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ORGANOSOLV PULPING OF *CALOTROPIS PROCERA* BY MONO ETHANOL AMINE

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ABSTRACT

In this study, usage of mono ethanol amine (MEA) as an organic reagent was considered in pulping of Milkweed compared with alkaline non-friendly pulping methods including Kraft and Kraft-AQ and soda-AQ. In this case, monoethanolamine was added in various ratios i.e. 100, 75, 50, 37.5 and 25% in replacement with water (MEA-water pulping). Besides, anthraquinone was added in parallel with MEA-water treatments (MEA-water -AQ) and its effect on pulp properties has been considered. The results indicated that replacement ratio of 75/25, 240 minutes of retention time and with0.1% usage of anthraquinone showed the optimum conditions based as yield and kappa number of the pulp samples. Moreover, at the same degree of delignification, the MEA pulps showed about 15-20% higher yield based on raw material. Total unbleached MEA pulp yield is very high, ranging between 48 to 54% with kappa number of 58. For Kraft, the yield varied between 38 to 43%.

KEYWORDS: Organosolv pulping, mono ethanol amin, alkaline pulping, yield, reject, kappa No.

INTRODUCTION

Paper as a strategic commodity is closely related to various issues in case of official, educational, economical and etc. Thus, it would be economical if countries could produce required paper by the national mills and in fact without using imported sources. Besides, an increment has been appeared in consumption of pulp and paper based products in recent decades even in the countries which has not enough lignocellulosic sources (FAO reports 2009). Surely, population growth will increase pressure on forests and other resources and intensify destruction of these vital areas; therefore, because of restrictions on harvesting of forests and the declining resources, excessive use of these resources will create a critical situation for environment and humans in a deep way. Thus, new alternatives especially planting of fast-growing species could partly resolve the lack of forest species. In the case of cultivation, selection of the appropriate species is so important since that just eight percent of total Iran area is covered with forest; actually, more than half of Iran's land area is desert and semi-desert. The species which require low biological needs i.e. low water and humidity are suitable for planting in these areas. In fact, it is expected that these species should supply the requirement of wood and paper industry. The last studies have shown that among drought-friendly species, milkweed with binomial nomenclature of *Calotropis procera* is growing automatically and without irrigation which is greatly compatible to the dry conditions and high temperatures of southern areas of Iran. Naser et al (2011) considered chemical and biometrical characteristics of milkweed. As the results, percentage of chemical components including cellulose, hemicellulose, lignin and ash were evaluated 47.88%, 27.88%, 24.25% and 2.1%, respectively. Besides, the lowest and highest value of fiber is about 0.742 and 1.67 mm, respectively. As a matter of fact, the values are in the range of other hardwoods and therefore, from this point of view, milkweed has acceptable potential of pulping (Naser et al. 2011).

Greenpeace groups in various countries are restricting the classical pulping processes which use sulfur-containing reagents. In this way, organosolv methods could be suggested. Usage of organic solvents i.e. methanol, ethanol, mono ethanol amine, diethanolamine, triethanol amine and some other kinds has showed some valuable advantages including recoverability of chemicals and environmentally friendly base of the process (Harlow and Wise, 1938, Wise et al. 1939). This disclosure prompted several studies on the use of MEA for the production of pulp. Mostly, these investigations were focused on the use of wood as raw material and MEA was only added in alkaline pulping to support the delignification process. Extensive studies on the use of MEA as the only delignifying agent in cooking of hardwood (*Eukalyptus grandis*) and softwood (*Pinus elliottii*) were carried out by Wallis (1976, 1978a, 1978b, 1980). A literature review is given by Claus et al. (2004) and Claus (2005). Ghahremani et al. (2014) used mono ethanol amine for pulping of kenaf whole-stem in different cooking conditions. Based on the results, 75% MEA ratio, 90 min. cooking time, 160°C cooking temperature and liquor/kenaf ratio of 4/1were realized as optimum cooking conditions whereas the whole stem was delignified to a low kappa number of 19.8 and the pulp yield of 55.1%. In addition, this newly developed pulping process provided superior mechanical properties in comparison with soda-AQ pulp. The delignification behavior of wheat straw and rye straw using various MEA-water and liquor/straw ratios was studied by Salehi et al (2013). In this case, the impacts of mono-, di-, tri-ethanolamine/water mixtures and addition of KOH to the cooking liquor were monitored. The best results were achieved with a MEA-water ratio of 50/50 at a liquor/straw ratio between 3:1 and 4:1. The use of the mixture of mono-, di-, tri-ethanolamine instead of MEA only was not effective for straw pulping. The effect of adding KOH to the MEA pulping liquor was negligible. Besides, in comparison with soda and soda/AQ as the reference pulps, the MEA pulps showed 10% higher yield at similar degree of delignification.

All in all, ex-researches have shown that the MEA pulping method results to more selectivity in delignification and higher protection of carbohydrates. In fact, compared to other processes, kappa number was lower and yield was higher; moreover, it is possible to recover the chemical in a friendly and safe way.

For all above mentioned reasons, in this study, MEA pulping process has been evaluated in case of milkweed.

MATERIAL AND METHODS

Milkweed samples were prepared from planted area of Kerman city in Iran and they were then transported to Alborz research center. Firstly, the samples were chipped to achieve the acceptable fragments (3 centimeters in width and length and 5 mm in thickness). After being well air-dried, the moisture content was measured. The pulping operation was carried out in a set of cylindrical digester (3.7 L each) rotating in a heated glycerin bath in laboratory of Tehran University.

Mono ethanol amine (MEA) was used as a main pulping reagent which should be mixed with deionized water in a variety of ratios. At first, 25% of MEA was combined with 75% of the deionized water. In then, four other respective ratios were defined based as an increase in MEA ratio and a decrease in water ratio; the rates include 37.5 to 62.5, 50 to 50, 75 to 25 and finally 100% of MEA without usage of water. It is worth noting that all cooks were carried out using by 50 gram of milkweed as a raw material with 5 to 1 as the ratio of cooking liquor to wood. Besides, 120 and 240 minutes were selected as the two retention time of cooking at a constant maximum temperature of 160°C. Nevertheless high temperature about 170 to 190°Cwere required to obtain bleachable pulp grades with low kappa number, but also because of mono ethanol amine decomposition at these temperatures and besides production of dark pulp, 160°Cwas selected as constant temperature of MEA pulp. The all MEA based treatments were illustrated in Tab. 1. Next step, the effect of anthraquinone (AQ) was evaluated in all above mentioned treatments. 0.1% of AQ were added to the white liquor. The MEA-AQ treatments were brought in Tab. 2.

Tab. 1 : Condition of MEA pulping.

MEA (%)	Water (%)	Time at temp. (min)
25	75	240
37.5	62.5	
50	50	
75	25	
100	0	

Tab. 2: Condition of MEA AQ pulping.

MEA (%)	Water (%)	Time at temp. (min)
25	75	120 and 240
37.5	62.5	
50	50	
75	25	
100	0	

The main motivation of all organosolv pulping is being environmentally-friendly base of these methods. In addition, recoverability of the reagents is another advantage. Actually, the conventional process for hardwoods is the Kraft and soda-AQ pulping methods to some extent; well, every new pulping method for hardwoods has to compete with these two process. Therefore, in next three steps, soda-AQ, Kraft and Kraft-AQ pulping's of milkweed was carried out in order to compare with the MEA and MEA-AQ pulp samples. In this way, 22 and 24% has been selected as active alkaline (AA) for soda-AQ method. In Kraft and Kraft-AQ methods, AA was determined equal 18, 20, 22 and 24 percent. Also, two level of sulfidity about 20 and 25% has been considered. All three alkaline cooking was considered in four different times of 120, 135, 150 and 240 minutes at two of maximum temperatures about 165 and 170°C. Besides, dosage of AQ was fixed in 0.1% for Kraft-AQ, soda-AQ and MEA-AQ.

Totally, three parallel pulping methods of the milkweed were designed: MEA, MEA-AQ, soda-AQ, Kraft and Kraft-AQ. At the end of cooking time, the pulps were thoroughly was hed by water on a 20 mesh screen and collected on a 200 mesh screen in order to determine the yield based as accepted part and rejects. Afterwards, the kappa number was measured according to TAPPI Method T 236 om-85. Based as yield and kappa amounts, optimum ratio of MEA and water mixing would be determined. In addition, the amount of yield, screen rejects and kappa number were compared for three pulp samples including MEA, MEA-AQ and Kraft.

RESULTS

Tabs. 3 and 4 show the pulp properties of MEA-water and MEA-water-AQ treatments, respectively. The values of kappa and yield including total and acceptable and screen reject has been brought.

Tab. 3: The results of MEA-water pulping (without AQ).

Code	MEA	Water	Time (min)	Kappa No.	Total yield (%)	Acceptable (%)	Screen reject (%)
1	100	0	240	80.6	54.32	52.99	1.33
2	75	25		77.4	55.14	54.33	0.81
3	50	50		88.4	55.27	50.65	4.62
4	37.5	62.5		93.7	56.67	47.92	8.75
5	25	75		95.3	57.45	48.29	9.25

Tab. 4: The results of MEA-water-AQ pulping (with 0%.1 AQ).

Code	MEA	Water	Time (min)	Kappa No.	Total yield (%)	Acceptable (%)	Screen reject (%)
1	100	0	120	74.8	53.17	52.95	0.22
2	75	25		65.2	54.43	54.28	0.15
3	50	50		84.7	54.51	53.16	1.35
4	37.5	62.5		88.5	56.13	52.57	3.56
5	25	75		91.3	56.22	50.6	5.62
6	100	0	240	61.9	52.90	52.9	0
7	75	25		58	53.49	53.49	0
8	50	50		73.8	53.45	53.45	0
9	37.5	62.5		78.6	54.32	54.32	0.31
10	25	75		86.2	55.64	55.64	2.81

Effect of MEA-water ratio

As seen in both Tabs. 3 and 4, with an increase in the ratio of MEA to water, the reject value was significantly increased (from less than 0.5% to more than 5%). Besides, the acceptable yield has been increased, too. In fact, more usage of MEA in cooking liquor caused to lessen the reject value. It could be concluded that, replacement of water with MEA in cooking liquor had a positive effect on yield improvement. Among the five MEA ratios, the highest acceptable yield and least screen reject was observed with 75% of mono ethanol amine.

In the case of kappa evaluation, an expectable trend was observed; so that, with an increase in water ratio in cooking liquor, the kappa numbers were significantly increased. However, the lowest kappa number was related to 25/75% of MEA-water ratio. It means that, if more MEA is used, less lignin will remain in text of the pulp.

Effect of retention time

In this step, the effect of cooking time was considered on pulp properties. In case of MEA-water-AQ treatments, 120 and 240 minutes were considered as the two of cooking time. But for MEA-water treatments, the cooking time was fixed in 120 minutes. The results of Tabs. 3 and 4 indicated that with an increase of cooking time from 120 to 240 minutes, the total yield and acceptable yield was enhanced. In opposite, the amount of screen reject was decreased.

Since, more delignification is the main objective of the chemical pulping process, it is so important to measure the amount of delignification as a main criterion of a chemical process evaluation. It has been showed that an increment in the time caused to decrease the average of kappa number. It means that less lignin amount has been remained in text of the pulp. As well as, the results indicated positive effect of mono ethanol amine in development of delignification. In fact, with an increase in the amount of water in cooking liquor, the kappa number and subsequently residual lignin amount was increased. In this case, lowest and highest kappa values were related to the ratio of 75/25% and 25/75%, respectively.

Effect of AQ addition

Based as Tab. 4, usage of anthraquinone had a positive effect on the delignification rate. As well as, MEA-water-AQ treatments showed lower kappa values in comparison to MEA-water treatments. Among all treatments, lowest kappa number was obtained about 58 related to 240 minutes cooking time at 160º C and 75/25%MEA-water with 0.1% added of AQ.

Kraft, kraft-AQ and soda-AQ treatments

The amounts of kappa and total yield have been illustrated in table 5.As seen, the lowest kappa number (65.4) was obtained with 24% of AA and 25% of sulfidity. This process has been carried out for 120 minutes in maximum temperature of 1650°C. As well as, the highest total yield (42.5%) related to 18% of AA, 20% of sulfidity which has been carried out for 135 minutes in maximum temperature of 165˚C. However, the amount of screen reject was about 22% that is too high to select as the optimum treatment.

Tab. 5: The results of Kraft pulping.

Code	AA (%)	Sulfidity (%)	Time (min)	Kappa No.	Total yield (%)
1	24	25	120	65.4	37.66
2	24	20	150	66.7	37.57
3	24	20	120	72.3	39.51
4	24	20	135	87.8	42.5
5	24	20	135	85.6	41.4
6	24	20	135	69.7	39.49

The results showed that among Kraft-AQ treatments, treatment 4 showed the optimum condition. In fact, with 24% usage of active alkaline (AA), 20% of sulfidity and cooking time of 240 minutes showed the lowest kappa number (38.5) and highest amount of total yield (39.95%). Tab. 6 shows the results of all Kraft-AQ treatments.

Tab. 6: The results of Kraft-AQ pulping.

Code	AA (%)	Sulfidity (%)	Time (min)	AQ dosage (%)	Kappa No.	Total yield (%)
1	24	20	120	0.1	47.6	36.68
2	24	20	120	0.1	51.2	37.06
3	24	20	120	0.1	66.5	38.11
4	24	20	240	0.1	38.5	39.95
5	24	20	150	0.1	45.2	38.52
6	24	20	150	0.1	49.5	36.66
7	22	25	120	0.1	60.1	39.33
8	24	25	120	0.1	47.7	36.04

The results of soda-AQ treatments showed that the highest amount of lignin solution has been related to the treatment with 24% AA, and 240 minutes as a cooking time. The kappa number and total yield were reported about 70.7 and 37.46%. In contrary, highest amount of total yield (38.48%) was obtained with 24% usage of active alkaline in the cooking time of 120 minutes. In this case, the kappa number was calculated about 75.6. Tab. 7 shows the amounts of kappa number and total yield for the soda-AQ treatments.

Tab. 7: The results of soda-AQ pulping.

Code	AA (%)	Temp. (°C)	Time (min)	AQ dosage (%)	Kappa No.	Total yield (%)
1	24	165	120	0.1	75.6	38.48
2	24	170	240	0.1	70.7	37.64
3	24	165	120	0.1	78.8	37.92
4	24	170	120	0.1	76.4	37.32

Statistical analysis indicated significant effect of active alkaline on the kappa number. Based as Tab. 5, an increase of AA from 18 to 20 and from 18 to 24% led to decrease the kappa value about 2.2 and 18.1, respectively. Also, based as yield results in the mentioned Tab. 5, the highest total yield related to 18% of AA consumption. However, the screen reject of this sample was about 19.5% which is so high to select as an optimum treatment. As seen in Figs. 1 and 2, usage of more active alkaline led to improve acceptable yield and lessen the screen reject. As expected, lowest yield amount was 39.49% with AA of 24%.

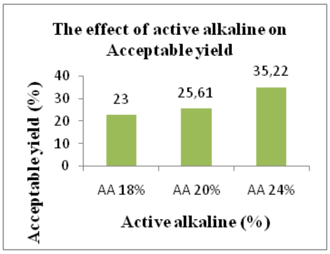

Fig. 1: The effect of active alkaline on acceptable yield.

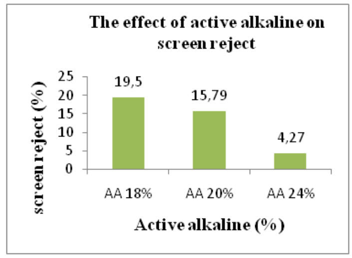

Fig. 2: The effect of active alkaline on screen rejects.

Usage of anthraquinone decreased the kappa value. As seen in Tabs.5 and 6, 0.1% addition of AQ caused to 21.1units decline in kappa value. In other words, AQ usage had a positive effect in lignin solution in the pulping process. As well as, it has been showed that usage of AQ improved the total yield up to 2.45%; the screen reject was approximately vanished and acceptable yield improved up to 3.66% (Figs. 3 and 4). Chai et al. (2007) claimed that anthraquinone increases the delignification rate and improves the yield. The mechanism is based on protection of polysaccharides via the conversion of aldehydes groups to aldonic acid groups. So, anthraquinone is converted to anthrahydroquinone and it will oxidize the lignin. In fact, less amount of lignin and more amount of polysaccharide will be remained in the pulp.

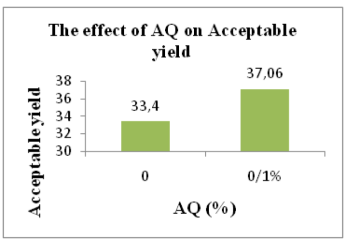

Fig. 3: The effect of AQ on acceptable yield.

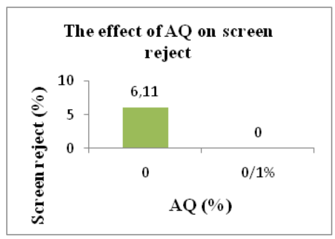

Fig. 4: The effect of AQ on screen rejects.

Based as Tab. 5, increment of sulfidity leads to remove more lignin in the Kraft-AQ pulping process. As seen with 5 percent increase in sulfidity value, kappa number decreased about 6.4 units. This result is significantly remarkable.

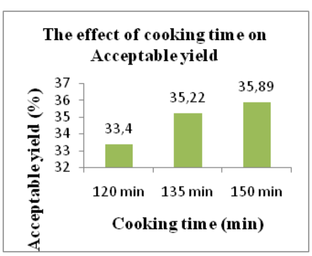

Fig. 5: The effect of time on acceptable yield.

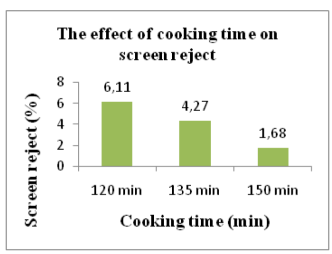

Fig. 6: The effect of time on screen rejects.

It would be concluded that more chemical consumption either active alkaline or sulfidity had a negative impact in total yield. As well as, the screen reject value was decreased and the acceptable yield was improved. Besides, the kappa value decreased with more chemical consumption. The results showed that increment of the cooking time had a similar effect on the yield and kappa parameters (Tab. 5). Three cooking time including 120, 135 and 150 minutes had been considered. As illustrated, increase of cooking time about 15 and 30 minutes led to lessen kappa value up 2.6 and 5.6 units. Also, the acceptable yield has been improved and screen reject has been decreased with the time increase. There was not observed any remarkable difference in the amount of total yield.

DISCUSSION

In Fig. 7, the total yield has been illustrated together with kappa number for the MEA-water treatments. As seen, the MEA-water ratio of 75/25% has been showed the best results based as yield and kappa value. It indicates positive effect of mono ethanol amine as a reagent of pulping; so that with an increase of mono ethanol amine portion in cooking liquor from 25 until to 75%, the yield has been improved and the kappa value has been decreased. In fact, an increment in MEA consumption has been lead to expand the cooking process; less remained lignin and less screen reject would verify this result. The yield and kappa value for ratio of 100/0% are after ratio of 75/25%. It has been probably resulted from the reduction of cooking liquor concentration (Ghahremani 2014). Wallis (1978) stated that usage of vapor instead of water in MEA pulping of eucalyptus could solve more lignin relative in less relative amount of the time.

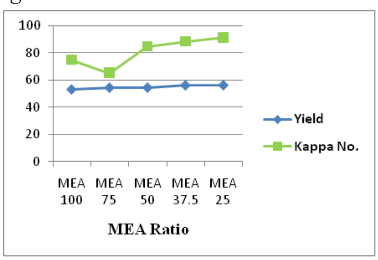

Fig. 7: The total yield (acceptable and reject) and kappa number.

In the case of cooking time in MEA-water-AQ treatments, there was no significant change in total value with an increment of the time (from 120 to 240 minutes). In contrary, the kappa value was decreased. As illustrated above, the lowest value was 58 that probably resulted from the ratio of liquor to milkweed. So in order to improve the delignification rate, the L/W ratio should be increased. Moreover, most likely, due to the complexity of lignin, delignification by mono ethanol amine is difficult (Hedjazi 2009). Besides, complicated structure of the hardwoods lignin is maybe another reason (Gahremani 2014).

Comparison of processes

Compared to other chemical pulping methods, high yield amount is an advantage of MEA pulping method. In this study, the lowest and highest values of the total yield were obtained 52.9 and 57.45. Actually, considering the amount of extractives about 13% in milkweed (Naser et al. 2012), these amounts are indicated as a valuable yield amount. Pulping of milkweed have considered based as a variety of the pulping processes including Kraft, Kraft-AQ and soda-AQ in comparison with MEA-water and MEA-water-AQ. As observed, the highest value was 42.5. This value is much less than the lowest yield among MEA-water treatments (<52.9%). As a matter of fact, the improvement of yield of 15-20% is a motivating phenomenon from industrial perspective. Figs. 8 and 9 shows the total yield and kappa number of the 5 different processes.

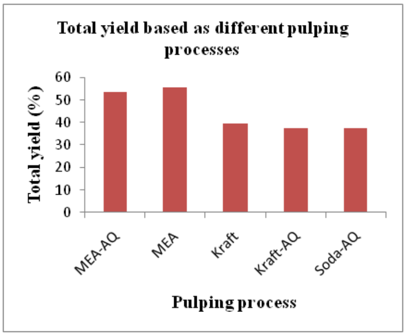

Fig. 8: Comparison of total yield.

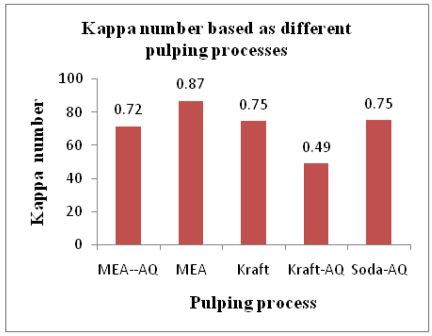

Fig. 9: Comparison of kappa number.

High yield of MEA-water pulping was reported by some researchers before; high selectivity of the MEA pulping is one of the reasons (Salehi 2014). Based on john (2001), in one hand, carbohydrates were protected via redox reaction, in the other hand, condensation reaction of the lignin is stopped and more relative lignin will be solved. Wallis (1978) and Hedjazi et al. (2009) have indicated similar results for MEA pulping of eucalyptus and wheat straw, respectively.

The average amount of kappa numbers has been calculated for the different processes according to tables 3, 4, 5, 6 and 7. Thus, the kappa number of Kraft-AQ pulp sample is less than others. In next, MEA-water-AQ, Kraft, soda-AQ and MEA-water samples are next category.

CONCLUSIONS

1. It has been observed that based as the yield amount and kappa number of the pulp sample, milkweed could be used as an exclusive raw material or in combination with other species.
2. Based on the values of yield and kappa in different treatments, the MEA-water ratio should be 75:25 or 100/0.
3. The presence of AQ in Kraft pulping decreased screened yield and simultaneously enhanced the delignification rate. In MEA pulping, AQ addition showed a similar effect. In fact, MEA/AQ pulping of milkweed provides a highly selective delignification with low kappa numbers.
4. Total unbleached MEA pulp yield is very high, ranging between 48 to 54%. For Kraft, the yield varied between 38 to 43%. In fact, at the same degree of delignification, the MEA pulps showed about 15-20% higher yield based on raw material. The main reasons for the much higher yield of MEA pulp could be relative lower alkalinity and the higher selectivity of this solvent.
5. Nevertheless the kappa number of MEA-water pulp sample are too high compared to non-friendly pulping such as Kraft, Kraft-AQ and soda-AQ, but as mentioned above with little charge of anthraquinone, it could be reduced to an acceptable amount. Besides, due to high yield amount, the MEA pulping method is evaluated as economical and friendly process.

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