production (e.g., saving in cooking chemicals, bleachability and pollution), the ratio should be kept at 15%.

Cooking time has important effects on pulping yield and physical properties. In order to have a yield over 70%, as well as good physical properties, a cooking time of 20 to 40 minutes is considered to be an optimal choice. After cooking, the quantity of residual SO_2 in spent liquor is high, about 60% of the initial charge, being a disadvantage of the liquid-phase process.

5.2 VAPOR-PHASE CM PULPING OF REED

The pulp (about 75% yield) produced by vapor-phase process displays characteristics similar to those of the pulp produced by liquid-phase process. The strength properties are: burst index, 2.0 $kPa.m^2/g$; breaking length, 5.0 km; tear index, 6 $mN.m^2/g$; and the optical properties are: brightness, 36.5%; and opacity, 94%. A comparison of specific refining energy between the vapor-phase and liquid-phase CM pulps indicates that the specific energy consumption for the former is about half of that for the latter (0.4 vs. 0.8 MJ/kg for refining to 150 mL CSF).

5.3 RECYCLING OF SPENT IMPREGNATION LIQUOR FOR PULP PRODUCTION

Recycling of spent liquor for pulp production could be practised without limit in the number of times. In comparison with liquid-phase cooking, the vapor-phase cooking combined with spent liquor recycling would bring in substantial savings in chemicals and heating energy, and would also generate much less water pollution. In this study, on the basis of one kg o.d. chip, the discharged liquor volume and quantity of SO_2 from vapor-phase process were, respectively, 0.8 litre and 3.75 g, while 4.0 litres and 100 g from liquid-phase process.

5.4 BLEACHING

Reed CM pulp responds well to two-stage HP bleaching. Under optimal bleaching conditions (i.e., NaClO: 8 to 10%; peroxide: 2%, and NaOH: 1.5%), more than 40 points of brightness gain could be achieved (e.g., from 32% to 78%). Physical properties of pulp are significantly improved by bleaching, while the overall yield (with respect to o.d. chip) can be maintained over 70%. The final brightness depends not only on bleaching method and conditions but also on cooking conditions; using a cooking liquor of pH 9 and a SO_2 charge of 15% would subsequently result in a high brightness gain by bleaching.

5.5 GENERAL REMARKS

With respect to the characteristics of other conventional chemical pulping processes for reed, CM pulping might lead to an uncomplicated operation with acceptable production cost, as well as the savings in chemicals and heating energy, and a significant reduction of environmental impact. It is therefore a promising pulping method for the countries where the shortage of wood-fibre raw materials for papermaking is a continuously unsolved problem.

When considering pulping yield, physical properties and bleachability, reed CM pulp has a potential to be used in the manufacturing of printing, writing and fine papers, or it might be used as the major furnish for the production of these papers.

Much work is still needed to be undertaken concerning other characteristics of reed CM pulp, such as ink receptivity and linting. Further exploration of CM pulping process for reed with the use of different chemical treatments is also worthwhile. Furthermore, the future work should involve the investigation of the runnability of such CM pulp on paper machine. Several vapor-phase pilot-plant trials have already been carried out in a Chinese mill as a follow-up of the program sponsored by the Canadian International Development Agency.

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APPENDIX

Presented in Figures A1 to A4 are the results from a preliminary test related to the investigation of the refining compatibility between a PFI mill and a blender (Model Osterizer 14, Sunbeam).

As shown, the blender used was similar to a PFI mill with regard to refining function, in terms of burst index (Figure A1), breaking length (Figure A2), tear index (Figure A3), and bulk (Figure A4).

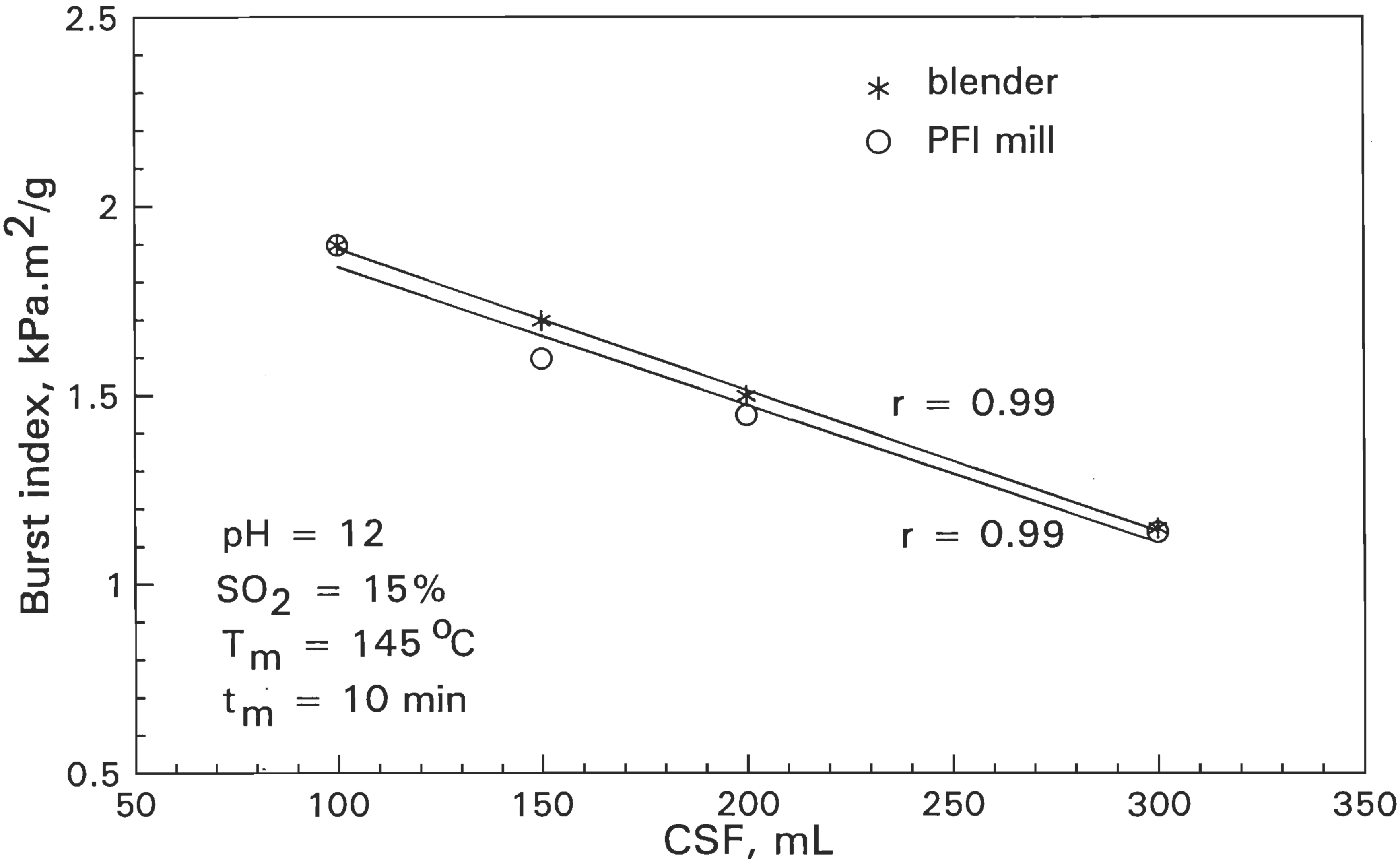

Figure A1 Burst index versus CSF for pulp refined with blender and with PFI mill.

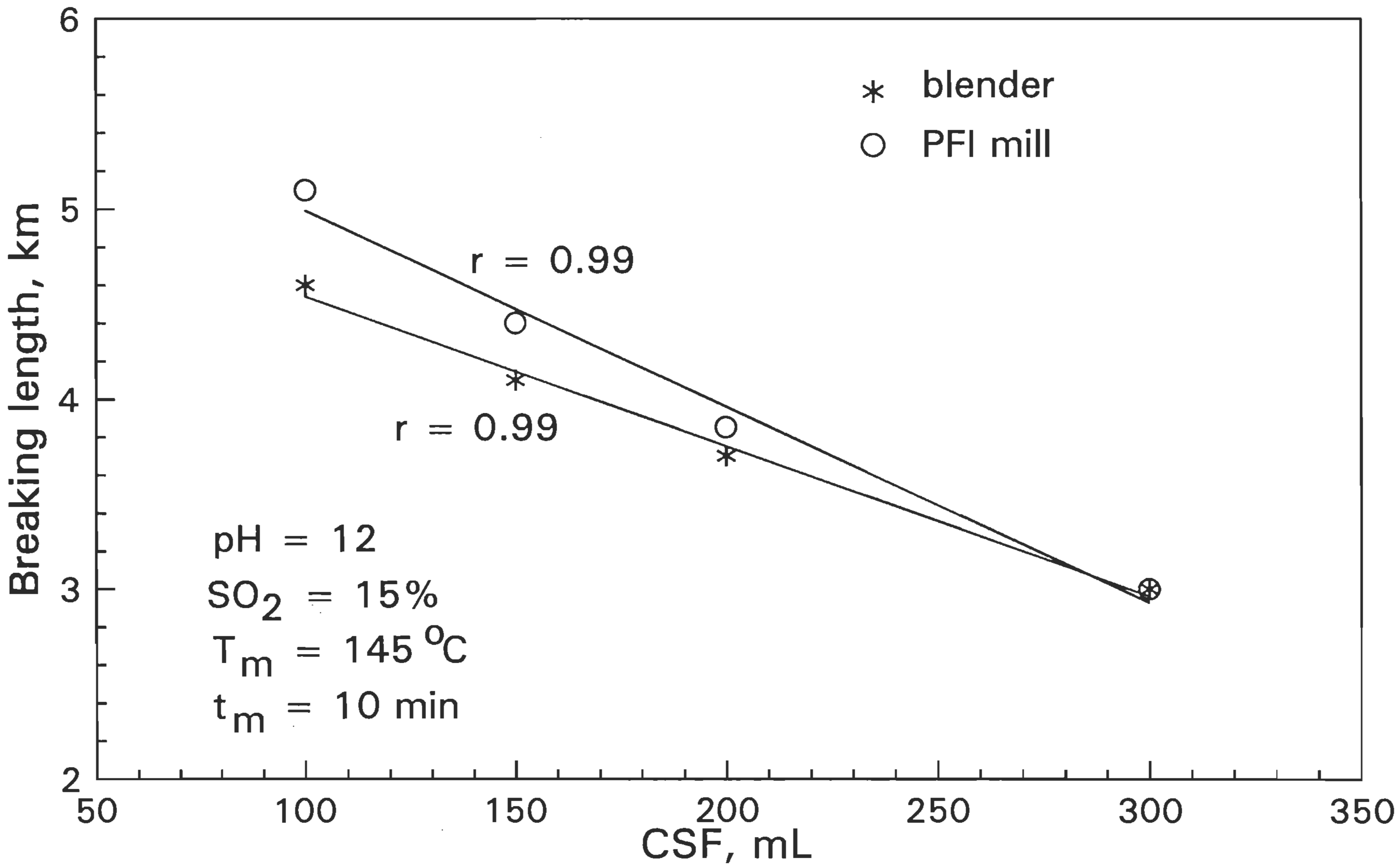

Figure A2 Breaking length versus CSF for pulp refined with blender and with PFI mill.

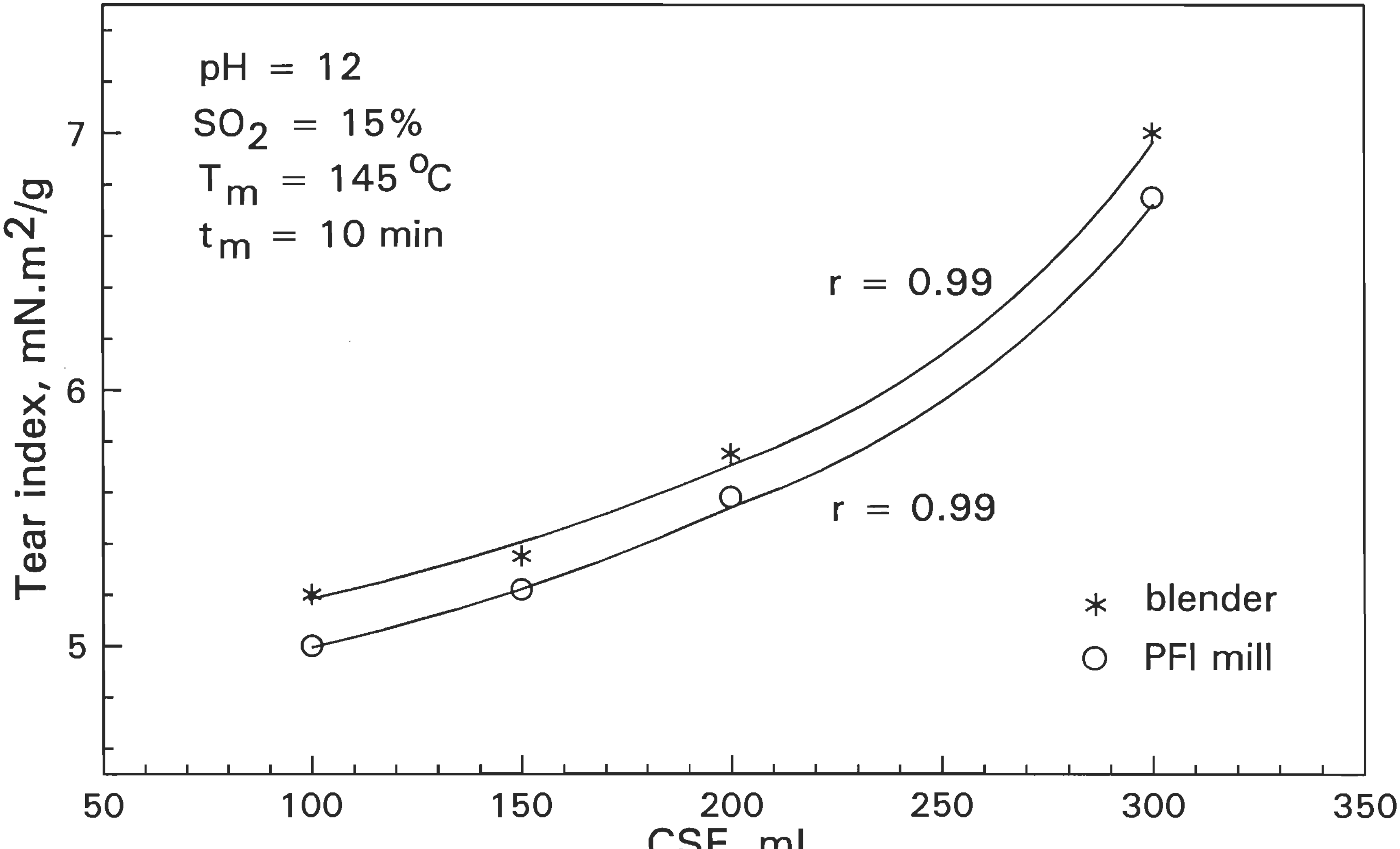

Figure A3 Tear index versus CSF for pulp refined with blender and with PFI mill.

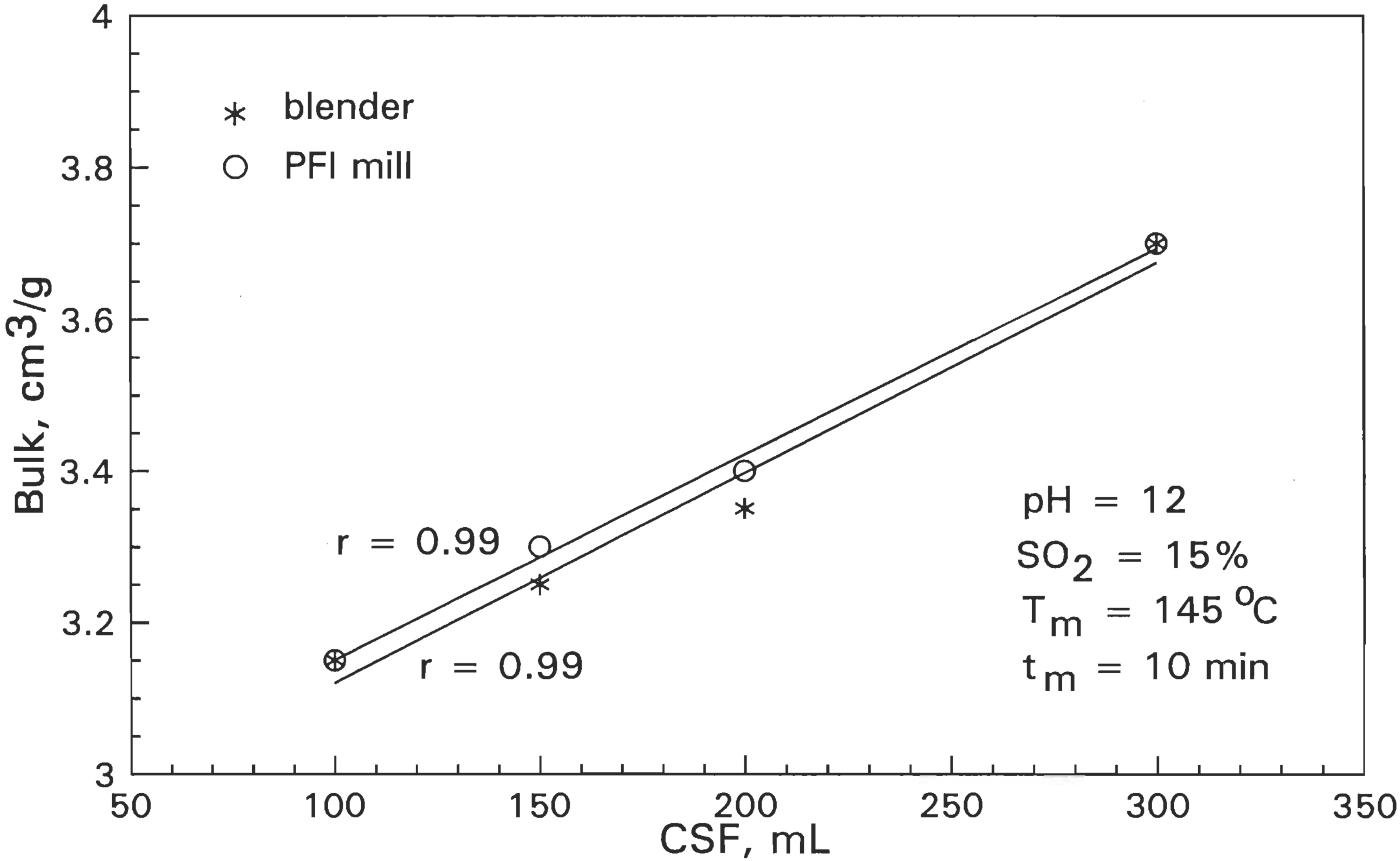

Figure A4 Bulk versus CSF for pulp refined with blender and with PFI mill.