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REVUE DE LA FACULTÉ FORESTIÈRE
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ALADAĞ'DA (BOLU) BAZI SARIÇAM MEŞCERELERİNDE YILLIK YAPRAK DÖKÜMÜ MİKTARI VE BU YOLLA TOPRAĞA VERİLEN AZOT'UN TESPİTİ ÜZERİNE ARAŞTIRMALAR

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Kısa Özet

Bu araştırma ile yurdumuzun önemli bir orman yetişme bölgesi olan Bolu - Aladağ civarında, önemli yerli ağaç türlerimizden sarıçam meşcereleri altındaki mevcut ölü örtü ve yıllık yaprak dökümü ile toprak yüzeyine varan organik madde miktarları tesbit edilmiş, ölü örtünün ve yıllık yaprak dökümünün ihtiva ettiği azot besin maddesi % ve total miktarları olarak hesaplanmıştır.

GİRİŞ

Orman topraklarının üzerinde bitkisel ve hayvansal artıklardan ibaret bir organik tabaka mevcuttur. Ölü örtü denilen bu tabaka ve bunun ayrışma ürünleri olan humus maddeleri toprağın birçok özelliklerini ve dolayısıyla verimini önemli ölçüde etkilemektedir. Gerçekten orman ölü örtüsü öncelikle toprağın strüktürünü düzeltir, böylece köklerin gelişimini ve toprağın su tutma kapasitesini arttırır. Ayrıca ölü örtünün ayrışması sonucunda bitkiler tarafından kökler vasıtasıyla derin toprak tabakalarından alınıp yapraklara gelen besin maddeleri tekrar toprağa iade edilmiş olur. Bu olaylar sonucunda üst toprakta bazı besin maddelerinin artış kaydetmesi de bahis konusudur. Şu hale göre; ölü örtünün ve onun ayrışma ürünü olan humus'un bitki beslenmesi bakımından en önemli fonksiyonu tabii bir gübre maddesi olarak toprağa çeşitli besin maddelerini ve bu arada azot'u vermesidir. Ayrıca toprak organik maddeleri mikroorganizmalar için bir besin maddesi ortamıdır, bu suretle toprağın biyolojik aktivitesinde önemli bir fonksiyonu vardır (Irmak, A., Çepel, N., 1974).

Yukarıda işaret edildiği gibi orman ölü örtüsü mineral toprağın üzerini örten ve çoğunluğu yıllık yaprak dökümü ile meydana gelen bir organik madde tabakasıdır. Bu tabaka içinde kabuk ve dal parçaları, kozalak pulları, tohum karpelleri ve buna benzer bitki artıkları da bulunur (Irmak, A., Çepel, N., 1974). Her yıl

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dökülen yaprak vb. organik maddeler bu tabakaya eklenir. Böylece en üstte taze ve parçalanmamış bitki artıkları altta da derine doğru ayrışma derecesi tedricen artan artıklar bulunur. Bu şekilde ölü örtüde görünüş bakımından farklılıklar gösteren ve «yaprak tabakası», «çürüntü tabakası» ve «humus tabakası» olarak adlandırılan üç tabaka tefrik edilebilir. Bu sebeple ölü örtüyü «mineral toprağın üzerinde yatan; yaprak, çürüntü ve humus tabakalarından oluşan organik madde topluluğu» olarak tanımlamak da mümkündür (Irmak, A., Çepel, N., 1974). Bu üç tabakanın kalınlığı veya esasen varlığı ölü örtünün ayrışma hızı hakkında bir fikir verir ve bu hususta bir hükümlendirme yapılabilme olanağı sağlanır.

Buraya kadar kısaca açıklanmaya çalışıldığı gibi orman ölü örtüsü çok yönlü ve önemli fonksiyonlara sahiptir. Onun sadece tabii bir gübre kaynağı olarak orman beslenmesindeki önemini belirtmek amacıyla yapılan araştırmalar; yaprak dökümü ile toprağın yüzüne varan ölü örtü uzaklaştırıldığı takdirde orman ağaçlarının artımının azaldığını ve hatta bazı hallerde tamamen durduğunu göstermiştir (Wittich, W., 1951, 1954, Wehrmann, J., 1961, Süchting, H., 1943).

Bu araştırmamızda Bolu - Aladağ mıntıkasındaki sarıçam ormanlarında; aşağıdaki soruların cevaplandırılmasına çalışılmıştır:

1. Meşcerelerde mevcut ölü örtü miktarı ne kadardır?
2. Yıllık yaprak dökümü miktarları ne kadardır?
3. Ölü örtüde ve her yıl dökülen yapraktaki azot miktarları % ve kg/ha olarak nedir?

DENEME ALANLARININ TANITIMI

Bu araştırma Bolu - Aladağ mıntıkasındaki sarıçam ormanlarında seçilen dört deneme alanında yapılmıştır. I ve II numaralı deneme blokları Aladağ Orman İşletmesi Kartalkaya Bölgesinin Karapınar deresi mevkiinde, III ve IV numaralı deneme blokları aynı işletme hudutları içinde yeralan Şerif Yüksel Araştırma Ormanının Harmancık Deresi mevkiinde bulunmaktadır. Meşcerelerin aslı ağaç türü sarıçam olup göknar sarıçam'ın muhtelif yaş safhalarında çam'ın altına bir alt tesis olarak tabii bir şekilde gelmiş bulunmaktadır. Üst tabakayı teşkil eden sarıçamlar I, II ve III numaralı deneme bloklarında 80 - 110, alt ve ara tabakadaki göknarlar 50 - 90 yaşlarındadır. IV numaralı deneme bloku ise daha genç olup sarıçamlar 50 - 70, göknarlar 20 - 30 yaşları arasındadır.

I ve II numaralı deneme bloklarında toprak kumlu killi balçık tekstüründe, III ve IV numaralı bloklarda ise kil ve killi balçık türündedir. Her dört deneme blokunda reaksiyon asidik ortamdadır (Tablo 1). Ölü örtü örneklerinde yapılan pH ölçmeleri de toprak reaksiyonuna yakın değerler vermiş bulunmaktadır. Toprak analiz sonuçları 0 - 10 cm derinlikler arasındaki azot muhtevasının da genellikle yüksek değerlere ulaştığını göstermektedir.

ARAŞTIRMA METODU

Meşcerelerde mevcut total ölü örtü miktarlarını tesbit etmek için 1 m² (1.0 m × 1.0 m) yüzeyli kasalar kullanılmıştır. Bir deneme bloku içindeki her parselde üç ayrı yerde 1 m² yüzeyli kasa tatbik edilmek suretiyle ölü örtü örnekleri toplanmıştır. Aynı şekilde yıllık dökülen yaprak miktarını tayin edebilmek için her parsele gelişigüzel üç ayrı yere üst yüzeyi yatay duracak şekilde 0.25 m² (0.5 m × 0.5 m) yüzeyli ve kenar yüksekliği 20 cm olan kasalar yerleştirilmiştir. Kasalar 5 yıl süreyle deneme alanlarında bekletilmiş ve bir yıl içersinde dökülen yapraklar belirli zamanlarda toplanmıştır. Gerek ölü örtü ve gerekse yıllık yaprak dökümü miktarını tesbit amacıyla her parsel için üç ayrı değer bulunmuş ve bu değerlerin ortalamasından hektardaki ölü örtü ve yıllık yaprak dökümü miktarı hesaplanmıştır. Aynı şekilde azot konsantrasyonu ve miktarının hesaplanmasında üç ayrı analiz sonucunun ortalamasından yararlanılmıştır. Tablo 2 ve tablo 3 bu ortalama değerleri göstermektedir. Analiz metodları aşağıda kısaca açıklanmış bulunmaktadır.

Mekanik analiz : Toprakların tekstür tayini hidrometre metoduna göre yapılmıştır.

pH tayini : Toprak ve ölü örtü reaksiyonu (pH değeri) Beckman pH ölçeri ile 1 : 2.5 oranında H_2O ile sulandırılmış çözelti içersinde cam kalomel elektrotla yapılmıştır.

Azot tayini : Azot tayini Kjeldahl metoduna göre total azot olarak yapılmıştır.

ARAŞTIRMA SONUÇLARI

Bu araştırmaya beş yıl devam edilmiş olup sonuçlar 1967 - 1968, 1968 - 1969, 1969 - 1970, 1970 - 1971, 1971 - 1972 yıllarının yaprak dökümüne ait periyodları kapsamaktadır. Ölü örtü tesbitleri araştırmanın başlangıç yılı olan 1967 sonbaharında deneme alanlarında mevcut yaprak, çürüntü ve humus tabakalarının tamamına ait miktarları birarada göstermektedir. Bir hektarlık orman alanında mevcut ölü örtü miktarları 115.4 - 50.6 ton arasında değişmektedir (tablo 2, sütun 1). IV numaralı deneme blokunda bulunan değerler diğer deneme bloklarına göre oldukça düşüktür ve örneğin I numaralı deneme blokundaki miktarın ancak % 50'si kadardır. Bu durum blok IV'ün diğerlerine göre daha genç oluşundan ileri gelmektedir. Yıllık yaprak dökümü miktarları da IV numaralı deneme blokunda bir hayli azdır (1963 - 2760 kg/ha). I, II ve III numaralı deneme bloklarındaki yıllık yaprak dökümü miktarları 3429 - 5337 kg/ha arasında değişmektedir. Yine 1967 - 1972 yılları arasındaki toplam yaprak dökümünün miktarları bakımından 23378 kg/ha ile I numaralı deneme bloku başta gelmekte, 11848 kg/ha ile IV numaralı deneme bloku sonuncu sırayı almaktadır. IRMAK, A., ve ÇEPEL, N., 1968'in yaptıkları bir araştırmaya göre Belgrad Ormanında karaçam meşcerelerinin, 5 yıllık tesbitlerin ortalamasına göre, yıllık yaprak dökümü miktarları 4300 - 4824 kg/ha arasında değişmektedir. Tablo 2'deki değerler ayrıca 5 yıllık periyod içersindeki yaprak dökümü miktarının mevcut ölü örtünün yaklaşık olarak % 20'sine baliğ olduğunu da göstermektedir.

Tablo 3'ün sol yarısı ölü örtüdeki ve yaprak dökümü ile toprağa ulaşmış olan azot konsantrasyonunu (100 gr mutlak kuru yaprak maddesindeki miktar), sağ yarısı ise azotun kg/ha değerlerini göstermektedir. N konsantrasyonları gerek bloklar içinde ve gerekse bloklar arasında önemli ölçüde değişmemektedir. Ölü örtüdeki ortalama azot miktarları 369.0 - 941.3 kg/ha arasında bulunmaktadır. Ölü örtünün ihtiva ettiği kg/ha azot miktarları bakımından da 1 numaralı deneme bloku başta gelmekte, blok IV ise sonuncu sırayı almaktadır. Yıllık dökülen yapraklardaki azot miktarları 16.3 - 45.0 kg/ha arasında değişmekle beraber genellikle 35 - 40 kg/ha arasında bulunmaktadır. Yıllık yaprak dökümü ile toprağa intikal eden azot ve diğer besin maddelerinin, sadece orman beslenmesi yönünden bir gübre maddesi olarak oynadığı rol çok büyüktür. Zira 100 kg Amonyum Sulfat $(NH_4)_2SO_4$ gübresi ile toprağa 21 kg N intikal ettirilmiş olmaktadır. Şu hale göre deneme bloklarının çoğunda yıllık yaprak dökümü sayesinde hektar başına yaklaşık olarak 20 kg Amonyum Sulfat gübrelemesine muadil azot verilmiş olmaktadır. Başlangıçta organik halde bağlı olan bu miktar azot zamanla bitkilerce alınabilecek amonyum veya nitrat azotuna dönüştürülerek tekrar bitkilerin istifadesine sunulmaktadır. Orman ağaçlarının yıllık besin maddesi ihtiyacı konusunda yurdumuz şartlarında yapılmış araştırmalar yoktur. Bu bakımdan yıllık yaprak dökümüyle toprağa verilen azotun meşcerelerin ihtiyacının nekadarını karşılayabileceğini söylemek mümkün değildir. Ancak bir fikir edinmek ve kıyaslama yapabilmek maksadıyla diğer ülkelerde yapılan araştırma sonuçlarından yararlanılabilir. Goussone (1964) gençlik çağındaki sarıçamların yıllık azot ihtiyacının 60 - 80 kg/ha arasında değiştiğini bildirmektedir. Wittich'e (1961) göre geniş yayılışa sahip olan çam, lâdin ve kayın gibi orman ağaçları II. bonitetteki yetişme muhitlerinde topraktan her yıl hektarda 30 - 50 kg azot alırlar. Bu iki araştırıcının verdiği değerler arasındaki fark önemli görülmektedir. Ancak gençlik çağında orman ağaçlarının ağaçlık çağına kıyasla besin maddesi ihtiyacının çok yüksek olduğu da bilinen bir gerçektir. Diğer taraftan muhtelif yetişme muhitlerinde, münferit ağaç türlerinin azot ihtiyacının büyük değişiklikler gösterdiği de bilinmektedir. Örneğin: kavak, karaağaç ve akçaağaç gibi ağaç türlerinin azot ihtiyacı iyi topraklarda hektarda 1 yıl için 100 - 150 kg olup şeker pancarının ihtiyaç gösterdiği miktara yaklaşmaktadır (FIEDLER, REISSIG 1964). Yapılan bu açıklamalardan da anlaşılacağı gibi orman ağaçlarının besin maddesi alımında lokal yetişme muhiti koşulları önemli ölçüde etkili olmaktadır. Ancak bu durum bizim diğer araştırma sonuçlarından yararlanmamıza da tamamen engel değildir. Bu düşünüşün ışığı altında Aladağ mıntıkasındaki sarıçam ormanlarının yıllık azot ihtiyacını 40/50 kg/ha olarak kabul edebiliriz. Tablo 3'ün tetkikinden de görüleceği gibi yıllık yaprak dökümü ile her yıl toprağa yaklaşık olarak 35/40 kg/ha azot verilmektedir. Bu miktar azot'un sadece ağaçların toprak üstü organlarına ait olduğu, ölen köklerin de toprağa önemli ölçüde organik madde verdiği gözönünde tutulursa Aladağ mıntıkasındaki sarıçam meşcerelerinin yıllık azot ihtiyacının büyük ölçüde bu yolla karşılandığı sonucuna varılabilir.

Tablo 1. Toprak - ölü örtü analiz sonuçları.
Tabelle 1. Analysenergebnisse von Böden und Streu.

Blok	Parsel	Derinlik Tiefe cm	İskelet hacmi Skelet-anteil %	İnce toprak ağır. Gewicht der Feinerde kg	N %	Kum Sand %	Toz Schluff %	Kil Ton %	Toprak sınıfı Bodenart	pH H_2O toprakta in Boden	pH H_2O ölü örtüde in Streu
I	1	0-10	19.5	0.665	0.174	53.71	16.67	29.62	Kumlu killi bal. Sandig toniger Lehm	5.15	4.82
	2	»	10.0	0.670	0.229	53.71	15.23	31.06		5.27	5.22
	3	»	25.5	0.615	0.301	54.34	15.91	29.75		5.75	5.85
II	1	»	20.5	0.585	0.206	57.94	16.09	25.97	» » »	5.77	5.95
	2	»	12.5	0.795	0.213	50.31	18.97	30.72	» » »	5.92	5.85
	3	»	14.0	0.660	—	49.07	18.02	32.91	» » »	5.97	6.15
III	1	»	13.5	0.520	0.398	42.95	9.90	47.15	Kil (Ton)	5.35	5.65
	2	»	4.5	0.795	0.234	36.73	24.89	38.38	» »	5.65	5.65
	3	»	6.5	0.655	0.311	35.85	27.89	36.26	Killi balçık (Toniger Lehm)	5.67	5.65
IV	1	»	10.5	0.665	0.283	38.56	35.05	26.39	Balçık (Lehm)	5.70	5.87
	2	»	9.0	0.615	0.269	42.98	22.34	34.68	Killi balçık (Toniger Lehm)	5.60	5.65
	3	»	13.0	0.580	0.230	43.42	22.92	33.66	» »	5.60	5.77

Tablo 2. Deneme alanlarında mevcut ölü örtü ve yıllık yaprak dökümü miktarları.
Tabelle 2. Streumenge und Jährlicher Streuabfall in den Versuchsflächen.

Blok	Parsel	Mevcut örtü Streu ton/ha	Yıllık yaprak dökümü Jährlicher Streuabfall kg/ha					
			19.10.1967 - 24.10.1968	24.10.1968 - 25.10.1969	25.10.1969 - 28.10.1970	28.10.1970 - 25.10.1971	25.10.1971 - 26.10.1972	1967 - 1972
I	1	115.4	3692	4947	5079	4537	6500	24755
	2	106.8	4147	4586	4317	4067	4180	21297
	3	110.7	4820	4144	5513	4275	5330	24082
	Ø	111.0	4220	4559	4970	4293	5337	23378
II	1	99.1	3705	3176	3935	3154	4540	18560
	2	104.6	3747	3847	4555	4105	5520	21774
	3	97.8	3580	3265	3420	4145	4939	19349
	Ø	100.5	3677	3429	3987	3801	5000	19894
III	1	89.5	4152	4393	4780	3880	5091	22296
	2	86.1	4484	4693	3595	4451	4847	22070
	3	85.4	3394	4413	4907	4472	3660	20846
	Ø	87.0	4010	4500	4427	4268	4533	21737
IV	1	50.6	2300	1744	2956	2623	2480	12103
	2	58.5	1868	2407	2740	2195	2260	11470
	3	54.3	1720	2355	2585	2493	2819	11972
	Ø	54.5	1963	2169	2760	2437	2520	11848

lo 3. Ölü örtü ve yıllık yaprak dökümündeki N miktarları.

elle 3. N-Werte in Streu und in abgefallenen Streu.

ok	Parsel	Ölü örtüde in Streu	Yıllık dökülen yaprakta in Jährlich abgefallenen Streu					Ölü örtüde in Streu	Yıllık dökülen yaprakta in Jährlich abgefallenen Streu					
			1967-968	968-969	969-970	970-971	971-972		967-968	968-969	969-970	970-971	971-972	967-972
									Kg/ha					
I	1	0.832	0.881	0.904	0.956	0.915	0.880	960.1	32.5	44.7	48.6	41.5	57.2	224.5
	2	0.815	0.962	0.956	0.875	0.912	0.830	870.4	39.9	43.8	37.8	37.1	34.7	193.3
	3	0.897	0.854	0.834	0.858	0.865	0.809	993.0	41.2	34.6	47.3	37.0	43.1	203.2
	Ø	0.848	0.899	0.898	0.896	0.897	0.840	941.3	37.9	40.9	44.5	38.5	44.8	206.6
II	1	0.864	0.879	1.100	0.916	0.897	0.905	856.2	32.6	34.9	36.5	28.3	41.1	173.4
	2	0.817	1.002	0.979	0.997	0.965	0.919	854.6	37.5	37.7	45.4	39.6	50.7	210.9
	3	0.715	0.890	0.879	0.895	0.819	0.875	699.3	31.9	28.7	30.6	33.9	43.2	168.3
	Ø	0.799	0.924	0.986	0.936	0.894	0.900	803.0	34.0	33.8	37.1	34.0	45.0	183.9
II	1	0.612	0.861	0.911	0.880	0.868	0.868	547.7	35.7	40.0	42.1	33.7	44.2	195.7
	2	0.865	0.981	0.868	0.929	0.939	0.897	744.8	44.0	40.7	33.4	41.8	43.5	203.4
	3.	0.629	0.700	0.879	0.719	0.826	0.893	537.2	23.8	38.8	35.3	36.9	32.7	167.5
	Ø	0.702	0.847	0.886	0.843	0.878	0.886	610.7	34.0	39.9	37.3	37.5	40.2	188.9
V	1	0.715	0.897	0.719	0.957	1.125	0.881	361.8	20.6	12.5	28.3	29.5	21.8	112.7
	2	0.648	0.830	0.764	0.847	0.875	0.837	379.1	15.5	18.4	23.2	19.2	18.9	95.2
	3	0.667	0.897	0.767	0.812	0.845	0.795	362.2	15.4	18.1	21.0	21.1	22.4	98.0
	Ø	0.677	0.875	0.750	0.872	0.948	0.838	369.0	17.2	16.3	24.1	23.1	21.1	101.8

UNTERSUCHUNGEN ÜBER DEN JÄHRLICHEN STREUABFALL UND DADURCH IN DEN BODEN ANGELANGTEN STICKSTOFFGEHALT IN DEN KIEFERNWÄLDERN VON ALADAĞ (BEI BOLU)

Doz. Dr. Münir DÜNDAR

Abstract

Diese Arbeit wurde durchgeführt um jährlich abfallenden Streumengen in den Kiefernwäldern von Aladağ festzustellen und auf diese Weise in den Boden zugeführten N-Mengen zu bestimmen.

ZUSAMMENFASSUNG

Wir wissen, dass der organischer Substanz wesentlichen Einfluss auf viele Eigenschaften der Böden ausübt und in ungedüngten Böden, vor allem der Nährstoffgehalt der organischen Substanz für die Ernährung der Pflanze von grosser Bedeutung ist. Unter den Nährstoffen hat Stickstoff eine Schlüsselstellung. Da der N - Gehalt der Böden von Ihren Gehalt an organischer Substanz abhängt, gewinnt ihr Gehalt an organischer Substanz auch für die Versorgung der Pflanze mit Stickstoff eine dominierende Rolle.

Die Arbeit wurde in den Kiefernbeständen von Aladağ (bei Bolu) durchgeführt um folgende Fragen zu beantworten:

1. Wie hoch ist die Menge an organischer Substanz in den Kiefernbeständen?

2. Wie verläuft der Streuabfall in diesen Beständen?

3. Wie hoch ist die N-Menge, die durch den jährlichen Streuabfall in den Boden gelangt?

Für die Untersuchungen wurde je zwei Versuchsflächen in Revier Kartalkaya und im Versuchswald Şerif Yüksel gewählt. Jede Versuchsfläche bestand aus drei Parzellen. In jeder Parzelle wurde in drei verschiedenen Stellen mit Hilfe von Holzkasten in 1 × 1 m (1 m^2) Grösse, Gesamtmenge des organischen Substanz bestimmt. Ausserdem wurde in drei Stellen jeder Parzelle, durch Holzkasten in der Grösse von 0.5 × 0.5 m (0.25 m^2) fünf Jahre lang Jährlich abgefallene Streumenge festgestellt. Auf diese Weise wurde drei Werte für jede Parzelle erhalten und durch Mittelwerte von organischer Substanz und von Jährlich abgefallene Streumenge die Werte pro Hektar errechnet. Der N-Gehalt als % und als kg pro Hektar. wurde auf gleicher Weise bestimmt.

Die Analysenergebnisse von Böden und Streu sind in der Tabelle 1 ersichtlich. Tabelle 2 enthält die vorhandene organischer Substanz und jährlich abgefallene Streumenge in den Versuchsflächen. In die Tabelle 3 sind die N-Werte als % und als kg pro Hektar in dem vorhandenen organischen Substanz und in der abgefallenen Streu eingetragen.

Die Ergebnisse der Untersuchungen zeigen, dass die Menge an organischer Substanz zwischen 50.6 - 115.4 t/ha wechselt (Tabelle 2). Jährlicher Streuabfall liegt zwischen 1720 - 6500 kg/ha. Der Mittelwert von 5 jährigen Streuabfall wechselt zwischen 11848 - 23378 kg/ha. Tabelle 3 zeigt die N-Werte im vorhandenen organischen Substanz, sowie in abgefallenen Streu als % und als kg pro Hektar. N-Gehalte in organischer Substanz liegen zwischen 0.677 - 0.848 %; die N-Werte als kg pro Hektar zwischen 369.0 - 941.3. Gesamt N-Mengen in der jährlich abgefallenen Streu sind im Mittel 16.3 - 45.0 kg/ha. Nach den Literaturangaben liegen jährlicher N-Bedarf von Kiefern in Jugendstadium zwischen 60 - 80 kg/ha (GUSSONE 1964); bei Kiefer, Fichte und Buche zwischen 30 - 50 kg/ha (WITTICH 1961). Wenn man oben erwähnten Werte als Mass vor Auge hält, kann gesagt werden, dass der N - Bedarf von Kiefernbeständen in Aladağ, zum grössten Teil, allein durch die N-Menge von jährlichen Streuabfall gedeckt wird.

KAYNAKLAR

FIEDLER, H.J., REISSIG, H., 1964. Lehrbuch der Bodenkunde. VEB Gustav Verlag Jena.

GOUSSONE, H.A., 1964. Naehrstoffbedarf in Beständen s. 29

BÜCHTING, H., 1943. Die Ernaehrungsverhältnisse des Waldes. Allg. Forst und Jagdzeitung 119, Heft 2, 3.

IRMAK, A., ÇEPEL, N.. 1968. Belgrad Ormanında Seçilen Birer Kayın, Meşe ve Karaçam Meşceresinde Yıllık Yaprak Dökümü Miktarı ve Bu Yolla Toprağa Verilen Besin Maddelerinin Tesbiti Üzerine Araştırmalar. İ.Ü. Orman Fakültesi Dergisi, Seri A, Cilt XVIII, Sayı 2.

IRMAK, A., ÇEPEL, N., 1974. Bazı Karaçam, Kayın ve Meşe Meşcerelerinde Ölü Örtünün Ayrışma ve Humuslaşma Hızı Üzerine Araştırmalar. İ.Ü. Yay. No. 1973, Orman Fakültesi Yayın No. 204.

WEHRMANN, J., 1961. Mineralstoffernaehrung der Kiefer auf Heideböden. Jahresbericht des BEV.

WITTICH, W., 1951. Der Einfluss der Streunutzung auf den Boden. Forstw. Cbl. 70, Heft 2.

WITTICH, W., 1954. Die Melioration Streugenützter Böden. Forstw. Cbl. 73. Jahrg. Heft 7/8.

WITTICH, W., 1961. Die Grundlagen der Stickstoffernaehrung des Waldes und Möglichkeiten für ihre Verbesserung. In: Der Stickstoff - seine Bedeutung für die Landwirtschaft und die Ernaehrung der Welt. Verlag Stalling, Oldenburg.

THE DILUTE ACID HYDROLYSIS OF WOOD

Dr. Güneş UÇAR [1]

Abstract

Aspen (Populus tremuloides) was hydrolyzed with dilute sulphuric acid in a flow reactor. By considering the organic acids formed at elevated temperatures a correspondency could be attained between determined glucose yields and predicted values calculated by means of kinetic parameters for cellulose and glucose decomposition respectively.

1. INTRODUCTION

Currently the renewed interests are arising in utilization of wood and wood residues as a source of energy and chemical intermediates. The ethyl alcohol production from wood is regarded as the most promising way since it is a clean liqued fuel on one hand and the ethanol is a valuable starting material in the industry to synthesize many other chemicals.

Fermenting the sugar solutions to alcohol is one of the oldest technique known by the mankind. Nearly half of wood consists of cellulose which is the important structural component of the plant cells. There are also other polysaccharides (polyoses) in the cell wall so that together with cellulose 2/3 - 3/4 of wood is composed of sugars in polymer forms. The cellulose and some polyoses can deliver -after being converted into their monomers- sugar solutions that are readely fermentable to ethyl alcohol.

The convertion of cellulose into glucose can be accomplished by means of acid - and enzymatic hydrolyses. Acid hydrolysis of wood can be carried out using either dilute acid at elevated temperatures or concentrated acid at lower temperatures. Both systems have been practised during the World War I and II (STAMM, HARRIS, 1953, WENZL, 1970, GOLDSTEIN, 1980). Today only in the USSR over 40 plants are in operation on wood and agricultural residues (FENGEL, WEGENER, 1984). Dilute acid hydrolysis has found wider applications than the concentrated acid because of recovery and corrosion problems in the last processes. In many case a prehydrolysis step is connected to remove easely hydrolyzed polyoses under milder conditions. Thus, relatively pure glucose streams were obtained from residual cellulose during subsequent hydrolysis called also cellulose saccharification (CEDERQUIST, 1952, SPRINGER, 1985, HARRIS et al., 1985).

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The acid hydrolysis of cellulose occurs in two steps as a heterogeneous reaction. First the oxygen atom of glycosidic bond between anhydroglucose units is protonated rapidly. A more slow scission of the bond takes place afterwards. At elevated temperatures, i.e. above 150°C a part of cellulose called amorphous fraction and the most polyoses can be hydrolyzed much faster than the crystalline, resistive cellulose. However at these conditions the decomposition of monomeric sugars is also unavoidable. Another type of reactions of glucose in the aqueous acid solutions are referred to as reversion which covers the forming of reversible products (= reversion products) such as disaccharides, oligosaccharides and anhydrosugars. After evaluating some recently announced works the Figure 1 was prepared to show the possible reactions of wood polysaccharides (cellulose, polyoses) in dilute acid (GRETHLEIN et al. 1980, HARRIS, 1981, CONNER et al. 1985).

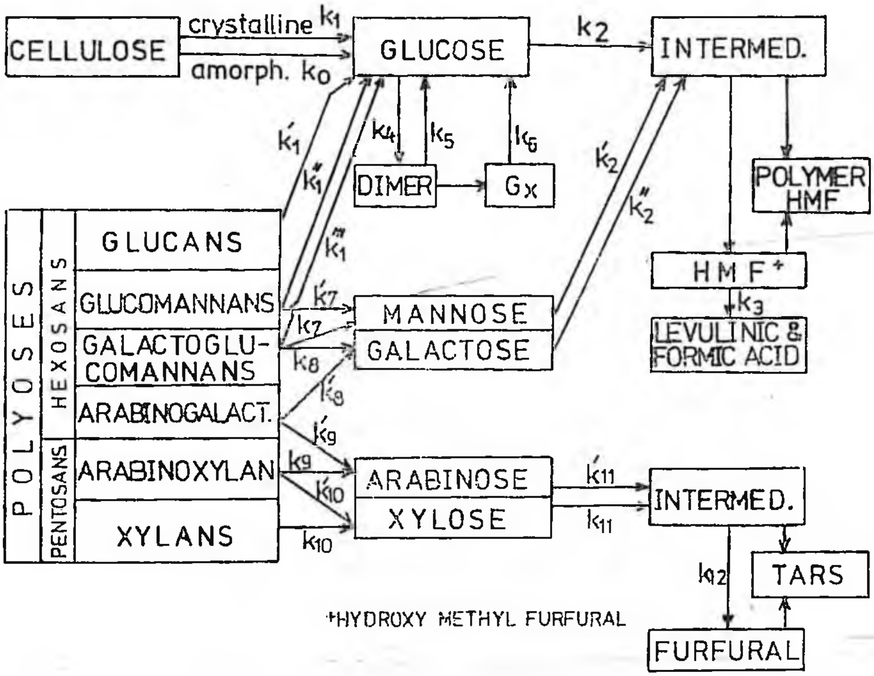


Figure 1. The reactions of wood polysaccharides in dilute acid.

Although the acid hydrolysis of cellulose is a heterogeneous reaction earlier works showed it could be expressed as a first order, homogeneous one (SEAMAN, 1945, YOUNG, 1949, KIRBY, 1948). The consecutive reastions can be given then as follows :

$$\underset{\text{(resistant)}}{\text{Cellulose}} \xrightarrow{k_1} \text{glucose} \xrightarrow{k_2} \text{decomposition products}$$

The k_1 and k_2 rate constants are to be determined acc. to the equations :

$$\frac{dC}{dt} = -k_1C \qquad (1)$$

$$\frac{dG}{dt} = k_1C - k_2G \qquad (2)$$

On the other side the rate constants k_1 and k_2 have an Arrhenius temperature dependence and an additional acid concentration dependence :

$$k_1 = P_1 A^m \exp(-E_1/RT) \qquad (4)$$

$$k_2 = P_2 A^n \exp(-E_2/RT) \qquad (3)$$

The isothermal solution of the rate equations also needs to incorporate another glucose fraction (G_0) which is assumed to be available at zero times as a result of the instantenous hydrolysis of amorphous cellulose and polyoses (glucomannans). Thus, the integration of equation (2) with G_0 fraction taking into account gives:

$$G = C_0 \left(\frac{k_1}{k_1-k_2}\right)(\exp^{(-k_2t)} - \exp^{(-k_1t)}) + G_0 \exp^{(-k_2t)} \qquad (5)$$

where :

G = predicted glucose, as % of potential glucose
C_0 = resistant cellulose, as % of potential glucose
G_0 = readily hydrolyzed cellulose fraction, as % of pot. glu.
t = time, minutes
k_1 = cellulose decomposition rate constant, min^{-1} (Eq. 3)
k_2 = glucose decomposition rate constant, min^{-1} (Eq. 4)
A = acid concentration, wt %
m = exponent on acid concentration in cellulose decomposition
n = exponent on acid concentration in glucose decomposition
T = temperature, Kelvin
R = gas constant, 8.31441 $J\ K^{-1}\ mol^{-1}$
E_1 = activation energy for cellulose decomposition, J/gmol
E_2 = activation energy for glucose decomposition, J/gmol
P_1 = pre exponential constant in Eq. 3, min^{-1}
P_2 = pre exponential constant in Eq. 4, min^{-1}

The parameter vector (m, n, E_1, E_2, P_1, P_2 and G_0) are estimated from the experimental data using some algorithms or regression analyses. Table 1 gives some selected parameters from earlier works carried out in various systems such as glas bombs or ampules (SAEMAN, 1945, MC KIBBINS, 1958), flow reactors (GRETHLEIN, et al. 1980).

Table 1. Experiment Conditions and Kinetic Parameters of Glucose-and Cellulose Decomposition.

Conditions

No.	Substrate	Temp. (°C)	Time (min	H_2SO_4 con. (%)	Type of Reactor	Reference
1	Glucose	170 - 190	0.5 - 30	0.4 - 1.6	Glas bomb	Saeman, Saeman,
2	Douglas	170 - 193	0.5 - 40	0.4 - 1.6	Glas bomb	(1945) (1945)
3	Glucose	180 - 260	0.3 - 60	0.12 - 3.8	Glas ampule	McKibbins (1958)
4	Glucose	180 - 260	0.06 - 0.27	0.6 - 3.75	Flow Reactor	Grethlein Grethlein
5	Alpha Cel.	180 - 240	0.2 - 0.3	0.5 - 2.1	Flow Reactor	et al (1980) et al (1980)
6	Poplar	180 - 265	0.08 - 0.14	0.34 - 1.6	Flow Reactor	Grethlein, Conv. (1982)

Parameters

No.	Pre-exponential (min^{-1})	Acid exponent	Activ. Energy (J/gmol)	G_0 (%)
1	2.38×10^{14}	1.02	137620.1	100
2	1.735×10^{19}	1.34	179613.7	0
3	1.83×10^{14}	0.8634	136096.1	100
4	3.83985×10^{19}	0.5687	87872.5	100
5	5.331×10^{16}	1.1355	154892.3	3
6	6.122×10^{15}	0.9874	147165.2	1.1

The kinetic modeling of reactions is being considered a useful device for designing, developing and operating of chemical processes. In the very recent works the effects of ash constituents on the sulfuric acid as catalyst and the reversion reactions were emphasized and incorporated into the model to improve the performance of kinetic equations (CONNER et al. 1985, HARRIS et. al. 1984, SPRINGER, HARRIS, 1985). During the last decade there are also intensified studies on the fermentation of pentoses to ethanol (WANG et al. 1980 JEFFRIES, 1981, 1985, MALESZKA, SCHNEIDER, 1982, DELLWEG et al. 1984). In this way, the prehydrolysis field of especially hardwoods is receiving more and more attention. Many rate studies performed in this area indicate that the hydrolysis of xylan also fits into the first order homegeneous reactions (CONNER, 1984, CONNER et al. 1985, CONNER, LORENZ, 1986, MALONEY et. al, 1985, SPRINGER, 1966).

2. MATERIAL AND METHODS

The aspen wood (Populus tremuloides), growing in New Hampshire, U.S.A. was Wiley milled and the fraction passing through 60 mesh is used for preparing of the 7 % slurries for the acid hdyrolysis experiments in a plug flow reactor which was developed by GRETHLEIN et al (1980). Two series of runs were carried out by acidifying the slurry in the tank with various amounts of sulfuric acid resulting in 0.37 and 1 % acid concentrations and by elevating the temperatures stepwise from 220° up to 255°C. At the beginning and end of each run the slurry tank was sampled to determine the acid and the solid concentration more accurately by titrating with 0.1 N NaOH or oven drying at 102° ∓ 2°C respectively.

The potential glucose value of the poplars for the 1. and 2. run was determined by hydrolyzing the wood with 72 and 77 % sulfuric acid first, then neutralyzing with $BaCO_3$ and analyzing at the HPLC (High pressure liquid chromatography) for different kind of sugars. The poplar used for the first series contained 45.0 % and that for the second series 47.6 % potential glucose respectively.

The desired reactor temperatures were reached by increasing the amount of steam, consequently the system pressure. From reactor outlet the samples (hydrolyzates) were taken and the sampling time was also measured. The collected samples were then subjected to different analyses, namely determination of acid concentration (calculated as % sulfuric acid), solid concentration and the amout of glucose (HPLC method and glucose analyzer).

The yield of glucose achieved during each run was estimated acc. to the equation :

$$\text{Yield } (\%) = \frac{G_2 \,.\, 100}{F \,.\, G_1}, \text{ where}$$

G_1 = the amount of potential glucose (mg/ml) in the slurry (pumped in the system),

G_2 = the potential glucose in the hydrolyzate (mg/ml), F = dilution factor.

To estimate the dilution factor a simple way was developed. An exact amount of 1 % sulfuric acid solution was pumped in the system and the elapsed time was measured. At the same time the sample from reactor outlet was collected, thus enabling to calculate the flow in-and flow out-rates of the system. Flow in rate/flow out rate ratio simply gave then the dilution factor for a certain reactor temperature.

By increasing the amount of steam in the reactor but keeping the flow-in rate constant a dilution factor curve was obtained. On the other side by changing the moyno pump speed and proceeding in similar way several dilution factor curves were drawn.

Figure 2 shows an example of dilution factor curve obtained as described above. Another curve was olsa drawn here using the following empiric formula suggested by MC PARLAND (1980),

$$F = -1.690 \,.\, 10^{-3}\, T = 1.055$$

which seems to be unable to reflect adequately the pump performance especially at higher temperatures.

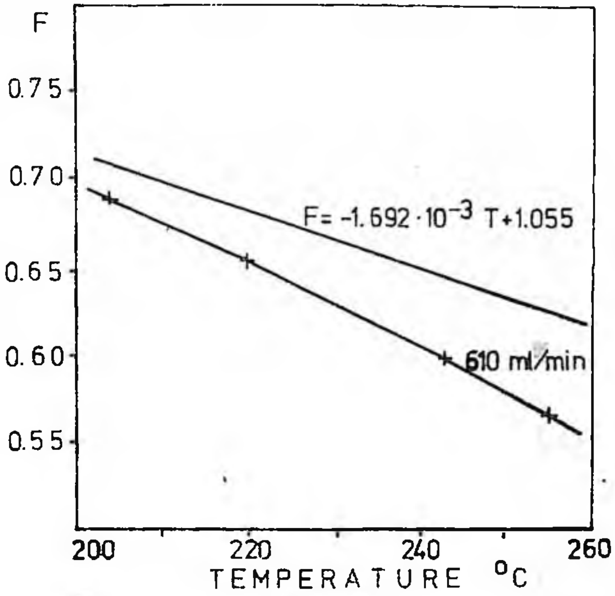


Figure 2. The dilution factor curves for the plug flow reactor.

Table 2. The results of acid hydrolysis of aspen in the plug flow reactor.

Run No	Temp. (°C)	A. con. (%)	F	Residue (mg/ml)	Residue (%)	G_1F (mg/ml)	G_2 (mg/ml)	Glu Yield (%)
1 - 0	Start	0.367	1.000	73.93	100.0	33.27	0.0	0.0
1 - 1	220	0.308	0.661	26.97	55.2	21.99	1.71	7.8
1 - 2	230	0.314	0.641	25.33	53.5	21.32	2.56	12.0
1 - 3	240	0.318	0.620	24.03	52.4	20.63	3.77	18.3
1 - 4	250	0.315	0.597	20.49	46.4	19.86	5.42	27.3
2 - 0	Start	0.99	1.000	67.88	100.0	32.31	0.0	0.0
2 - 1	230	0.78	0.636	22.26	51.6	20.55	4.68	22.8
2 - 2	241	0.75	0.611	13.99	33.7	19.74	8.08	40.9
2 - 3	250	0.75	0.588	10.24	25.7	19.00	9.85	51.8
2 - 4	256	0.74	0.573	8.09	20.8	18.51	10.25	55.4

3. RESULTS AND DISCUSSION

Table 2 summarizes the data obtained from both runs series. In Figure 3 the potential glucose yields were plotted vs. temperatures to obtain correlations (Table 2, Figure 3).

While the curve of first series (initial acid con. = 0.367 %) is showing a steady increase at the second series where more acid applied (0.99 %) the nearly maximum glucose yield was achieved at 256°C. The small difference between glucose yields of runs at 250° and 256°C (run no: 2 - 3 and 2 - 4) supports also this opinion.

The amount of residues in hydrolyzates was included in Table 2. To ease a comparison the solid concentration of the slurry was taken 100 %. The residue concentrations of hydrolyzates based on this were calculated by equation :

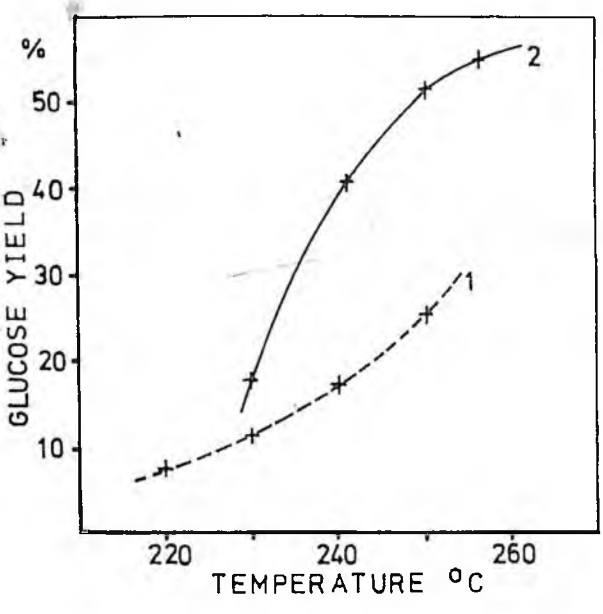


Figure 3.

$$\text{Residue con. (\%)} = \frac{\text{The solid con. of hydrolyzate . 100}}{\text{The initial con. of slurry . F}}$$

The dilute acid hydrolysis apparently involves the solubility of wood. Even at the most mild conditions applied here (run 1 - 1) nearly the half of wood was dissolved where the glucose yield is only 8 %. The dissolved part of wood makes up more than half of wood at 250°C (run no: 1 - 4) and this time 27 % glucose yield is obtained. Most likely the polyoses of wood are readely being hydrolyzed and the lignin itself rises as the most resistant wood component to the acid hydrolysis. Probably it remains almost quantitatively in the residues.

The poplar contains roughly 20 % lignin which is still unsoluable at such high temperatures (UÇAR, 1982). Asuming the rest of cellulose would be in the residue without further decomposition ($\simeq$ 33 % of wood), so the amount of residue should be 53 % during the run at 250°C (run no: 1 - 4). The difference is about 7 % (53 - 46 %) which indicates no critical glucose decomposition occurs under these conditions. On the other side the maximum glucose yield of 55 % was achieved during the second series-run at 256°C. This corresponds 26 % of wood. Under the logical assumption, that the residue obtained after this run consisted of only the rest of cellulose and lignin, it would amount to 46 %. The determined residue of 21 % clearly shows serious glucose losses. The HMF was detected on the HPLC - chromatograms of the same hydrolyzate which also verifies these results.

The kinetic parameters were estimated for solka floc hydrolysis and glucose decomposition in the plug flow reactor by GRETHLEIN et al. (1980). These parameters given in Table 1 (line alpha cellulose) were used to calculate the reaction rate constants, k_1 for cellulose hydrolysis, k_2 for glucose decomposition. The predicted glucose yields were then obtained for the first and second series runs using the equation (5). The G_0 fraction of cellulose (readily hydrolyzed cellulose was assumed to be 0 %, 1.15 %, 3 %, 5 % and 10 % by evaluating the different related works (FAGAN et al. 1971, SAEMAN, 1945, GRETHLEIN, CONVERSE, 1982).

«t» reaction times were also found out by dividing the flow out rates through the reactor volume (112.9 cm^3). Table 3 represents then reaction times, calculated and observed yields for each run.

Table 3. Observed and predicted glucose yields.

					YIELDS (%)					
Temp	A. con	Time	K_1	K_2	PREDICTED (G_0 values)					OBS.
(°C)	(%)	(min)	(1/min)	(1/min)	0.00	1.15	3.00	5.00	10.00	
220	0.308	0.0990	0.54998	0.96888	5.05	6.04	7.62	9.34	13.63	7.80
230	0.314	0.0977	1.19101	1.49971	10.20	11.08	12.49	14.01	17.82	12.00
240	0.318	0.0945	2.48604	2.27458	18.76	19.47	20.62	21.86	24.95	18.30
250	0.315	0.0922	4.92266	3.35374	31.02	31.50	32.29	33.14	35.26	27.30
230	0.780	0.1035	3.34678	2.51616	25.58	26.17	27.13	28.16	30.73	22.80
241	0.750	0.1017	7.06800	3.85668	41.43	41.73	42.41	42.73	44.04	40.90
250	0.750	0.1010	13.18257	5.49271	53.16	53.21	53.29	53.37	53.59	51.80
256	0.740	0.0990	19.44167	6.85412	55.82	55.77	55.67	55.57	55.31	55.40

$P_1 = 5.331 E + 16$ $P_2 = 3.83985 E + 09$ $m = 1.1355$ $n = .5687$

$E_1 = 154892.4$ $E_2 = 87872.56$ $R = 8.31441$

At the first glance a tendency can be observed that the predicted yields are somewhat higher than the experimental determined yields in many cases. Particularly taking G_0 values more than 3 % and at higher temperatures with lower acid concentration (1. series), or at lower temperatures with higher acid concentration (2. series) these excesses are noticeable.

To explain these differences attention was paid to the acid concentrations determined by the titration method. Finding out the concentration of H+ ions which really participate in the catalytic cleavege of ether bonds between anhydroglucose units of cellulose molecules is considered rather difficult. The determined acid concentrations affect the rate constants k_1 and k_2 from which then the predicted yields are estimated. As known, the hardwoods, also poplars, contain acetyl groups, uronic acids bound on the xylan molecules in appreciable amounts. The percentage of acetyl groups and uronic acids in aspen wood is 3.7 and 4.3 respectively (TIMELL, 1967). The acetyl groups splitt off easily at high temperatures whereas the uronic acids seem to be more resistant at low temperatures but above 200°C they are subjected to hydrolysis too. Besides these acids under the conditions here some other organic acids should be expected to occur which also contribute to increase of H+ ions in reactor medium.

If all H+ ions from organic acids were formed at the beginning or whether they all really acted on oxygen bonds between glucose units to cleavege them is disputable. But it might be deduced under logical consideration, that either the half amount of the H+ ions (originating from organic acids) could take part in the hydrolysis or the whole H+ ions excess would play its catalytic role for a half time of the reaction.

By using the dilution factor «F» and the initial sulfuric acid concentration of slurry it is possible to find out the mineral acid concentration of medium in the reactor. On the other side the acid concentration values of the hydrolyzates should be consequently higher than those obtained this way because of the organic acids. By subtracting the half value of difference from determined acid concentrations a correction was made and then the Table 3 was rearranged again showing the predicted and observed yields for both determined and corrected acid concentrations (Table 3 A).

From Table 3 A is obvious a better aggreement between observed and calculated yields was achieved. At lower temperatures the readily hydrolyzed fraction of cellulose has a considerable influence on the glucose yields and this becomes more effective during the experiments where the glucose decomposition rate constants are small respectively where the hydrolysis with more diluted acid (1. series) taking place. On the other side in the case taking G_0 value as 10 % high predicted glucose yields are obtained particularly at lower temperatures with lower acid concentrations because the glucose decomposition under these conditions is also very small.

Therefore it would not be wrong to conclude that the appropriate G_0 values for cellulose hydrolysis would lie between 3 - 4 %.

Recently the cellulose decomposition parameters for the New Hampshire poplar hydrolyzed in the plug flow reactor under different conditions were estimated by

Tablo 3A.

Temp (C)	A. con (%)	Time (min)	K_1 (1/min)	K_2 (1/min)	YIELDS (%) PREDICTED (G_0 values) 0.00	1.15	3.00	5.00	10.00	OBS.
220	0.308	0.0990	0.54998	0.96888	5.05	6.04	7.62	9.34	13.63	7.80
220	0.275	0.0990	0.48357	0.90840	4.47	5.47	7.08	8.82	13.16	7.80
230	0.314	0.0977	1.19101	1.49971	10.20	11.08	12.49	14.01	17.82	12.00
230	0.275	0.0977	1.02451	1.39076	8.90	9.80	11.25	12.82	16.74	12.00
240	0.318	0.0945	2.48604	2.27458	18.76	19.47	20.62	21.86	24.95	18.30
240	0.273	0.0945	2.09057	2.08553	16.22	16.97	18.19	19.51	22.81	18.30
250	0.315	0.0922	4.92266	3.35374	31.02	31.50	32.29	33.14	35.26	27.30
250	0.267	0.0922	4.08011	3.05279	27.09	27.64	28.54	29.51	31.92	27.30
230	0.780	0.1035	3.34678	2.51616	25.58	26.17	27.13	28.16	30.73	22.80
230	0.705	0.1035	2.98382	2.37558	23.41	24.04	25.05	26.15	28.89	22.80
241	0.750	0.1017	7.06800	3.85663	41.43	41.73	42.21	42.73	44.04	40.90
241	0.677	0.1017	6.29214	3.63850	38.74	39.09	39.65	40.25	41.77	40.90
250	0.750	0.1010	13.18257	5.49271	53.16	53.21	53.29	53.37	53.59	51.80
250	0.666	0.1010	11.51925	5.13392	51.05	51.15	51.31	51.48	51.90	51.80
256	0.740	0.0990	19.44167	6.85412	55.82	55.77	55.67	55.57	55.31	55.40
256	0.654	0.0990	16.89695	6.38909	55.24	55.22	55.18	55.13	55.03	55.40

$P_1 = 5.331 E + 16$ $P_2 = 3.83985 E + 09$ $m = 1.1355$ $n = .5687$

$E_1 = 154892.4$ $E_2 = 87872.56$ $R = 8.31441$

GRETHLEIN and CONVERSE (1982). These parameters were tested for aspen and Table 3 B represents the calculated data with new parameters.

This time the predicted yields are showing some deficits for almost all runs. To explain the unsuitability of the new kinetic data for aspen we could consider first the higher amount of lignin found in NH - poplar (23.7 % vs. 21.8 %), whereas the aspen has more polyoses i.e. xylan. Furthermore Grethlein and Converse describes that another reactor tubes with less volume (106.3 and 72.56 ml) was used and the Moyno pump, the pressure let down orifice were also replaced to facilitate to run the slurries with high solid concentration. Probably these all factors resulted in obtaining rather different, somewhat substrate but more reactor specific parameters.

On the other hand the kinetic data for alpha cellulose (solka floc) can also be applied on aspen wood with enough accuracy. Thus the Table 3 A gives evidence that the reactions taking place during the decomposition of cellulose and glucose can be expressed by means of 1. order homogeneous reactions.

Table 3B. Predicted and observed glucose yields.

Temp	A. con	Time	K_1	K_2	YIELDS (%)					
					PREDICTED (G_0 values)					
(C)	(%)	(min)	(1/min)	(1/min)	0.00	1.15	3.00	5.00	10.00	OBS.
220	0.308	0.0990	0.49502	0.96888	4.56	5.55	7.15	8.87	13.19	7.80
220	0.275	0.0990	0.44261	0.90840	4.10	5.10	6.72	8.46	12.83	7.80
230	0.314	0.0977	1.02964	1.49971	8.89	9.78	11.22	12.77	16.64	12.00
230	0.275	0.0977	0.90326	1.39076	7.89	8.80	10.27	11.86	15.83	12.00
240	0.318	0.0945	2.06932	2.27458	15.93	16.67	17.87	19.16	22.40	18.30
240	0.273	0.0945	1.77991	2.08553	14.01	14.79	16.06	17.42	20.82	18.30
250	0.315	0.0922	3.96363	3.35374	26.08	26.63	27.50	28.45	30.82	27.30
250	0.267	0.0922	3.36665	3.05279	23.09	23.69	24.66	25.71	28.33	27.30
230	0.780	0.1035	2.52857	2.51616	20.16	20.81	21.86	23.00	25.85	22.80
230	0.705	0.1035	2.28834	2.37558	18.61	19.29	20.39	21.59	24.57	22.80
241	0.750	0.1017	5.16306	3.85668	33.22	33.61	34.25	34.93	36.65	40.90
241	0.677	0.1017	4.66652	3.63850	31.12	31.56	32.26	33.02	34.92	40.90
250	0.750	0.1010	9.33476	5.49271	44.87	45.01	45.25	45.50	46.12	51.80
250	0.666	0.1010	8.30166	5.13392	42.72	42.92	43.23	43.56	44.41	51.80
256	0.740	0.0990	13.51920	6.85412	49.71	49.72	49.74	49.76	49.81	55.40
256	0.654	0.0990	11.96666	6.38909	48.36	48.42	48.51	48.60	48.84	55.40

$P_1 = 6.12221\ E + 15$ $P_2 = 3.83985\ E + 09$ $m = 0.987416$ $n = .5687$

$E_1 = 147165.2$ $E_2 = 87872.56$ $R = 8.31441$

After coincidence of observed and predicted data in Table 3 A another attempt was made to investigate the maximum glucose yields and the required reaction times under different conditions. Since under these circumstances G_0 fraction of cellulose would not impact on the yields and to ease the calculations, it was not taken into consideration. Thus the following equations are used :

$$G_{max} = \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}} \quad . \quad t_{max} = \frac{k_2 - k_1}{\ln k_2 - \ln k_1}$$

Table 4 shows maximum glucose yields and related times estimated for assumed acid concentrations from 0.25 up to 2 % at various high temperatures (180° - 300°C). Furthermore the Figure 4 was prepared for instance to visualize the correlation between yield, time and temperature respectively.

The highest yield obtainable in terms of kinetic parameters is around 80 %. But achieving this success indeed depends upon that several difficulties had to be overcome. Some such constraints are being discussed here briefly :

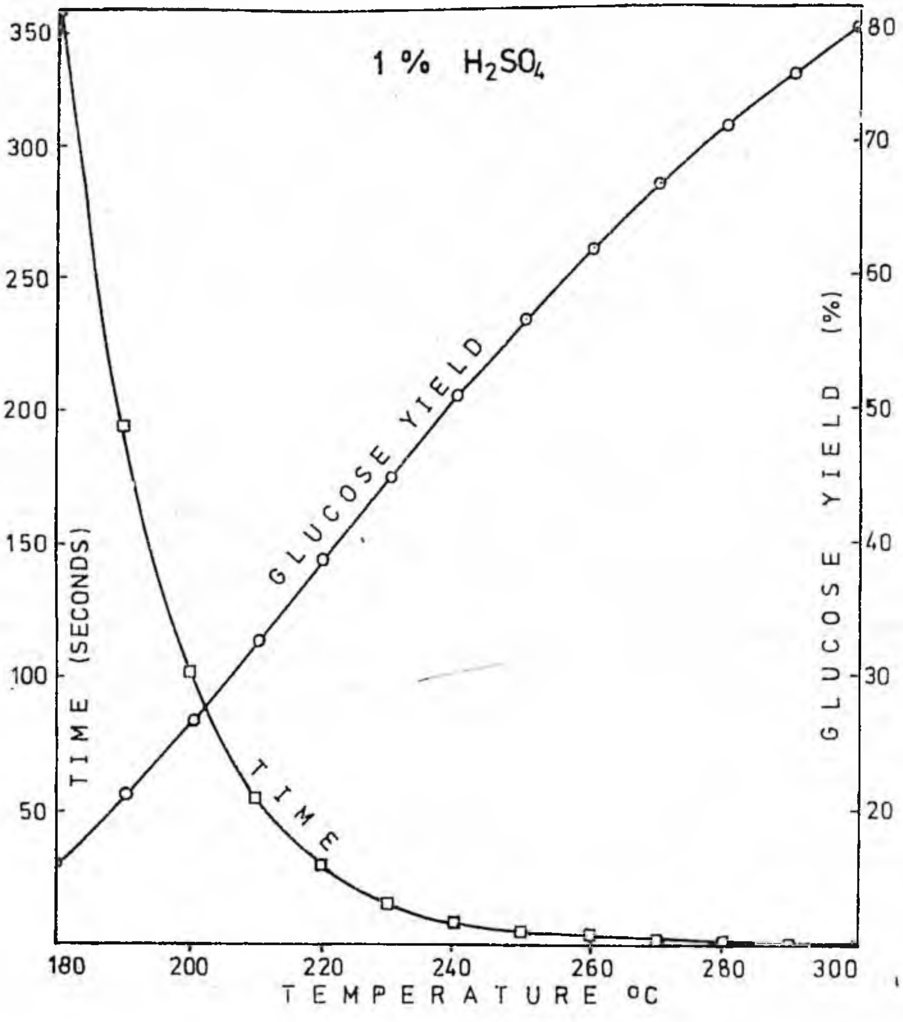
Table 4. Predicted maximum glucose yields and times.

ACID CON. (%)	TEMP. (C)	RATE CONS. (K_1) (1/min)	RATE CONS. (K_2) (1/min)	TMAX (sec.)	GMAX (%)
0.2500	180.0	0.01546	0.12978	1116.539	8.936
0.2500	200.0	0.08790	0.34780	317.522	15.873
0.2500	210.0	0.19857	0.55221	173.530	20.248
0.2500	220.0	0.43397	0.86048	96.295	25.133
0.2500	230.0	0.91942	1.31738	54.225	30.404
0.2500	240.0	1.89174	1.98371	30.970	35.918
0.2500	250.0	3.78642	2.94068	17.933	41.523
0.2500	260.0	7.38396	4.29541	10.525	47.074
0.2500	280.0	26.11865	8.79565	3.770	57.544
0.2500	300.0	84.59068	17.13203	1.420	66.661
0.5000	180.0	0.03398	0.19249	656.508	12.171
0.5000	200.0	0.19312	0.51586	182.660	20.795
0.5000	210.0	0.43624	0.81903	98.737	25.981
0.5000	220.0	0.95841	1.27624	54.201	31.572
0.5000	230.0	2.01992	1.95392	30.200	37.401
0.5000	240.0	4.15605	2.94221	17.073	43.291
0.5000	250.0	8.31855	4.36158	9.790	49.082
0.5000	260.0	16.22214	6.37088	5.693	54.638
0.5000	280.0	57.38121	13.04558	2.005	64.671
0.5000	300.0	185.84103	25.40998	0.744	72.968
0.7500	180.0	0.05384	0.24240	478.746	14.454
0.7500	200.0	0.30604	0.64964	131.438	24.096
0.7500	210.0	0.69133	1.03144	70.582	29.720
0.7500	220.0	1.51089	1.60723	38.497	35.657
0.7500	230.0	3.20100	2.46066	21.317	41.718
0.7500	240.0	6.58617	3.70525	11.980	47.720
0.7500	250.0	13.18257	5.49271	6.831	53.508
0.7500	260.0	25.70753	8.02312	3.951	58.961
0.7500	280.0	90.93312	16.42883	1.378	68.570
0.7500	300.0	294.50580	31.99983	0.507	76.295
1.0000	180.0	0.07464	0.28549	381.743	16.261
1.0000	200.0	0.42428	0.76511	103.799	26.617
1.0000	210.0	0.95841	1.21478	55.477	32.524
1.0000	220.0	2.09460	1.89291	30.120	38.665
1.0000	230.0	4.43766	2.89804	16.605	44.841
1.0000	240.0	9.13064	4.36386	9.293	50.871
1.0000	250.0	18.27547	6.46904	5.278	56.607
1.0000	260.0	35.63927	9.44921	3.041	61.943
1.0000	280.0	126.06380	19.34904	1.054	71.190
1.0000	300.0	408.28381	37.68775	0.386	78.482

1.2500	180.0	0.09617	0.32412	319.810	17.771
1.2500	200.0	0.54662	0.86863	86.300	28.668
1.2500	210.0	1.23479	1.37915	45.955	34.774
1.2500	220.0	2.69862	2.14903	24.861	41.047
1.2500	230.0	5.71736	3.29016	13.659	47.282
1.2500	240.0	11.76366	4.95431	7.620	53.303
1.2500	250.0	23.54560	7.34433	4.315	58.971
1.2500	260.0	45.91665	10.72774	2.479	64.194
1.2500	280.0	162.41716	21.96706	0.855	73.132
1.2500	300.0	526.02173	42.78712	0.312	80.078
1.5000	180.0	0.11829	0.35953	276.488	19.075
1.5000	200.0	0.67236	0.96354	74.144	30.402
1.5000	210.0	1.51881	1.52983	39.362	36.655
1.5000	220.0	3.31935	2.38382	21.233	43.017
1.5000	230.0	7.03245	3.64962	11.634	49.281
1.5000	240.0	14.46950	5.49559	6.473	55.274
1.5000	250.0	28.96148	8.14673	3.656	60.870
1.5000	260.0	56.47823	11.89979	2.096	65.987
1.5000	280.0	199.77576	24.36704	0.720	74.656
1.5000	300.0	647.01532	47.46176	0.261	81.318
1.7500	180.0	0.14091	0.39247	244.313	20.228
1.7500	200.0	0.80097	1.05182	65.167	31.905
1.7500	210.0	1.80934	1.66999	34.508	38.272
1.7500	220.0	3.95431	2.60223	18.569	44.694
1.7500	230.0	8.37769	3.98400	10.150	50.968
1.7500	240.0	17.23738	5.99910	5.635	56.926
1.7500	250.0	34.50155	8.89314	3.176	62.450
1.7500	260.0	67.28201	12.99006	1.818	67.468
1.7500	280.0	237.99097	26.59957	0.622	75.901
1.7500	300.0	770.78320	51.81025	0.225	82.320
2.0000	180.0	0.16399	0.42344	219.377	21.263
2.0000	200.0	0.93211	1.13480	58.245	33.234
2.0000	210.0	2.10557	1.80175	30.774	39.688
2.0000	220.0	4.60171	2.80754	16.524	46.153
2.0000	230.0	9.74930	4.29833	9.015	52.425
2.0000	240.0	20.05950	6.47242	4.995	58.342
2.0000	250.0	40.15018	9.59480	2.811	63.796
2.0000	260.0	78.29749	14.01496	1.606	68.723
2.0000	280.0	276.95508	28.69826	0.548	76.946
2.0000	300.0	896.97723	55.89802	0.198	83.155

$P_1 = 5.331$ E + 16 $P_2 = 3.83895$ E + 09 $m = 1.1355$ $n = .5687$

$E_1 = 154892.4$ $E_2 = 87872.56$ $R = 8.31441$



Şekil 4.

At high temperatures particularly above 220°C 1 % sulfuric acid itself causes considerable corrosions in the reactor thus making necessary to use special steel alloys for reactor building. However the reactor section made from best available alloys has its durability and should be replaced after a certain time. The restrictions and problems related to the slurry pumping into the system at high pressures and high temperatures were evalueted by GRETHLEIN and CONVERSE (1982). Arising the temperature gives rises to drastic increase of rate constants where k_1 (cell. decomposition) is much more boosted than k_2 (glu. decomposition), thus resulting in higher glucose yields. But the high temperature acid hydrolysis needs very short reaction times indeed as can be seen from Figure 4 and Table 4 too. To assure isothermal conditions in the reactor the acidified slurry must be heated up and cooled down in very short times such 1/10 of whole reaction time at least. By means of steam injection in the reactor too short heating times were reached such as 0.7 seconds from 20° to 240°C and 0.4 sec. for the critical region from 160 - 240°C in the plug flow reactor (GRETHLEIN et al. 1980). Otherwise the pressure let down orifice enables practically instanteneous cooling of the slurries in the same system. But the Table 4 dictates much more shorter reaction times for better glucose yields over 75 % for instance. Perhaps it is the most serious problem at this time to build such reactor that enables very short time hydrolysis at high temperature in pilot scale. By using the continuous plug flow reactor at 263°C the highest glucose yields obtained were 65.1 % for mixed hardwood and 66.6 % for poplar (GRETHLEIN, CONVERSE, 1982).

4. CONCLUSIONS

The kinetic model developed by Saeman can be successfully used to simulate the dilute sulfuric acid hydrolysis of aspen wood in the flow reactor as gathered from the comparison of the experimental data with the predicted values under the given conditions. The coincidence was much better if the calculated data were based on the kinetic parameters obtained for the alpha cellulose (solka floc) and as the acid concentrations determined by titration were corrected considering the organic acids formed in the reactor. The available glucose at zero time is around 3 - 5 % as evaluated from the predicted and observed data. Applying the kinetic parameters for poplar itself which were determined later on resulted in lower yield values that might be attributed to the subsequent improvements on the flow reactor.

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REFERENCES

CEDERQUIST, K.N., 1952. Some Remarks on Wood Hydrolyzation. Report of a Seminar held at Lucknow, India, pp. 193-198.

CONNER, A.H., 1984. Kinetic Modeling of Hardwood Prehydrolysis, P.I. Xylan Removal by Water Prehydrolysis. Wood and Fiber Science, 16. pp. 268-277.

CONNER, A.H.. LORENZ, L.F., 1986. Kinetic Modeling of Hardwood Prehydrolysis, P. III. Water and Dilute Acetic Acid Prehydrolysis of Southern Red Oak. Wood and Fiber Science, 18, pp. 248-263.

CONNER, H.A., LIBKIE, K., SPRINGER, E.L., 1985. Kinetic Modeling of Hardwood Prehydrolysis, P. II. Xylan Removal by Dilute Hydrochloric Acid Prehydrolysis. Wood and Fiber Sci., 17, pp. 540-548.

CONNER, A.H., WOOD, B.F., HILL, C.G., HARRIS, J.F.. 1985. Kinetic Model for the Dilute Sulfuric Acid Saccharification of Lignocellulose. Journal of Wood Chemistry and Technology, 5(4), pp. 461 - 489.

DELLWEG, H., RIZZI, M., METHNER, H., DEBUS, D., 1984. Xylose Fermentation by Yeast 3. Comparison of Pachysolen Tannophilus and Pichia Stiptis. Biotechnol. Lett. 6, pp. 395-400.

FAGAN, R.D.. GRETHLEIN, H.E., CONVERSE, A.O., PORTEOUS, A., 1971. Kinetics of the Acid Hydrolysis of Cellulose Found in Paper Refuse. Environmental Science and Techn. 5, pp. 545-547.

FENGEL, D., WEGENER, G., 1984. Wood. Chemistry, Ultrastructure, Reactions. Walter de Gruyter, Berlin, New York.

GOLDSTEIN, I.S., 1980. The Hydrolysis of Wood. Tappi, 63, pp. 141-143.

GRETHLEIN, H.E., CONVERSE, A.O., 1982. Second Annual Report on Acid Hydrolysis of Cellulosic Biomass. Thayer School of Eng., Dartmouth College.

GRETHLEIN. H.E., CONVERSE, A.O., MC PARLAND, J.J., SMITH, P.C., 1980. Acid Hydrolysis of Cellulosic Biomass in a Continuous Plug Flow Reactor, Final Report for U.S. Dep. of Energy/Seri.

HARRIS, J.F., 1981. Cellulose Hydrolysis, Yields of Glucose and Reversion Products. unpublished private notice.

HARRIS, J.F., SCOTT, R.W., SPRINGER, E.L., WEGNER, T.H., 1984. Factor Influencing Dilute Sulfuric Acid Prehydrolysis of Southern Red Oak Wood. In: Tillman, David A.J., Edwin C. eds. Progress in Biomass Conversion, V. 5. Orlando FL, Academic Press, pp. 102-141.

HARRIS, J.F., BAKER. A.J., CONNER, A.H., JEFFRIES, T.W., MINOR, J.L., PETTERSEN, R.C., SCOTT, R.W., SPRINGER, E.L., WEGNER, T.H., ZERBE, J.I., 1985. Two Stage, Dilute Sulfuric Acid Hydrolysis of Wood. An Investigation of Fundamentals, FPL - 45, General Technical Report.

JEFFRIES, T.W., 1981. Conversion of Xylose to Ethanol under Aerobic Conditions by Candida Tropicalis, Biotechn. lett. V. 3, pp. 213-218.

JEFFRIES. T.W., 1985. Emerging Technology for Fermenting D-Xylose. Trends in Biotechnology, 3, pp. 208-212.

KIRBY, A.M.Jr., 1948. Kinetics of Consecutive Reactions Involved in Wood Saccharification. Research and Marketing Act Studies Rep. No, 14 (CF. Univ. of Wisc. Master Thesis).

MALESZKA, R., SCHNEIDER, H., 1982. Concurrent Production and Consumption of Ethanol by Cultures of Pachysolen Tannuphilus Growing on Xylose. Appl. Environ. Microbiol., 44, pp. 909-912.

MALONEY, M.T., CHAPMAN, T.W., BAKER, A.J., 1985. Dilute Acid Hydrolysis of Paper Birch, Kinetics Studies of Xylan and Acetyl Group Hydrolysis. Biotechn. Bioeng. 37, pp. 355-361.

MC KIBBINS, S.W., 1958. Kinetics of the Acid Catalyzed Conversion of Glucose to 5-Hydroxymethyl 2-Furaldehyde and Levulinic Acid. Univ. of Wisc. Ph. D. Thesis.

MC PARLAND, J.J., 1980. The Acid Hydrolysis of Cellulosic Biomass, A Bench Scale System and Preliminary Plant Design. Master of Eng. Thesis, Thayer School of Eng. Dartmouth College.

SAEMAN, J.F., 1945. Kinetics of Wood Saccharification, Hydrolysis of Cellulose and Decomposition of Sugars in Dilute Acid at High Temperature. Ind. and Eng. Chem. 37, pp. 43-52.

SPRINGER. E.L., 1966. Hydrolysis of Aspenwood Xylan with Aqueous Solutions of Hydrochloric Acid. Tappi, 47, pp. 102-106.

SPRINGER, E.L., 1985. Prehydrolysis of Hardwoods with Dilute Sulfuric Acid. Ind. Eng. Chem. Prod. Res. Dev. 24, pp. 614-623.

SPRINGER, E.L., HARRIS, J.F., 1985. Procedures for Determining the Neutralization Capacity of Wood during Hydrolysis with Mineral Acid Solutions. Ind. Eng. Chem. Prod. Res. Dev. 24, pp. 485-489.

STAM, A.J., HARRIS, E.E., 1953. Chemical Processing of Wood, Chemical Publishing, New York, Chap. 16.

TIMELL, T.E., 1967. Recent Progress in the Chemistry of Wood Hemicelluloses. Wood Sci. and Techn. Vol. 1, pp. 45-70.

UCAR, H., 1982. (Investigations on Wood Hydrolysis with Regard to the Chemical Utilization), Habilitationsthesis, Faculty of Forestry Blacksea Technical University. (Turkish).

WANG, P.Y., SHOPSIS, C., SCHNEIDER, H., 1980. Fermentation of Pentose by Yeast, Biochem. Biophys. Res. Comm., 94, pp. 248-254.

WENZL, H.F.J., 1970. The Acid Hydrolysis of Wood, In: The Chemical Technology of Wood. Academic Press, New York, London, pp. 158-252.

YOUNG, E.P., 1949 The Effect of Temperature on the Yield of Sugar from Cellulose. Res. and Mark. Act Studies. Rep. No: 15.